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April 19, 1999

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The Honorable John T. Conway
Chairman
Defense Nuclear Facilities Safety Board
625 Indiana Avenue, NW
Suite 700
Washington, DC 20004

Dear ~~Mr.~~ John Chairman:

Enclosed is a document entitled *Technical Handbook of ^{233}U Material Properties, Processing, and Handling Guidelines* (ORNL/TM-13600). It represents the deliverable for Commitment 13 of the Department's Implementation Plan for addressing the Defense Nuclear Facilities Safety Board's (DNFSB) Recommendation 97-1 concerning the safe storage of ^{233}U material.

The handbook is designed to serve as a single comprehensive information resource for use by the Department's federal and contractor technical workforce involved with the processing, handling, and storage of ^{233}U and ^{233}U bearing materials. It is intended to be an integral part of the Department's training efforts to meet the objective of retaining long-term expertise necessary to assure safe handling and storage of ^{233}U.

If you have any questions, please contact me, or have your staff contact Hoyt Johnson of my staff at (202) 586-0191.

Sincerely,

Dave Huizenga

David G. Huizenga
Acting Deputy Assistant Secretary for
Nuclear Material and Facility Stabilization
Office of Environmental Management

Enclosure

cc: (w/encl)
M. Whitaker, S-3.1

99-0001024

ORNL/TM-13600

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Technical Handbook of ^{233}U Material Properties, Processing, and Handling Guidelines

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ORNL-27 (3-96)

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March 31, 1999

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DNF SAFETY BOARD

Mr. Hoyt C. Johnson
U.S. Department of Energy
Office of Nuclear Material Stabilization
Forrestal Building, Room GA-242, EM-66
1000 Independence Avenue, SW
Washington, DC 20585-0001

Dear Mr. Johnson:

Contract No. DE-AC05-96OR22464: ^{233}U Technical Handbook

Enclosed are four (4) copies of our completed report, *Technical Handbook of ^{233}U Material Properties, Processing, and Handling Guidelines* (ORNL/TM-13600), for approval and transmittal to the Defense Nuclear Facilities Safety Board (DNFSB) by April 30. This handbook satisfies DNFSB 97-1 deliverable HQ-13-013. Contributors to the handbook are cited in the acknowledgments section of the document, and Steve Storch served as the principal investigator for this task.

We are distributing copies of the handbook to the 97-1 technical team members who contributed to this document. Following submittal of the document to the DNFSB, we will make wider distribution. Our Classification and Information Control Officer has recommended that the 97-1 program control the distribution list for this document. We are preparing a proposed distribution for your review.

Please contact me if you have any questions about the handbook.

Sincerely,

James E. Rushton, Manager
ORNL 97-1 ^{233}U Safe Storage Technical Team
Chemical Technology Division

cc: C. W. Forsberg
A. M. Krichinsky
B. D. Patton

cc w/o enc: J. M. Begovich
S. N. Storch

ORNL/TM-13600

Technical Handbook of ^{233}U Material Properties, Processing, and Handling Guidelines

Compiled by

Oak Ridge National Laboratory*
Oak Ridge, Tennessee

March 1999

Prepared for
U. S. Department of Energy
Office of Nuclear Material Stabilization
Washington, D.C.

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*Managed by Lockheed Martin Energy Research Corp., under contract DE-AC05-96OR22464 for the U.S. Department of Energy.

PREFACE

This technical handbook has been prepared to satisfy a need for an authoritative, single-volume compilation of information and data on the characteristics of the ^{233}U radionuclide and materials containing the ^{233}U isotope. The ^{233}U technical handbook presents basic data associated with the properties, processing, and handling guidelines of ^{233}U-bearing materials.

The document has been planned for easy reference with an introductory section (Sect. 1), which serves as a guide for the entire report. Organization of the report and a summary description of the topics covered are described in Sect. 1. Suggestions for revising or including additional relevant material in this document are always welcome and should be conveyed to:

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This technical handbook on ^{233}U-bearing materials could not have been prepared without the support, assistance, and input of many people. Appreciation is expressed to the following individuals.

- Special thanks to Jim Rushton and Brad Patton, who provided administrative guidance, encouragement, and helpful review comments.

Contributors to various sections included the following:

- Robert Sadlowe: Confinement and containment
- Calvin Hopper: Nuclear criticality
- Robert Coleman: Radon generation and control, off-gas filtration
- Ron Pope, Larry Shappert, and Rick Michelhaugh: Transportation
- Walt Bond, Mac Toth, and Fred Peretz: Physical and chemical properties
- Loong Yong: Radiation protection
- Lee Trowbridge: Special chemical hazards
- Pete Bereolos: Package and storage requirements
- Tatum Fowler: Nuclear material control and accountability
- William Rich: Nuclear material safeguards
- Fred Peretz: Molten Salt Reactor Experiment (MSRE) Program/operation and MSRE fuel stabilization
- Jim Nehls: Uranium metal fabrication, summary of ^{233}U production at Hanford and Savannah River

Grateful appreciation is expressed to members of a special review group, who provided insightful reviews and comments on many different sections of this document:

- Rowland E. Felt (DOE-EH)
- Charles W. Forsberg
- Alan M. Krichinsky
- Leroy C. Lewis (INEEL)
- Fred J. Peretz
- Mac Toth

- Special thanks to Carl Detrick and Don Connors, of Bettis Atomic Power Laboratory, for providing and reviewing information on the Light-Water Breeder Reactor Development Program.
- Thanks to Alan Krichinsky, Billy Starnes, and Judy Butler, who provided helpful suggestions, comments, and documents that contained useful information.

- Thanks to Robert Brooksbank (retired), for providing review comments that were most helpful in developing the format and structure of this handbook.
- Thanks to Charles Barton (retired), of Oak Ridge, for providing information on the handling of radioactive materials in glove boxes.

Other individuals provided technical, clerical, and editing/document format assistance:

- Scott Ludwig, for providing information and sources documenting past ^{233}U processing.
- Linda Gilpin, for reviews and providing information on shielding.
- Janet Westbrook, for providing information on confinement and shielding.
- Jim McGehee and Ed Rosenbaum, for providing review comments on training information.
- David Kocher, for reviewing and providing information and data on the radiological properties of ^{233}U and ^{233}U-bearing materials, potential exposure pathways for humans, and issues of radiation protection.
- Alan Icenhour and Guillermo D. Del Cul, for providing information and figures on MSRE fuel stabilization.
- Tatum Fowler, for review of information on safeguards and nuclear material control and accountability.
- Michael Murray, for providing review comments and information on off-gas filtration.
- Oren Webb, for reviews and providing information on ^{233}U medical applications and thorium ingrowth removal.
- Ray Cooperstein (DOE–DP), John Evans (DOE–S), Leroy Lewis and Roger Henry (INEEL), and David Karraker (SRTC), for providing review comments and helpful suggestions.
- Carlisle E. Pickett, Major C. Thompson, and Anthony P. Gouge of WSRC, who provided documents on past ^{233}U production experience at SRS.
- Robert Watrous (Lockheed Martin Hanford Corporation) and Rick Stutheit (DOE-RL), who provided documents on past ^{233}U production experience at the Hanford Site.
- Special thanks to Sue McDaniel, for preparing and typing drafts of this report and preparing all of the figures.
- Special thanks to Donna Brooksbank, for typing final versions of the document and for preparing the report in its final form.
- Special thanks to Ralph Sharpe, for editing, document layout, and numerous suggestions that were extremely helpful (and crucial) for facilitating the publication of this document.
- Special thanks to the ORNL Library staff (in particular Bill Myers, Debbie Cole, Bob Conrad, Becky Rushton, Gabrielle Boudreau, Mark Dickey, Cynthia Manley, Joan Van Riper, Terry Depp, and Ta-Chang Liu), who were very helpful in locating and providing many of the information sources that were used to prepare this handbook.
- Finally, special thanks to the DOE 97-1 ^{233}U Safe Storage Technical Team, chaired by Hoyt Johnson (DOE-EM-66), for their helpful comments in reviewing this document prior to its publication.

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LIST OF ABBREVIATIONS, ACRONYMS, AND INITIALISMS

The following is a list of acronyms, abbreviations, and initialisms (including chemical symbols and units of measure) used in this document.

ACB	Auxiliary charcoal bed
ACS	American Chemical Society
ADU	Ammonium diuranate $[(NH_4)_2U_2O_7]$
AEA	Atomic Energy Act of 1954
AEC	U.S. Atomic Energy Commission
AGS	American Glovebox Society
ALARA	As low as reasonably achievable
ALI	Annual limit on intake
ANL	Argonne National Laboratory, Argonne, Illinois
ANL–E	Argonne National Laboratory–East, Argonne, Illinois
ANL–W	Argonne National Laboratory–West, Idaho Falls, Idaho
ANS	American Nuclear Society
ANSI	American National Standards Institute, Inc.
ASME	American Society of Mechanical Engineers
BAPL	Bettis Atomic Power Laboratory, West Mifflin, Pennsylvania
BMP	Best management practice
BNL	Brookhaven National Laboratory, Upton, New York
BP	Boiling point
BWR	Boiling-water reactor
B&W	Babcock and Wilcox
C/S	Containment and surveillance
CEUSP	Consolidated Edison Uranium Solidification Program
CFR	Code of Federal Regulations
CNEN	Comissao Nacional de Energia Nuclear
COMED	Commonwealth Edison Dresden Reactor–Unit 3
CTD	Chemical Technology Division (at Oak Ridge National Laboratory)
CY	Calendar year
DAC	Derived air concentration
DBA	Design basis accident
Dc	Dose to critical organ
DEB	Diethylbenzene $[C_6H_4(C_2H_5)_2]$
DIQ	Design information questionnaire
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DOE–EH	U.S. Department of Energy, Office of Environment, Safety, and Health
DOE–EIA	U.S. Department of Energy, Energy Information Administration

DOT	U.S. Department of Transportation
Ds	Dose to skin
DSBPP	Di-sec-butyl phenyl phosphonate $[(C_4H_9O)_2P(O)H]$
DU	Depleted uranium
D&D	Decontamination and decommissioning
EIS	Environmental Impact Statement
EM	Environmental management
ENDF	Evaluated Nuclear Data File
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ERR	Elk River Reactor
ES&H	Environment, Safety, & Health
FSVR	Fort St. Vrain Reactor
FTIR	Fourier-transform infrared
GA	General Atomics Laboratory, San Diego, California
GCR	Gas-cooled reactor
GET	General employee training
GI	Gastrointestinal
HEPA	High-efficiency particulate air (filter)
HEU	Highly enriched uranium
HLLW	High-level liquid waste
HLW	High-level waste
HTGR	High-temperature, gas-cooled reactor
HVAC	Heating, ventilation, and air-conditioning
IAEA	International Atomic Energy Agency
ICPP	Idaho Chemical Processing Plant, Idaho Falls, Idaho
ICRP	International Commission on Radiological Protection
ID	Inner diameter
IDMS	Isotope dilution mass spectrometry
IIA	International Inspection Area
INEEL	Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho
INPO	Institute of Nuclear Power Operations
IP	Indian Point (reactor)
ISFSI	Independent Spent Fuel Storage Installation
ITREC	Italian Reprocessing Corporation
IX	Ion exchange
KAPL	Knolls Atomic Power Laboratory, Schenectady, New York
LA	Limited area
LANL	Los Alamos National Laboratory, Los Alamos, New Mexico
LBNL	Lawrence Berkeley National Laboratory, Berkeley, California
LET	Linear energy transfer

LEU	Lowly enriched uranium
LLI	Lower large intestine
LLNL	Lawrence Livermore National Laboratory, Livermore, California
LLLW	Low-level liquid waste
LLW	Low-level waste
LSA	Low-specific activity
LWBR	Light-water breeder reactor
LWR	Light-water reactor
MAA	Material access area
MBA	Material balance area
MC&A	Material control and accountability
MCL	Maximum concentration level
Mound	Mound Plant, Miamisburg, Ohio
MOX	Mixed oxide [nuclear fuel (uranium and plutonium)]
MP	Melting point
MPC	Maximum permissible concentration
MSR	Molten Salt Reactor
MSRE	Molten Salt Reactor Experiment
NA	Not applicable
NBL	New Brunswick Laboratory, Argonne, Illinois
NCRP	National Council on Radiation Protection
NDA	Nondestructive assay
NEA	Nuclear Energy Agency
NEPA	National Environmental Policy Act
NESHAPs	National Emission Standards for Hazardous Air Pollutants
NFPA	National Fire Protection Association
NFS	Nuclear Fuel Services
NPDES	National Pollutant Discharge Elimination System
NRC	U.S. Nuclear Regulatory Commission
NSR	National security requirements
NUMEC	Nuclear Materials and Equipment Corporation
OD	Outer diameter
OECD	Organization for Economic Cooperation and Development
OG	Off-gas
ORELA	Oak Ridge Electron Linear Accelerator
ORNL	Oak Ridge National Laboratory, Oak Ridge, Tennessee
O/M	Oxygen/metal (ratio)
PA	Protected area
PBR	Peach Bottom reactor
PCB	Polychlorinated biphenyl
PHWR	pressurized heavy-water reactor
PIDAS	Perimeter Intrusion Detection and Assessment System

PNNL	Pacific Northwest National Laboratory, Richland, Washington
PPA	Property protected area
PWR	Pressurized-water reactor
QA	Quality assurance
QC	Quality control
RCP	Remote canister package
RCRA	Resource Conservation and Recovery Act of 1976
RFETS	Rocky Flats Environmental Technology Site, Golden, Colorado
ROD	Record of Decision
RPP	Radiological protection procedure
RTPC	Radkowsky Thorium Power Corporation
RTR	Radkowsky Thorium Reactor
RXA	Recrystallization annealed
RWMC	Radioactive Waste Management Complex (located at Idaho National Engineering and Environmental Laboratory)
R&D	Research and development
SAR	Safety analysis report
SCGM	Sodium-cooled, graphite-moderated (reactor)
SCO	Surface-contaminated object
SGMP	Sol-gel microsphere pelletization
SI	Système International (International System of Units)
SISMP	Site Integrated Stabilization Management Plan
SNF	Spent nuclear fuel
SNM	Special nuclear material
SQ	Significant quantity
SRA	Stress relief annealed
SRE	Sodium Reactor Experiment
SRP	Savannah River Plant (now Savannah River Site)
SRS	Savannah River Site, Aiken, South Carolina
SS	Stainless steel
S&S	Safeguards and security
STP	Standard temperature and pressure
SX	Solvent extraction
TBP	Tributyl phosphate [$(C_4H_9)_3PO_4$]
TID	Tamper-indicating devices
TQPP	Training and Qualification Program Plan
TRU	Transuranic
TRULW	Transuranic liquid waste
TSA-RE	Transuranic Storage Area-Retrieval Enclosure
TVL	Tenth-value layer
URL	Uniform resource locator

VA	Vulnerability assessment
VOG	Vessel off-gas
VVER	A Russian acronym for a water-cooled, water-moderated power reactor (a Russian pressurized-water type reactor)
WAC	Waste acceptance criteria
WG	Weapons grade
WGP	Weapons-grade plutonium
WIPP	Waste Isolation Pilot Plant, Carlsbad, New Mexico
WSRC	Westinghouse Savannah River Company
WVNFS	West Valley Nuclear Fuel Services
WWW	World wide web
YM	Yucca Mountain
Y-12	Oak Ridge Y-12 Plant, Oak Ridge, Tennessee
ZPPR	Zero-Power Physics Reactor

1. INTRODUCTION

1.1 BACKGROUND

Uranium-233 (^{233}U) is a man-made isotope produced by the irradiation of thorium with thermal neutrons in a nuclear reactor. Because ^{233}U is fissile [special nuclear material (SNM)], it has been studied for its use as a nuclear-weapon material and as a fuel for nuclear power reactors. This isotope was discovered by John Gofman and others during the time of the Manhattan Project (1944), and its application as a fissile material in atomic bombs was immediately recognized (Rhodes 1995). While ^{233}U is not naturally occurring like the fissile isotope ^{235}U, it can be produced readily by the transmutation of relatively abundant natural thorium by irradiating thorium with neutrons in reactors. The ^{233}U produced is then separated from irradiated thorium targets or thorium containing SNF.

In the late 1940s and early 1950s, concerns arose regarding the long-term availability of uranium as a nuclear fuel. As a result, the government turned its development efforts toward breeder reactors using the much more abundant element thorium (Brooksbank, Patton, and Krichinsky August 1994). In the 1960s, ^{233}U was investigated as a nuclear reactor fuel. Uranium-233 is associated with the thorium fuel cycle, which offers three major advantages over the uranium-plutonium fuel cycle: (1) the greater abundance of thorium, (2) the production of fewer long-lived radionuclides (e.g., ^{237}Np), and (3) very little plutonium is produced; thus, the risks of weapons production and proliferation are lessened. However, major disadvantages of the thorium fuel cycle have also been identified. Thorium does not readily undergo fission. Consequently, the thorium fuel cycle is not self-sustaining. Unlike ^{238}U, which breeds fissile plutonium (i.e., ^{239}Pu) , thorium is not naturally present in economical reactor fuels. Another major problem is that some neutron-irradiated thorium is transformed into another uranium isotope, ^{232}U, which has a decay product, ^{208}Tl, which emits a highly energetic ray when it decays. The latter difficulty complicates the handling of ^{233}U-thorium-based fuel. The intense radiation associated with ^{232}U that is produced with ^{233}U has also complicated the use of ^{233}U in nuclear weapons.

Between 1964 and 1970, when U.S. interest had expanded to include the possibilities of using ^{233}U as a fuel for producing electricity from commercial power reactors, the Atomic Energy Commission (AEC) directed the production and recovery of about 2 metric tons (t) of ^{233}U at the Savannah River Site (SRS) and the Hanford Site (Hanford). SRS produced ^{233}U during five different campaigns between 1964 and 1969 (Orth April 1979). Hanford ^{233}U production was conducted in two distinct campaigns: the first in 1966 [Atlantic Richfield Hanford Company (ARHC) Mar. 11, 1968] and the second in 1970 (Jackson and Walser 1977). Further information on SRS and Hanford ^{233}U production campaigns is provided in Sect. 3 of this handbook. Also, during this period, some ^{233}U was produced from ^{233}U-thorium-fueled commercial reactors, most notably Indian Point Unit 1 (IP-1) [Electric Power Research Institute (EPRI) July 1981].

The United States investigated the use of ^{233}U for weapons, reactors, and other purposes from the 1950s to well into the 1970s. Based on the results of these investigations, it was decided not to use ^{233}U on a large scale. Most of the ^{233}U-bearing materials were placed in long-term storage at various sites. About 2 t of ^{233}U-bearing uranium are in the current U.S. inventory, most of which resides at Oak Ridge National Laboratory (ORNL) and Idaho National Engineering and Environmental Laboratory (INEEL). About one-half of this material is considered high-quality ^{233}U with few impurities (i.e., low ^{232}U impurity contents).

The U.S. Department of Energy (DOE) Defense Programs (DP) Office has declared much of the stored ^{233}U material as excess to national security needs. However, in recent years, several potential uses for ^{233}U have been identified. The application with the greatest near-term potential involves using ^{213}Bi, a decay product of ^{233}U, in radioimmunotherapy. One current small-scale use for ^{233}U is a calibration spike in safeguards procedures for nuclear materials. These and other ^{233}U applications are discussed further in Sect. 5 of this handbook.

Materials containing ^{233}U have several unique radiological properties that require special attention and considerations during the processing and handling of these materials. Major examples of the relatively unique properties and handling characteristics of ^{233}U-bearing materials are:

1. alpha emissions that require containment (unlike the alpha emissions from other uranium isotopes);
2. buildup of gamma emissions from the decay chain of an associated radioisotope, ^{233}U; and
3. emission through off-gas filters of radioactive radon gas (^{220}Rn), whose decay provides external doses from alpha and gamma radiation.

1.2 PURPOSE

This document is an unclassified compendium reference on ^{233}U material properties, processing, and handling guidelines. It has been assembled for future reference in documenting the accumulated data and knowledge base gained throughout the DOE complex from experience with operations and programs involving ^{233}U-bearing materials. This handbook is also intended to serve as a useful and a convenient single comprehensive resource of information on ^{233}U- and ^{233}U-bearing materials to a broad range of users, including technicians and operators involved with the processing, handling, and storage of ^{233}U-bearing materials. For this reason, much of the information presented in the document is useful in training and certification programs. This handbook is intended to serve as a technical reference for a variety of individuals, including engineers, program managers, and workers being trained in the processing and handling of ^{233}U-bearing materials. The handbook is also intended to serve as a guidebook by indicating those resources that provide more detailed information on ^{233}U- and ^{233}U-bearing materials.

This handbook has also been prepared as a commitment identified in the DOE Implementation Plan for the Safe Storage of Uranium-233 (DOE Sept. 25, 1997) which was made in response to the Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 97-1 (DNFSB Mar. 3, 1997). Sub-recommendation 8 of the DNFSB's Recommendation 97-1 identifies the need for the DOE complex to retain the technical knowledge and competency needed to ensure safe storage of ^{233}U-bearing material in the short- and long-term. To assist in achieving that objective, this handbook presents information for four major areas: (1) technical information on the characteristics of ^{233}U, (2) operational information on past ^{233}U processes, (3) handling practices and facility features appropriate for safe ^{233}U operations, and (4) potential applications.

1.3 METHODOLOGY AND CONTENT

In general, this report was prepared by compiling ^{233}U information from unclassified documents and interviews with individuals knowledgeable of ^{233}U material properties, processing, and handling. Additional information provided as a result of expert reviews of drafts of this report have also been incorporated.

The major body of the current report is comprised of four major sections (2 through 5) and three appendixes. Section 2 documents the known properties of ^{233}U. Radiological, criticality, and physical and chemical characteristics are described, followed by a discussion of ^{233}U biochemistry and metabolic pathways. Section 3 is a summary of the processing history of ^{233}U materials and includes a discussion of the radiological and chemical characteristics of six specific ^{233}U material processes: (1) ^{233}U separation from thorium targets, (2) progeny ingrowth removal from ^{233}U materials, (3) ^{233}U oxide preparation, (4) test fuel fabrication, (5) ^{233}U metal preparation, and

(6) separation of ^{233}U from fission products. Handling guidelines for ^{233}U materials are discussed in Sect. 4, which covers the requirements and good practices for safely handling ^{233}U and its decay products. The handling guidelines specifically address (1) radiation protection practices; (2) shielding materials; (3) control of radon emissions; (4) off-gas filtration; (5) confinement in ^{233}U material processing; (6) special chemical hazards; (7) packaging materials and techniques; (8) storage requirements; (9) safeguards, security, and nuclear materials accountability; (10) transportation; (11) safe plant operations; and (12) worker training. Where appropriate, Sect. 4 provides a description of major facilities and equipment needed in various areas for safe ^{233}U material handling. Section 5 offers a discussion of major applications that have been identified for ^{233}U materials. The DOE Standard for storing ^{233}U-bearing materials is provided in Appendix A. This is followed by Appendix B, which provides a list of Internet sites that have information on ^{233}U-bearing materials. Appendix C presents a summary of the characteristics of the current DOE inventory of ^{233}U-bearing materials.

For ease and flexibility in organizing and in preparing this report, each of Sects. 2 through 5 is subdivided into several related topics. Each topic is discussed in a separate subsection wherein information is presented in the following sequence: narrative, figures, and tables. References associated with each topic discussed are listed at the end of each subsection narrative in two groups: references cited and references recommended for further reading on the topic. All references are listed in an author-date format.

For most topics, a basic summary level of information is provided. Coverage of many topics has been selective and restrictive in scope and content. The interested reader will find more detailed information presented in the references cited in each subsection.

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2. PROPERTIES OF ^{233}U AND ^{233}U-BEARING MATERIALS

Major radiological, physical, and chemical properties of ^{233}U and ^{233}U-bearing materials are described in this section. Specific radiological, criticality, physical, and chemical characteristics are first described followed by a discussion of ^{233}U biochemistry and metabolic pathways.

Uranium-233 is a fissile uranium isotope that can be used in nuclear reactors to generate heat and electricity. Nuclei of ^{233}U have 92 protons and 141 neutrons. Uranium-233 is not naturally found. In a thorium-fueled reactor, ^{233}U is formed by irradiating the thorium (mainly ^{232}Th) with neutrons. This reaction produces ^{233}Th, which undergoes two successive beta (negative electron) decays to produce ^{233}U:

$$n + {}^{232}\mathrm{Th} \rightarrow {}^{233}\mathrm{Th} + \gamma$$
$$\downarrow$$
$${}^{233}\mathrm{Th} \rightarrow {}^{233}\mathrm{Pa} + \beta \ (22.3\mathrm{m})$$
$$\downarrow$$
$${}^{233}\mathrm{Pa} \rightarrow {}^{233}\mathrm{U} + \beta \ (27.0 \ \mathrm{d})$$

Uranium-233 contains a parasitic impurity, ^{232}U, another synthetic uranium isotope formed along with ^{233}U during neutron irradiation in a thorium-fueled reactor. The three principal radiochemical reactions that produce ^{232}U are:

(1)

$$n + {}^{232}\mathrm{Th} \rightarrow {}^{231}\mathrm{Th} + 2n$$
$$\downarrow$$
$${}^{231}\mathrm{Th} \rightarrow {}^{231}\mathrm{Pa} + \beta \ (25.5 \ \mathrm{h})$$
$$\downarrow$$
$${}^{231}\mathrm{Pa} + n \rightarrow {}^{232}\mathrm{Pa} + \gamma$$
$$\downarrow$$
$${}^{232}\mathrm{Pa} \rightarrow {}^{232}\mathrm{U} + \beta \ (1.31 \ \mathrm{d})$$

(2)

$$n + {}^{230}\mathrm{Th} \rightarrow {}^{231}\mathrm{Th} + \gamma$$

$$\downarrow$$

$${}^{231}\mathrm{Th}\ \text{(decays as shown above)}$$

(3)

$$n + {}^{233}\mathrm{U} \rightarrow {}^{232}\mathrm{U} + 2n$$

Uranium-232 is also formed by the chain initiating neutron irradiation of ^{235}U, ^{236}U, and ^{237}Np:

(4)

$$n + {}^{235}\mathrm{U} \rightarrow {}^{236}\mathrm{U} + \gamma$$

$$\downarrow$$

$${}^{236}\mathrm{U} + n \rightarrow {}^{237}\mathrm{U} + \gamma$$

$$\downarrow$$

$${}^{237}\mathrm{U} \rightarrow {}^{237}\mathrm{Np} + \beta\ (6.75\ \mathrm{d})$$

$$\downarrow$$

$${}^{237}\mathrm{Np} + n \rightarrow {}^{236}\mathrm{Np} + 2n$$

$$\downarrow$$

$${}^{236}\mathrm{Np} \rightarrow {}^{236}\mathrm{Pu} + \beta\ (22\ \mathrm{h})$$

$$\downarrow$$

$${}^{236}\mathrm{Pu} \rightarrow {}^{232}\mathrm{U} + \alpha\ (2.85\ \mathrm{y})$$

The relative importance of these reactions is highly dependent on the reactor neutron spectrum, ^{230}Th levels in the ^{232}Th, reactor neutron flux, and irradiation time. Both the total amount and the ratio of ^{232}U to ^{233}U produced increases with increasing neutron flux and irradiation time.

The concentration of ^{232}U in ^{233}U materials is typically measured in parts per million (ppm) of the total uranium content. Several measures have been identified for minimizing ^{232}U concentrations. A simple improvement is to avoid using ores that are rich in ^{230}Th. Such ores are readily available. This helps reduce one of the reaction pathways to ^{232}U. Uranium-232 production is also minimized by lowering the exposure of the thorium targets to high-energy neutrons. There are two ways to accomplish this. First, a thorium-fueled reactor can be loaded so that the targets are exposed only to a low-energy neutron flux. Also, using short irradiation times will minimize the buildup of intermediate nuclides (such as ^{231}Th) and subsequent production of ^{232}U.

For a single core fueling cycle under reactor conditions, the resultant ^{232}U concentration is typically less than 0.05 wt % (500 ppm of total uranium). Multiple cycles can build ^{232}U concentration up to 0.15 wt % (1500 ppm of total uranium). At low reactor burnup and well-thermalized neutron production conditions, ^{232}U concentrations were held as low as 5 ppm.

2.1 RADIOLOGICAL PROPERTIES

2.1.1 Alpha and Beta-Gamma Activity

Once produced, ^{233}U undergoes a series of radioactive decays as shown in Fig. 2.1*a* (Carter December 1976). The radiations emitted in the ^{233}U decay chain include alpha (α) and beta (β) particles from the decay of the parent and its radioactive decay products. The ^{233}U decay chain is actually part of the Neptunium Series, shown in Fig. 2.1*b* (Salmon, Loghry, and Ashline November 1995). Uranium-233 is a long-lived (159,200 year half-life) isotope, and its major radiological characteristics are summarized with those of other fissionable isotopes in Table 2.1*a* (Parrington et al. 1996 and Browne and Firestone 1986). The first decay product, ^{229}Th, also has a long half-life (7340 years), and the remaining decay products of the ^{233}U chain are relatively short-lived. Four isotopes in this series also emit gamma rays: ^{233}U, ^{221}Fr, ^{213}Bi, and ^{209}Tl. (The isotope ^{213}Bi has a potential medical application, which is discussed in Sect. 5.1). The ^{233}U decay chain ends with the stable isotope ^{209}Bi. Table 2.1*a* shows that from the standpoint of specific activity, ^{233}U is more than three orders of magnitude more radioactive than ^{235}U and has an activity that is six times lower than that of ^{239}Pu. It should also be noted that the specific activity (9.64 × 10^{-3} Ci/g) of ^{233}U is considerably greater than most of the isotopes of natural uranium (^{238}U: 3.33 × 10^{-7} Ci/g, ^{235}U: 2.16 × 10^{-6} Ci/g, and ^{234}U: 6.248 × 10^{-3} Ci/g). In addition, the specific activity of an associated isotope, ^{232}U (discussed below) is significantly greater (21.4 Ci/g).

Alpha radioactivity can be a significant internal health hazard for persons handling fissionable uranium (^{233}U and ^{235}U) materials. To limit radiation doses to workers from ingestion and inhalation, this high-alpha radioactivity by itself can require glove-box handling for ^{233}U (discussed in Sect. 4). (As mentioned in subsequent sections of this document, ^{233}U-bearing materials usually contain sufficient quantities of ^{232}U, whose decay products emit highly energetic gamma radiation that can pose a significant health hazard to persons handling the material.)

Table 2.1*b* (Kocher May 1980 and U.S. DOE December 1997) summarizes and compares the major radiological characteristics of ^{233}U and its decay products (see also Fig. 2.1*a*). The ranges of radiation decay energies associated with these nuclides are reported in Table 2.1*c* (Kocher May 1980 and Browne and Firestone 1986).

2.1.2 Uranium-232 Presence and Effects

The amount of ^{232}U associated with ^{233}U in the current U.S. inventory of separated ^{233}U can be divided into eight major batches based on the characteristics of the ^{233}U. Table 2.1*d* (Forsberg and Krichinsky January 1998) lists these batches and their characteristics, including the levels of ^{232}U impurity. The quality of the batches can be measured by two indexes. Most batches are almost isotopically pure ^{233}U—except for Batches 1 and 8, both of which contain significant quantities of ^{235}U. For most applications requiring ^{233}U, the high ^{235}U content severely diminishes the value of the ^{233}U. The second index of quality is the concentration of ^{232}U in the ^{233}U. If the ^{232}U concentration is high, the longer-term radiation levels associated with these batches will be high. The concentration of ^{232}U in units of parts of ^{232}U per million parts of ^{233}U is shown in the parenthesis above each column. The first two batches have high ^{232}U concentrations.

Major radiological characteristics of ^{232}U are listed in Table 2.1*a*. Uranium-232 is important because of its decay chain, shown in Fig. 2.1*c*, and the significant impacts of the concentration of ^{232}U in ^{233}U on the handling of ^{233}U materials. Uranium-232 has a half-life of about 70 years followed by short half-lives of various alpha-emitting daughter products. This decay chain includes an unstable decay product, ^{208}Tl, which emits a beta particle accompanied by a penetrating gamma ray (2.6 MeV). It is this gamma radiation that is primarily responsible for the shielding requirements that are needed with ^{233}U materials. For ^{233}U-bearing materials with significant quantities of ^{232}U (e.g., 20 ppm or greater), the decay of ^{208}Tl can build in unwanted radiation levels in 4 to 6 weeks. Other, less energetic, gamma rays from ^{212}Bi and other radionuclides in the

^{232}U decay chain are also of concern, although they occur at considerably lower yields (intensities) than the thallium emissions. The final product in the ^{232}U decay chain is the stable isotope ^{208}Pb.

Table 2.1*e* (Kocher May 1980 and U.S. DOE December 1997) summarizes and compares the major radiological characteristics of ^{232}U and its decay products [see also Fig. 2.1*c* (Carter December 1976 and Parrington et al. 1996)]. The ranges of radiation decay energies associated with these nuclides are reported in Table 2.1*f* (Kocher May 1980 and Browne and Firestone 1986).

The relative abundance of ^{232}U and the alpha, beta, and gamma emissions associated with the ^{232}U decay chain dictate much of the handling practices for its sister isotope, ^{233}U. Handling guidelines for ^{233}U materials are discussed further in Sect. 4.

Another hazard associated with the ^{232}U decay chain is the presence of ^{220}Rn, a high-energy (6.4 MeV) alpha emitter. Because at normal temperatures and pressures, radon exists as a gas, this causes additional requirements for the storage and handling of ^{233}U materials. Further discussion of the problem of radon generation from ^{233}U materials is provided in Sect. 2.3.

2.1.3 References for Sect. 2.1

Listed below are the references cited in Sect. 2.1. This is followed by a list of additional sources providing more detailed information on the radiological properties of ^{233}U (and ^{232}U) materials.

2.1.3.1 References Cited

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Carter, W. L. December 1976. *HTGR Fuel Refabrication: Calculation of Radiation Dose to Uranium-Loaded Resin from ^{232}U, ^{233}U, ^{234}U, ^{235}U, ^{236}U, and Their Daughters*, GCR: 76-18, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Forsberg, C. W., and A. M. Krichinsky. January 1998. *Strategy for the Future Use and Disposition of ^{233}U: Overview*, ORNL/TM-13550, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Kocher, D. C. May 1980. *A Radionuclide Decay Data Base–Index and Summary Table*, NUREG/CR-1413, ORNL/NUREG-70, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Parrington, J. R., et al. 1996. *Nuclides and Isotopes—Chart of the Nuclides*, 15th ed., General Electric Co., San Jose, Calif.

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ORNL DWG 97-5710

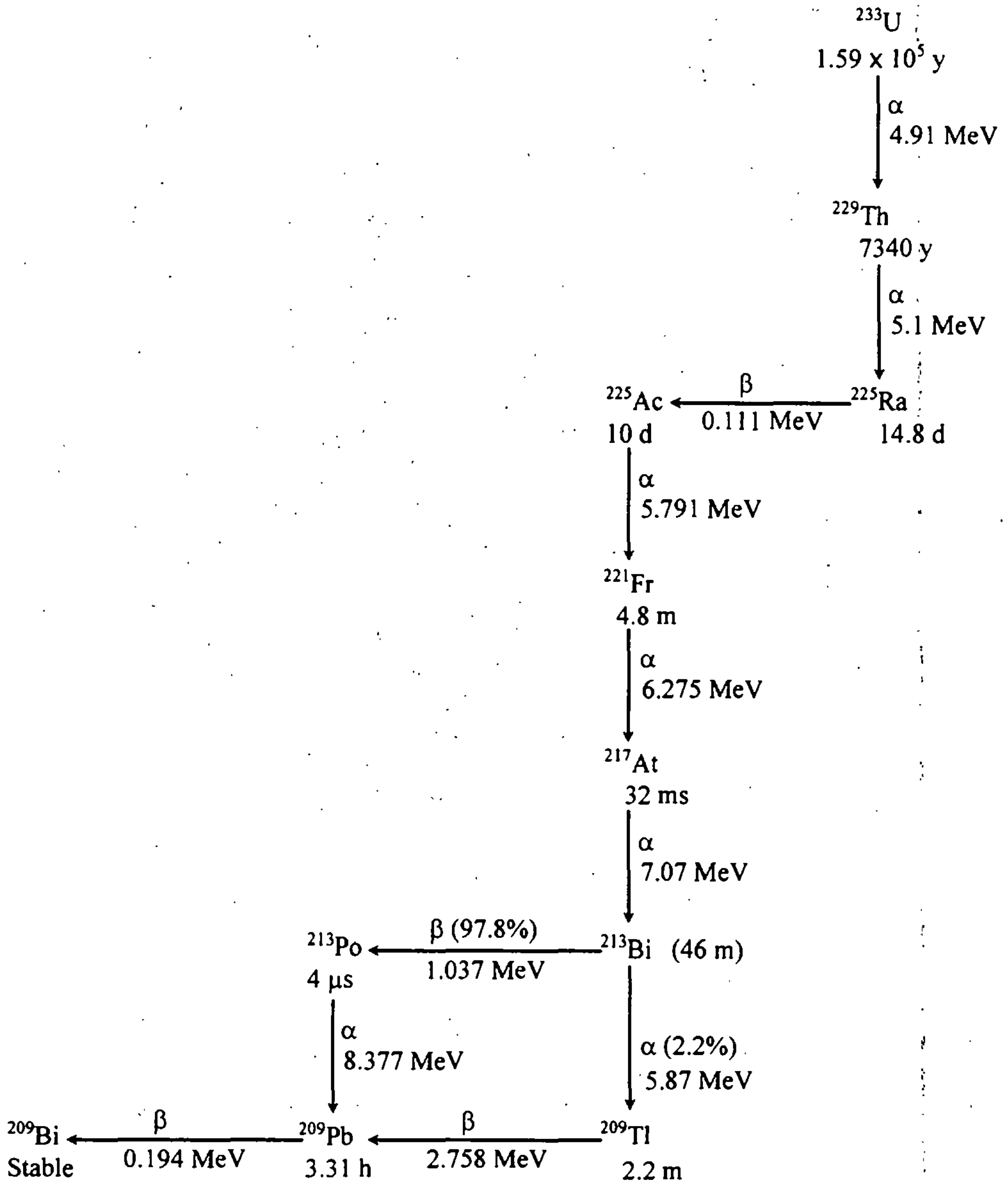

Fig. 2.1*a*. ^{233}U decay chain. *Adapted from Carter December 1976.*

ORNL DWG 97-5709

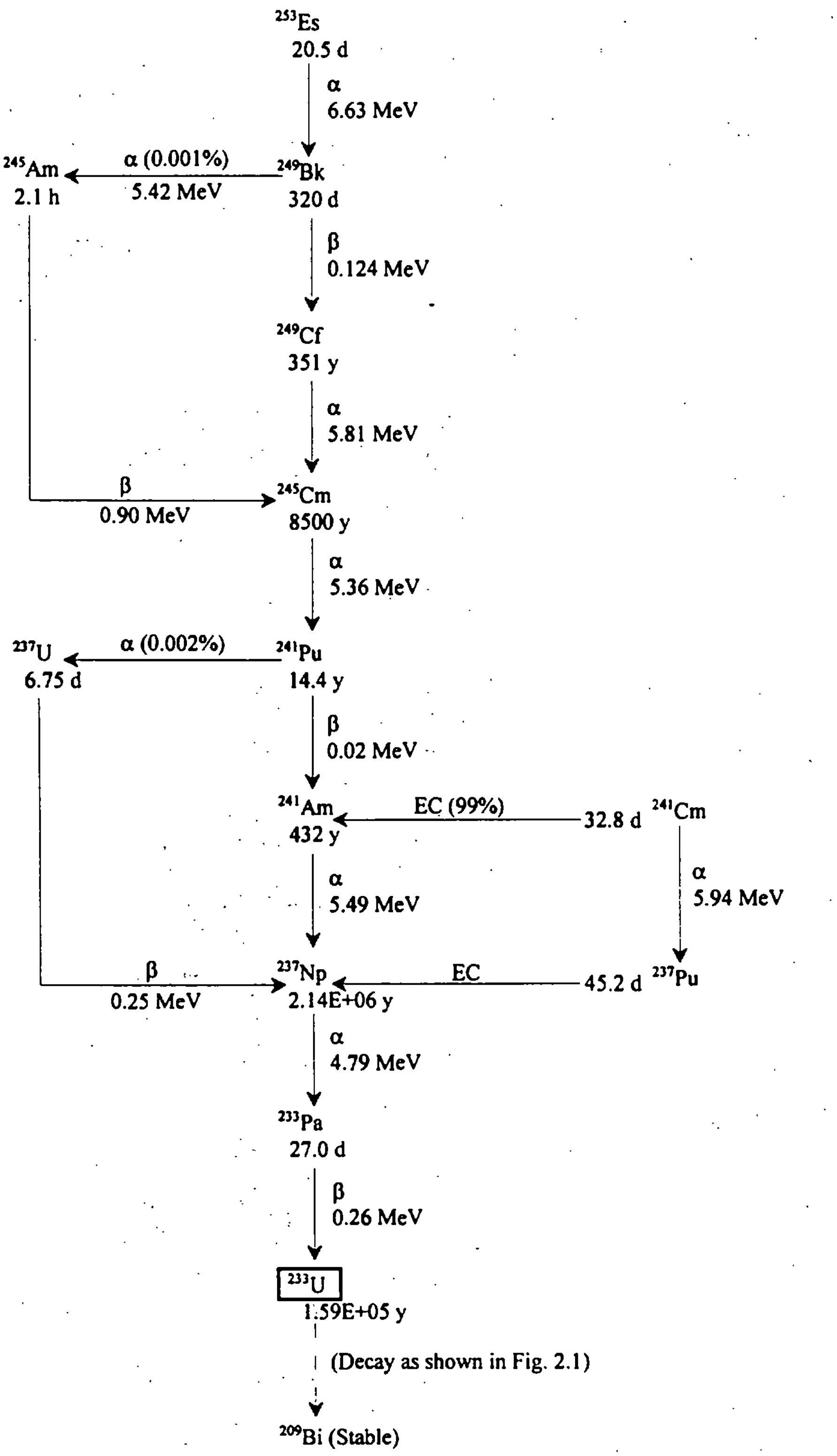

Fig. 2.1*b*. Decay chains for neptunium series of actinides. *Adapted from Salmon, Loghry, and Ashline November 1995.*

ORNL DWG 97-5711

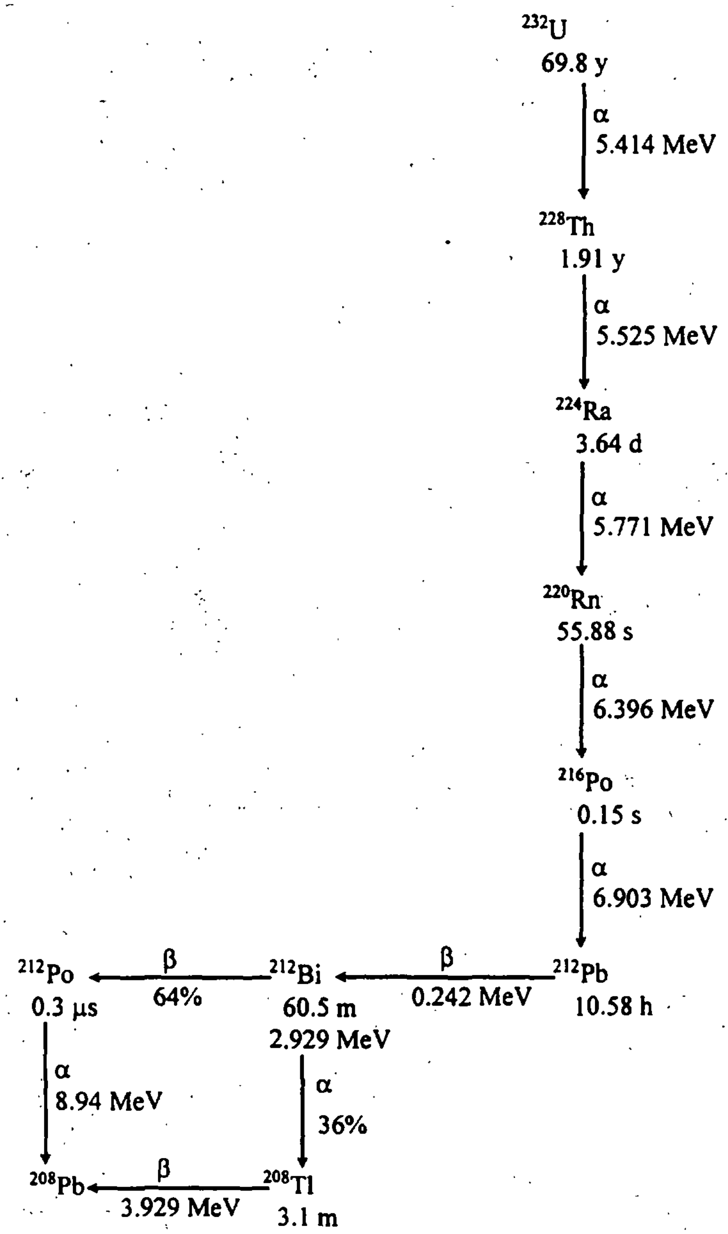

Fig. 2.1c. ^{232}U decay chain. *Adapted from Carter December 1976 and Parrington, et al. 1996.*

Table 2.1*a*. Major radiological characteristics of ^{232}U, ^{233}U, and other selected fissile radionuclides[a]

Property	^{233}U	^{232}U	^{235}U	^{239}Pu	^{241}Pu
Atomic number (Z)	92	92	92	94	94
Atomic mass number (A) (Isotopic mass, amu)	233 (233.039627)	232 (232.03713)	235 (235.043922)	239 (239.052156)	241 (241.05687)
Half-life (years)	159,200	69.8	703,700,000	24,110	14.4
Modes of radioactive decay and average energy (MeV) per disintegration					
Alpha (α) emissions	4.814	5.306	4.378	5.101	0.0001
Electron emissions (ϵ)	0.0055		0.0426		
Gamma (γ) and X-ray emissions	0.0013	0.0002	0.1561	0.0001	0.0052
Total[b]					
(MeV/disintegration)	4.821	5.307	4.577	5.101	0.0053
(W/Ci)	0.02857	0.03146	0.02713	0.03024	3.2E-05
Specific activity (Ci/g)	9.680E-03	21.40	2.161E-06	6.216E-02	103.0
Initial daughter product from decay	^{229}Th[c]	^{228}Th[d]	^{231}Th	^{235}U	^{241}Am

[a] Based on Parrington et al. 1996 and Browne and Firestone 1986.

[b] Also referred to as the "Q" value, which is the sum of the average energies for different radiation types in keV/disintegration or W/CI. Includes contributions from alpha and beta particles, discrete electrons, and photons. The "value" indicates the amount of energy (heat) that could be deposited in a radioactive material from each decay event if none of the radiation escaped from the material.

[c] See decay chains shown in Figs. 2.1*a* and 2.1*b*.

[d] See decay chain shown in Fig. 2.1*c*.

Table 2.1*b*. Major radiological characteristics of ^{233}U and its decay products[a]

Nuclide	Atomic number	Half-life[b]	Specific activity (Ci/g)	Principle modes(s) of decay		Average radiation energies (MeV)[d]			"Q" value[e]	
				Type[c]	Percent	α	ε	γ and X	(MeV/dis)	(W/Ci)
^{233}U	92	1.592E+05 y	9.680E−03	α	100	4.8141	0.0055	0.0013	4.821	2.857E−02
^{229}Th	90	7.340E+03 y	[f]	α	100	4.8620		0.0343	4.896	2.902E−02
^{225}Ra	88	14.2 d	[f]	β	100		0.1057	0.0137	0.119	7.08E−04
^{225}Ac	89	10.0 d	[f]	α	100	5.7501	0.0257	0.0176	5.793	3.434E−02
^{221}Fr	87	4.9 m	[f]	α	100	6.3571	0.0084	0.0277	6.393	3.789E−02
^{217}At	85	3.23E−02 s	[f]	α	100	7.0657		0.0002	7.066	4.189E−02
^{213}Bi	83	45.59 m	[f]	α β	2.16 97.84	0.1268	0.4563	0.0825	0.666	3.95E−03
^{213}Po	84	4.2E−06 s	[f]	α	100	8.3757			8.376	4.964E−02
(^{209}Tl)[g]	81	2.2 m	[f]	β	100		2.7580		2.758	1.634E−02
^{209}Pb	82	3.253 h	[f]	β	100		0.1980		0.198	1.17E−03
^{209}Bi	83	(stable)								

[a] Average energy per nuclide disintegration. Adapted from Kocher May 1980 and U.S. DOE December 1997.

[b] y = years, d = days, h = hours, m = minutes, and s = seconds.

[c] α = alpha emission, β = negative beta emission, and γ = gamma emission.

[d] α = alpha emission, ε = total electron emissions, and γ and X = gamma and X-ray photon emissions.

[e] The sum of the average energies for different radiation types in MeV/disintegration or W/Ci. Includes contributions from alpha and beta particles, electrons, and photons. The "value" indicates the amount of energy (heat) that could be deposited in a radioactive material from each decay event if none of the radiation escaped from the material.

[f] In a decay chain, the activity of each decay product is controlled by the activity of the parent. The activities of these decay products can never exceed the activity of the parent, taking into account any branching fractions.

[g] Daughter product from the alpha emission of ^{213}Bi in a branch of the ^{233}U decay chain.

Table 2.1*c*. Spectrum of major radiation decay energies (MeV/dis) for ^{233}U and its decay products[a]

Nuclide	Principle mode(s) of decay	Alpha (α) emissions		Total electron (ϵ) emissions		Gamma (γ) and X-ray emissions		Average total ("Q" value)[c]
		Range	Average[b]	Range	Average[b]	Range	Average[b]	
^{233}U	α	4.3072–4.8247	4.8141	0.0001–0.0062	0.0055	0.0011–1.1190	0.0013	4.821
^{229}Th	α	4.4783–5.0774	4.8620			0.0173–0.2900	0.0343	4.896
^{225}Ra	β			0.0000–0.3620	0.1057	0.0109–0.0403	0.0137	0.119
^{225}Ac	α	4.9015–5.8288	5.7501	0.0070–0.526	0.0257	0.0104–0.5260	0.0176	5.793
^{221}Fr	α	5.6893–6.4000	6.3571	0.0040–0.409	0.0084	0.0099–0.4091	0.0277	6.393
^{217}At	α	6.4835–7.0673	7.0657			0.0000–0.5940	0.0002	7.066
^{213}Bi	α, β	0.0000–5.8691	0.1268	0.0130–1.100	0.4563	0.0090–1.1001	0.0825	0.666
^{213}Po	α	7.6141–8.3800	8.3757					8.376
(^{209}Tl)[d]	β			0.0092–3.3800	2.7580			2.758
^{209}Pb	β			0.0010–0.6450	0.1980			0.198
^{209}Bi	(stable)							

[a] Adapted from Kocher May 1980 and Browne and Firestone 1986.

[b] Most probable or expected value in range specified.

[c] As defined in Table 2.1*b*.

[d] Daughter product from the α emission of ^{213}Bi in a branch of the ^{233}U decay chain.

Table 2.1d. Levels of ^{232}U impurities and quality of major batches of ^{233}U in inventory[a]

Batch No.	Site[b]	Material	Uranium isotopic composition				Measures of quality[c]	
			Total U (kg)	^{235}U (kg)	^{233}U (kg)	^{232}U (ppm)[d]	Total U (kg)/^{233}U (kg)	^{232}U (kg) × 10^6/^{233}U (kg)
1	ORNL	U_3O_8 monolith in >400 welded stainless steel cans [Consolidated Edison Uranium Solidification Program (CEUSP) material]	1042.6	796.3	101.1	140	10.3	1440
2	ORNL	UO_x powder in 140 welded inner aluminum cans	67.4	0.00	61.6	165	1.1	181
3	INEEL/RWMC	Unirradiated rods and pellets in 145 drums	35.1	0.00	34.2	21	1.03	22
4	ORNL	U_3O_8 monolith in 27 welded stainless steel cans placed in tin-plate cans	65.2	0.00	60.3	15	1.08	16
5	INEEL/ICPP	Unirradiated light-water breeder reactor (LWBR) fuel with 14 MT natural thorium	323.5	0.00	317.4	9	1.02	9
6	ORNL	UO_x powder in 174 stainless steel screw-top cans	96.5	0.00	91.2	7	1.06	7
7	ORNL	UO_x powder in 1743 welded stainless steel plates	45.7	0.00	44.8	7	1.02	7
8	Y-12[e]		42.6	38.7	0.8	0.113	53.2	6

[a] Adapted from Forsberg and Krichinsky January 1998. These data do not represent the entire inventory total because many small batches are not listed.

[b] The following site abbreviations are used: ORNL = Oak Ridge National Laboratory, INEEL = Idaho National Engineering and Environmental Laboratory, RWMC = Radioactive Waste Management Complex (located at INEEL), ICPP = Idaho Chemical Processing Plant (located at ICPP), and Y-12 = Oak Ridge Y-12 Plant.

[c] A low number implies a higher quality.

[d] Based on total uranium. These concentrations need to be decayed to a common date.

[e] May be classified as impure highly enriched uranium (HEU) or within the ^{233}U inventory.

Table 2.1*e*. Major radiological characteristics of ^{232}U and its decay products[a]

Nuclide	Atomic number	Half-life[b]	Specific activity (Ci/g)	Principle modes(s) of decay		Average radiation energies (MeV)[d]			"Q" value[e]	
				Type[c]	Percent	α	ϵ	γ and X	(MeV/dis)	(W/Ci)
^{232}U	92	6.89E+01 y	2.140E+01	α	100	5.3065		0.0002	5.307	3.146E-02
^{228}Th	90	1.913 y	*f*	α	100	5.3992	0.0201	0.0034	5.423	3.214E-02
^{224}Ra	88	3.66 d	*f*	α	100	5.6751	0.0022	0.0103	5.688	3.372E-02
^{220}Rn	86	55.6 s	*f*	α	100	6.2878		0.0005	6.288	3.727E-02
^{216}Po	84	1.50E-02 s	*f*	α	100	6.7785			6.779	4.018E-02
^{212}Pb	82	10.64 h	*f*	β	100		0.1752	0.1453	0.320	1.90E-03
^{212}Bi	83	1.0092 h	*f*	α β	35.94 64.06	2.1740	0.5025	0.1061	2.783	1.649E-02
^{212}Po	84	2.98E-07 s	*f*	α	100	8.7844			8.784	5.207E-02
(^{208}Tl)[g]	81	3.053 m	*f*	β	100		0.5979	3.3742	3.972	2.354E-02
^{208}Pb	82	(stable)								

[a] Average energy per nuclide disintegration. Adapted from Kocher May 1980 and U.S. DOE December 1997.

[b] y = years, d = days, h = hours, m = minutes, and s = seconds.

[c] α = alpha emission, β = negative beta emission, and γ = gamma emission.

[d] α = alpha emission, ϵ = total electron emissions, and γ and X = gamma and X-ray photon emissions.

[e] The sum of the average energies for different radiation types in MeV/disintegration or W/Ci. Includes contributions from alpha and beta particles, electrons, and photons. The "value" indicates the amount of energy (heat) that could be deposited in a radioactive material from each decay event if none of the radiation escaped from the material.

[f] In a decay chain, the activity of each decay product is controlled by the activity of the parent. The activities of these decay products can never exceed the activity of the parent, taking into account any branching fractions.

[g] Daughter product from the alpha emission of ^{212}Bi in a branch of the ^{233}U decay chain.

Table 2.1*f*. Spectrum of major radiation decay energies (MeV/dis) for ^{232}U and its decay products[a]

Nuclide	Principle mode(s) of decay	Alpha (α) emissions		Total electron (ϵ) emissions		Gamma (γ) and X-ray emissions		Average total ("Q" value)[c]
		Range	Average[b]	Range	Average[b]	Range	Average[b]	
^{232}U	α	4.5029–5.3203	5.3065			0.0000–0.8744	0.0002	5.307
^{228}Th	α	5.1384–5.4233	5.3992	0.0150–0.2160	0.0201	0.0000–0.2158	0.0034	5.423
^{224}Ra	α	5.0341–5.6856	5.6751	0.0000–0.6500	0.0022	0.0010–0.6510	0.0103	5.688
^{220}Rn	α	5.7486–6.2883	6.2878			0.0000–0.5498	0.0005	6.288
^{216}Po	α	5.9850–6.7785	6.7785					6.779
^{212}Pb	β			0.0000–0.9880	0.1752	0.0094–0.4152	0.1453	0.320
^{212}Bi	α, β	0.0000–10.5487	2.1740	0.0130–2.1970	0.5025	0.0090–2.2000	0.1061	2.783
^{212}Po	α	6.8420–11.6500	8.7844					8.784
(^{208}Tl)[d]	β			0.0130–2.6110	0.5979	0.0092–3.5000	3.3742	3.972
^{208}Pb	(stable)							

[a] Adapted from Kocher May 1980 and Browne and Firestone 1986.

[b] Most probable or expected value in range specified.

[c] As defined in Table 2.1*b*.

[d] Daughter product from the α emission of ^{212}Bi in a branch of the ^{233}U decay chain.

2.2 NEUTRON GENERATION OF RADIOLOGICAL CONCERN

2.2.1 Discussion

The artificial isotope ^{233}U is fissile. Consequently, the fissioning of ^{233}U like that of ^{235}U, ^{239}Pu, and ^{241}Pu generates neutrons. Both ^{233}U and ^{235}U are fissionable by thermal neutrons, which have an average speed of 2200 m/s and an average kinetic energy of 0.025 eV.

The fission of a heavy nucleus, such as ^{233}U, by the absorption of a thermal neutron, results in the splitting of that nucleus into two or more nuclei of intermediate mass and the average emission of 2 to 3 neutrons. In ^{233}U fission, the resulting fission fragments are formed with an average total kinetic energy of 163 MeV. In general, their masses are unequal—the most probable heavy mass number is 139. However, investigations such as Katcoff November 1960 have detected fission products throughout the mass region range 72 to 166. For comparison, Table 2.2*a* (Katcoff November 1960 and Lynch 1989) gives a breakdown of the average energy (MeV) released from the fission of selected uranium and plutonium radionuclides.

The primary nuclide products from the fission of ^{233}U by slow (thermal) neutrons are given in Table 2.9 and Fig. 2.12 of Benedict, Pigford, and Levi 1981. That reference also indicates that only a few of the primary ^{233}U fission products are stable, the rest being beta-emitting radionuclides. For comparison, the nuclear properties of ^{233}U and those of other fissile nuclides are listed in Table 2.2*b*. This is followed by Table 2.2*c* (Etherington 1958 and Benedict, Pigford, and Levi 1981), which is a list of capture and fission cross sections for ^{233}U and other nuclides which fission with thermal neutrons. Table 2.2*c* also gives the average number of neutrons produced per nuclide undergoing fission (ν) and per neutron absorbed (η). The value for η is higher for ^{233}U than for other fissile nuclides, and this property has given ^{233}U an important consideration as a potential nuclear fuel in thermal-neutron reactors (Benedict, Pigford, and Levi 1981). In fact, a thermal breeder is feasible only with ^{233}U in the fuel. In the early years of nuclear power development, it was felt that as natural uranium (and ^{235}U) became scarcer and the conservation of neutrons and fissile material became more important, the production of ^{233}U from the more abundant natural thorium offered the potential for greater long-term significance as a nuclear fuel.

The decay products of ^{232}U, shown in Fig. 2.1*c*, contribute not only an abundance of energetic alpha and beta emissions, but also an abundance of energetic gamma rays and a small number of neutrons from (γ, n) reactions with light elements that may contaminate uranium-bearing material. Shielding is also necessary because of the high-energy neutrons from alpha decay in ^{233}U-bearing materials. The alphas from the decay of ^{233}U, ^{232}U, and ^{228}Th interact with light elements such as beryllium (Be), carbon (C), oxygen (O), and fluorine (F) to form neutrons. This effect can add a neutron component to worker radiation exposure. The reactions of concern include:

$$\alpha + {}^{9}Be \rightarrow {}^{12}C + n$$
$$\alpha + {}^{13}C \rightarrow {}^{16}O + n$$
$$\alpha + {}^{17}O \rightarrow {}^{20}Ne + n$$
$$\alpha + {}^{19}F \rightarrow {}^{22}Na + n$$

Uranium-232 also has a slight tendency to fission upon neutron capture. However, its relatively dilute concentration (along with its association with the highly fissile ^{233}U) presents an insignificant contribution to nuclear criticality, which is discussed in Sect. 2.4.

2.2.2 References for Section 2.2

Listed below are references cited in Sect. 2.2. This is followed by a list of additional sources that provide more detailed information on neutron generation associated with ^{233}U-bearing materials.

2.2.2.1 References Cited

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Table 2.2*a*. Breakdown of energy released (MeV) for fission of various radionuclides[a]

Recoverable energy form	^{233}U	^{235}U	^{239}Pu
Light fission fragments[b]	97	98	100
Heavy fission fragments[c]	66	67	72
Fission product decay β-particles γ-rays	 9 14	 9 15	 9 14
Fission neutrons (kinetic energy)	5	4.9	5.8
Total recoverable energy (MeV)	191	194	201

[a] Adapted from Katcoff November 1960 and Sect. 11 in Lynch 1989.

[b] Nuclides of atomic mass number (A) < 120. The most probable light mass number is 95.

[c] Nuclides of A ≥ 120. The most probable heavy mass number is 139.

Table 2.2*b*. Properties of fissile radionuclides[a]

Nuclide	Half-life (years)	Principal mode(s) of decay	Effective decay energy (MeV)	Specific activity (Ci/g)	Fission thermal energy cross section[b] (barns)	Neutrons produced per fission	Major source
^{232}U	6.98E+01	α	5.414	2.140E+01	75	3.13	n capture by natural Th
^{233}U	1.592E+05	α	4.909	9.680E-03	531	2.492	n capture by ^{232}Th
^{235}U	7.037E+08	α	4.681	2.161E-06	582	2.418	Natural U (0.72 atom %)
^{239}Pu	2.411E+04	α	5.243	6.216E-02	743	2.871	n capture by ^{238}U
^{241}Pu	1.44E+01	β	0.007	1.030E+02	1009	2.927	n capture by ^{240}Pu

[a] Source: Benedict, Pigford, and Levi 1981.

[b] Variation of the fission factor η with neutron energy for ^{233}U, ^{235}U, and ^{239}Pu is shown in Fig. 2.4*a* in Sect. 2.4.

Table 2.2c. Properties of fissile nuclides for thermal (2200 m/s) neutrons[a]

Property	^{232}U	^{233}U	^{235}U	^{239}Pu	^{241}Pu
Cross sections (barns)					
Fission (σ_f)	75.2	531.1	582.2	742.5	1009
Capture (σ_c)	300	47.7	98.6	268.8	368
Absorption (σ_a)	375	578.8	680.8	1011.3	1377
σ_c/σ_f	4.0	0.0898	0.169	0.362	0.3647
Neutrons produced					
Per fission (ν)	3.13	2.492	2.418	2.871	2.927
Per neutron absorbed (η)	0.63	2.287	2.068	2.108	2.145

[a] Adapted from Etherington 1958 and Appendix C of Benedict, Pigford, and Levi 1981.

2.3 RADON GENERATION

2.3.1 Origin and Characteristics

Another hazard associated with the ^{232}U decay chain is the presence of the noble gas isotope ^{220}Rn, a high-energy (6.4 MeV) alpha emitter that has a short half-life of 55.3 s. Thorium-228 is the first and longest-lived decay product of ^{232}U and, having a half-life of 1.9 years, will reach 99% secular equilibrium with chemically separated ^{232}U within 13 years. The remainder of the decay chain, which includes ^{220}Rn and its progeny, will have the same activity as ^{228}Th when the only means of removal is radioactive decay—for example, the radon is not removed by ventilation or other means.

Radon's freezing points and boiling points are −71°C and −62°C, respectively. Thus, it is a gas at all practical conditions, which can cause problems during the storage and handling of ^{233}U materials. This necessitates special precautions for control and holdup of ^{220}Rn in ventilation systems to allow filtration of the radon and its progeny (U.S. DOE Jan. 2, 1998). If the holdup time for ^{220}Rn in a storage and ventilation system of ^{233}U-bearing materials is sufficiently long, the out-leakage of ^{220}Rn and its decay chain products can be prevented or at least substantially reduced. As with any other gas, the extent to which radon can be moved by ventilation will depend primarily on the physical form of the uranium matrix. Gas flow through a source could easily alter the concentration of radon and its progeny. The activity of ^{220}Rn in the source would be expected to re-equilibrate within minutes following the stop of such a purge, while its progeny would return to maximum activities within a few days.

Control of ^{220}Rn in off-gas cleanup systems is necessary to preserve as low as reasonably achievable (ALARA) conditions for workers handling ^{233}U-bearing materials. Inhalation of radon decay products, primarily those associated with ^{222}Rn, has been demonstrated to cause elevated levels of lung cancer due to direct irradiation of the respiratory system [National Council on Radiation Protection and Measurements (NCRP) 77 1984 and International Council on Radiological Protection (ICRP) 50 1987]. It should be noted that most research of lung cancer causation by radon has been performed for ^{222}Rn progeny; however, this is simply because of the relative abundance of the isotope in habited structures. The effect per unit exposure for ^{220}Rn progeny is considered to be approximately the same as for ^{222}Rn progeny and is reflected as such in radon-specific occupational exposure limits such as those used by the DOE (U.S. DOE Dec. 14, 1993).

The short half-life of ^{220}Rn implies that it will decay shortly after it is released to the environment, and therefore, most of the radiological impact in the vicinity of a facility emitting this nuclide is a result of the ^{212}Pb daughter and subsequent progeny (Till February 1976). Radon progeny will become charged and will usually attach very quickly to aerosols following creation. The fraction that remains unattached is usually quite small and highly reactive and will attach with high probability to the air passages of personnel breathing the air. As for attached progeny, most aerosol particles carry an electrical charge and are relatively massive, with median diameters typically greater than 0.1 μm. The particles are, therefore, capable of attaching to the surfaces of the respiratory tract either by impingement or by electrostatic precipitation. Essentially all dose, or risk, from radon is associated with alpha decays from radon progeny attached to tissues of the respiratory system.

The isotope ^{220}Rn can create a potential effluent treatment problem unique to facilities that handle ^{233}U. Depending on the original impurity level of ^{232}U, this can easily equate to a substantial amount of ^{220}Rn being produced. Additionally, some of the subsequent progeny following radon (e.g., ^{208}Tl) are strong gamma emitters, which means that a direct exposure hazard will be generated. This will occur at the storage location as well as at any point where the radon is purposely collected, such as an off-gas filtration system.

2.3.2 Comparisons of Radon from ^{233}U–^{232}U-Bearing Materials and Natural Uranium

The radon problem for ^{233}U–^{232}U-bearing materials differs in several ways from that associated with naturally occurring uranium. These differences include:

1. The nuclear decay chain of isotopically pure ^{233}U does not contain any radon isotope. The isotope ^{220}Rn is formed in the decay sequence of ^{232}U, which is typically present at ppm levels in the DOE inventory of ^{233}U.
2. Naturally occurring uranium contains the decay products that have grown into the host mineral over its entire existence. By contrast, ^{232}U in storage has been isolated from decay products through multiple chemical processing operations. However, the half-lives of ^{232}U decay products are sufficiently short such that the ^{232}U decay chain progeny can become a significant radiological source within a few months following chemical purification. The rate of activity build-in of the decay chain will be controlled by the 1.9-year half-life of ^{228}Th, meaning that more than 99% secular equilibrium will be attained within a period of 13 years.

3. The isotope ^{220}Rn, which is a direct decay product of ^{228}Th, has a half-life of only 55.6 s, while the principal isotope formed from natural uranium, ^{222}Rn, has a half-life of 3.82 d. Therefore, a much longer time period (by a factor of about 6,000) is available for the latter to diffuse out of the host environment.
4. The follow-on decay scheme for ^{220}Rn (from ^{232}U) to a stable isotope (^{208}Pb) is rapid, with the longest-lived member of the chain being ^{212}Pb, which has a half-life of 10.6 h. By contrast, the decay chain for ^{222}Rn (from ^{238}U) contains ^{210}Pb, which has a half-life of 22.3 years.
5. The differences in the residence times of the radon isotopes, ^{220}Rn and ^{222}Rn, is a result of the differences in their half-lives. Due to its 55-s half-life, ^{220}Rn can travel only short distances prior to decaying. By comparison, ^{222}Rn, which has a 3.8-day half-life, can travel great distances. Consequently, an off-gas delay system that would reduce the concentration of ^{220}Rn by an order of magnitude would have virtually no effect on an equivalent amount of ^{222}Rn activity.
6. Direct alpha irradiation of the respiratory system is the prime internal dose pathway for both ^{220}Rn and ^{222}Rn progeny. The detrimental effect from this type of exposure far outweighs the dose equivalent resulting from gamma or beta exposure from decay daughters. As for external radiation fields in the vicinity of a source or collection trap, both ^{220}Rn and ^{222}Rn can pose a significant external exposure hazard at high activities, although the gamma radiation from the ^{220}Rn chain is more penetrating, due in particular to ^{208}Tl, and has a higher relative emission abundance.

2.3.3 Treatment and Containment

Release of radon to the working environment could create both internal and external radiation hazards. Because ^{220}Rn is short-lived, a first line of defense for controlling the release of this gas is retention within the primary containment system. The functional requirement is that such a storage system should not necessarily require hermetic containment, but instead should attempt to achieve a hold-up time that is long enough to enable only a small fraction of radon to escape the system under typical operating conditions. Note also that the radon progeny will be electrically charged upon creation and are, therefore, not likely to travel very far in a turbulent system without plating to surfaces.

Use of activated carbon (charcoal) has been shown to be an excellent method for decontamination of ^{220}Rn from off-gas streams. As indicated in Ackley April 1975, activated (charcoal) appeared to hold promise, based on theoretical assumptions coupled with ^{222}Rn measurement data, as an effective adsorbent for ^{220}Rn holdup and removal. However, this application could be limited by charcoal's potential as a fire and explosion hazard. (Under certain conditions, the combination of NO_x compounds and charcoal constitutes a serious fire hazard). Use of an inorganic adsorbent in place of charcoal was also considered.

A summary of potential methods for the removal of ^{220}Rn from HTGR fuel-reprocessing and -refabrication off-gas streams is documented in Ackley April 1975. This source reviews available ^{222}Rn adsorption data (including materials used to retain radon at various concentrations) and identifies a useful theoretical treatment for adsorber design calculations. This document also provides a survey of documented investigations relating to ^{222}Rn adsorption on charcoal and then derives a predictive model for application to ^{220}Rn. Discussion of the problem of ^{220}Rn release during the carbonization, conversion, and coating steps of the refabrication of HTGR fuel has also been documented by Carter April 1975 and December 1976.

Actual measurements of ^{220}Rn adsorption onto activated charcoal from fast-moving gas streams were performed in 1998 (Coleman March 1999) to determine the effectiveness of a coconut-based activated charcoal on the decontamination of off-gas during remediation tasks at an ORNL facility where ^{233}U fuel was stored. The measurement information is summarized in Sect. 4 as part of the discussion covering off-gas filtration design. In summary, the charcoal proved to be a very effective material for reducing the concentration of ^{220}Rn in the off-gas stream.

The problem of ^{220}Rn release has been apparent during handling and storing large volumes of fissile solution. In the early 1970s, one such solution, which used soluble neutron adsorbers for criticality control, was tested at ORNL. This solution consisted of an aqueous nitrate of purified uranium product from the Consolidated Edison Indian Point Reactor. After two years, the radioactive daughters of ^{220}Rn were found in the vapor space of a 5,000-gal tank at ORNL. The tank was used to store nitrate solution. Subsequent deposition of these radionuclides were also found in unshielded off-gas piping. The problem was resolved by installing a de-entrainment device and a shielded Mini-Caisson™ filter near the storage tank (Parrott, Nicol, and Nichols 1971).

The off-gas system of the nitrate solution tank was modified to include a containment separator and a small absolute filter. Rerouting of the piping eliminated an additional problem of entrainment of solution that was occurring at a low point in the system. The entrainment separator, installed in a vertical section of the off-gas piping, provided four 180° direction changes for the air flow. The absolute filter had a capacity of 50 standard cubic feet per minute (scfm). Eventually 4 in. of lead shielding were added to the filter to reduce the radiation to a permissible level. As expected, the dominant daughter product from the ^{220}Rn decay in the off-gas system was found to be ^{212}Pb. Because of the 10.6-h half-life of ^{212}Pb, only a few days after the storage tank was sparged, the radioactivity level of the filter was reduced to background (Parrott, Nicol, and Nichols 1971).

From the standpoint of ^{233}U–^{232}U storage, ^{220}Rn is short-lived and, thus, does not contribute to container pressurization. Vacuum leak-tightness of primary and secondary containers is therefore not necessary if the holdup time for ^{220}Rn in the ^{233}U–^{232}U material storage configuration is long enough to prevent out-leakage of ^{220}Rn and its decay products.

The radiological contamination associated with the escape of ^{220}Rn from a containment system in a single incident is of a short-term nature. The longest-lived member of its decay chain is ^{212}Pb, which has a half-life of 10.6 h. The time required for the concentration of ^{212}Pb to decline to 0.1% (10^{-3}) of its initial value is 10 half-lives or 106 h, which equates to about 4 d.

2.3.4. References for Sect. 2.3

Listed below are the specific references cited in Sect. 2.3. This is followed by a list of additional sources providing more detailed information on ^{220}Rn generation.

2.3.4.1 References Cited

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2.3.4.1 Supplemental Resources

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Thomas, Jess W. January 1974. *Evaluation of Activated Carbon Canisters for Radon Protection in Uranium Mines*, HASL-280, U.S. Atomic Energy Commission, Health and Safety Laboratory, N.Y.

2.4 NUCLEAR CRITICALITY PROPERTIES

2.4.1 Nuclear Criticality Fundamentals and General Considerations

Four predominant isotopes are encountered in the nuclear industry that require special attention for the safety of personnel. They are ^{233}U; ^{235}U; ^{239}Pu; and, to a lesser extent, ^{241}Pu. These isotopes of uranium and plutonium are capable of maintaining self-sustaining, neutron-fission-chain reactions induced by neutrons of a broad range of kinetic energies. These isotopes are defined as fissile isotopes. This means that sufficient quantities (i.e., masses or concentrations) of ^{233}U can be accumulated such as to maintain a self-sustaining, neutron-fission-chain reaction ("criticality") with thermal neutrons (i.e., neutrons having kinetic energies of about 0.025 eV and velocities of about 2200 m/s); intermediate-energy neutrons (i.e., kinetic energies between about 0.025 eV and 10 keV); or fast neutrons (i.e., kinetic energies between about 10 keV and 15 MeV) or combinations thereof. This is to say that, on average, during the "critical" neutron fission-chain-reactions, precisely one neutron released from fission, or other fission-induced neutron (e.g., n-2n, γ-n), will cause subsequent fissions at a constant power rate. That is, the number of fissions per second will remain constant as the result of all neutrons, both prompt and delayed, that are released from each fission. Because the sum of prompt and delayed neutrons released from each fission is approximately 2.5, neutrons must be lost from the chain reaction to prevent an increase in the fission power rate known as "supercriticality" (i.e., a divergent, supercritical chain reaction). All neutron-fission-chain reactions can be initiated by neutrons that are released from the spontaneous fission of ^{233}U or other commingled fissile materials (e.g., ^{235}U, ^{239}Pu, and ^{241}Pu), or nonfissile fissionable materials (e.g., ^{234}U, ^{237}Np, ^{238}Pu, and ^{240}Pu) or fertile materials (e.g., ^{232}Th and ^{238}U). Table 2.4*a* gives the rate of neutron emission per nuclide mass from the spontaneous fissioning of certain nuclides.

Because people can be injured or killed by the substantial quantities of unshielded radiation that can be released from a criticality accident, ^{233}U must be processed, stored, or transported so that the neutron fission-chain reaction will not be self-sustaining or divergent. The prevention of criticality or supercriticality is achieved by causing sufficient neutrons to be lost from the fission-chain reaction so that the fission rate of the ^{233}U system will always digress to some relatively small multiple of the spontaneous fission rate of the ^{233}U and other fissile or fissionable and fertile material that is present. To varying degrees, this neutron loss can be caused by the presence of any commingled and/or intermingled materials having neutron-absorbing characteristics (such as cadmium) or extreme quantities of water relative to the ^{233}U content. Also, this neutron loss can be caused by the geometric shape and density of the system containing ^{233}U and by other materials surrounding the system. Favorable geometric shapes and densities cause neutrons to escape or leak from the system. High-density and/or thick materials can return or "reflect" neutrons to the ^{233}U system, whereas low-density and/or thin materials can allow neutrons to leak from the system.

The safety activity responsible for the prevention of criticality or supercriticality in operations with fissionable materials outside reactors is called "nuclear criticality safety." Nuclear criticality safety includes the integration of administrative facets (i.e., education and training, auditing and verification, policies and procedures, operating instructions and human factors, and regulations and standards) and technical and theoretical components (i.e., nuclear-reaction, cross-section data measurements and evaluations, critical-experiment benchmarking, theoretical modeling, computational programming, and calculations) to verify, validate, evaluate, analyze, specify, and document the basis of subcriticality and safety for fissionable material operations.

Nuclear criticality safety has proceeded and matured since the initiation of the first critical assembly on Dec. 2, 1942, by Enrico Fermi and others. The maturation process has evolved through national efforts for the designs of:

- fast neutron-driven, HEU and plutonium-fueled nuclear weapons,
- thermal energy neutron-driven ^{238}U-to-^{239}Pu production reactors,
- thermal energy neutron-driven, highly enriched uranium naval light-water reactors (LWRs),
- thermal energy neutron-driven lowly enriched commercial power LWRs,
- thermal energy neutron-driven ^{232}Th-to-^{233}U breeder reactors, and
- fast-energy neutron-driven ^{238}U-to-^{239}Pu breeder reactors.

Those national design efforts included substantial commitments of physical, intellectual, and fiscal resources to adequately and safely demonstrate the design objectives throughout the fuel cycle (i.e., fissionable material acquisition, processing and reprocessing, storage and transportation, and fueling and defueling). National efforts of theoretical analysis and modeling, physical experimentation, and benchmarking of fissile material systems were primarily focused on the fast- and thermal-energy-neutron applications of plutonium and lowly enriched uranium (LEU) and HEU. The influence and concern for intermediate-energy-neutron fission-chain reactions on nuclear criticality safety occurred in fuel-cycle operations, almost entirely out of reactors or weapons applications. For these intermediate-energy, neutron-type systems, required experimentation and benchmarking were frequently relegated to in situ subcriticality or remote criticality experiments on specific processing equipment or storage configurations.

Because there were very limited design applications and no production fuel-cycle facilities for ^{233}U, the needed physical experimentation and benchmarking for ^{233}U systems were restricted to thermal- and fast-energy-neutron research (i.e., criticality experiments and neutron cross-section measurements). Materials preparation and fabrication batch or unit masses and throughputs for the design applications were established conservatively low so as to avoid the need for experimentation and benchmarking of ^{233}U fissionable material systems outside the boundaries of the limited design applications. A review of the open literature referencing critical experiments and evaluations demonstrates the limited availability of intermediate energy-neutron research, in particular, for ^{233}U fissionable material systems [Paxton and Pruvost July 1987; Ozer et al. July 1982; Organization for Economic Cooperation and Development (OECD)-Nuclear Energy Agency (NEA) September 1998; and Koponen, Wilcox, and Hampel Apr. 24, 1979].

Regardless of the fissile material of concern, nuclear subcriticality and safety relies upon the specification and control of various factors that can affect criticality through neutron production, leakage, and absorption. These factors include:

- density of the fissile isotope (concentration or enrichment);
- neutron moderation (i.e., water neutron moderation causing neutron slow-down or thermalization);
- neutron reflectors (i.e., materials located externally to the fissionable material that can return neutrons to the system);
- geometry or shape and dimensions (including volume) of the fissionable material system, including reflector conditions;
- neutron interaction with other surrounding fissionable materials that may contribute to a critical neutron-fission-chain reaction;
- neutron absorber nature, concentration/density, or enrichment (e.g., thermal- or intermediate-energy neutron absorbers such as boron, cadmium, gadolinium, ^{238}U or ^{240}Pu, etc.); and
- mass of fissile isotope.

In the case of ^{233}U, the minimum required mass to achieve criticality (i.e., "critical mass") is as little as about 600 g ^{233}U if it is homogeneously distributed in a sphere of about 10 L of natural water that is surrounded by a 6-in. thickness of natural water (i.e., neutron reflector). More effective neutron reflectors, such as beryllium, and more effective neutron moderators, such as high-density polyethylene, can substantially reduce the critical mass below 600 g ^{233}U. In contrast, the critical mass of an unreflected, full-density ^{233}U metal sphere is approximately 16,500 g ^{233}U, but it is about 7,000 g ^{233}U when reflected with 6 in. of natural water. These remarkable variations in critical masses appear even more dramatic when an infinite mass of ^{233}U is overly diluted in an infinite volume with thermal-neutron-absorbing hydrogen, present in natural water, such that an infinite mass of ^{233}U is not critical as homogeneously distributed at less than 11 g ^{233}U per 1,000 g natural water. Contrarily, in the same infinite volume, ^{233}U at the same mass ratio with poorly neutron-absorbing silicon dioxide (i.e., 11 g ^{233}U per 1,000 g SiO_2) will be supercritical.

2.4.2 Basic Nuclear Criticality Safety Parameters for ^{233}U

The basic nuclear parameter that describes the attribute that is necessary for a fissionable material system to reach criticality is the so-called neutron regeneration factor, η. This factor is the number of neutrons produced divided by the number of neutrons absorbed within the fissionable material and is defined as:

$$\eta = \nu \times \frac{\sigma_f}{\sigma_a} ,$$

where

ν = number of neutrons produced per fission,
σ_f = neutron fission cross section,
σ_a = neutron absorption cross section = $\sigma_f + \sigma_c$, and
σ_c = neutron capture cross section.

Each of the above are neutron-energy-dependent parameters. The regeneration factors, shown in Fig. 2.4*a*, were taken from Ozer (July 1982), who provides the source data used by the nuclear industry for standard nuclear criticality safety computations. It is apparent that the fissile isotopes, ^{233}U, ^{235}U, and ^{239}Pu, have somewhat different values of η. More notable, however, is the difference in the magnitude and energy position of the neutron regeneration factor between 0.01 eV and about $1.0 \times 10^{+4}$ eV. As can be observed beyond about 60 eV for ^{233}U, no "resonance structure" is recorded in the Evaluated Nuclear Data File B, Release V (ENDF/B-V). This is also true for the most recent release VI of ENDF/B. In Fig. 2.4*b*, ENDF/B-VI values with recent ^{233}U neutron-fission cross-section measurements done in 1997 at the Oak Ridge Electron Linear

Accelerator (ORELA) facility are compared with those values from ENDF/B-VI that are used by the nuclear industry. As can be observed, there is substantial resonance structure to the fission cross section above 60 eV. The nearly straight-line behavior of the ENDF/B-VI values above 60 eV has been historically acceptable as a reasonable average value for any benchmarks (i.e., thermal- or fast-energy neutron) that were computationally tested. As a result of the 1997 ORELA measurements, a new "ad hoc" cross-section evaluation was done at ORNL (Wright and Leal September 1997). Because of the lack of intermediate-energy neutron-criticality experiments, the reevaluated nuclear data were tested with thermal- and fast-energy neutron-criticality benchmarks.

Comparative criticality parameters for ^{233}U, ^{235}U, and ^{239}Pu for water-reflected spheres, "infinitely long"cylinders, and "infinite" slabs were taken from Paxton and Pruvost (July 1997) and are plotted in Figs. 2.4*c*, 2.4*d*, and 2.4*e*, respectively. Some of the irregular curvatures for the ^{233}U parameters result from the lack of information over the range of data and the curve-fitting used to avoid overestimation of critical mass values. However, some of the values for ^{233}U reported from Paxton and Pruvost (July 1987) between 0.2–2.0 g ^{233}U/cm^3 may be somewhat in error. It is apparent from an inspection of these curves that process systems designed for ^{235}U are likely inappropriate for ^{233}U processes. Likewise, many process systems designed for plutonium are likely inappropriate for ^{233}U processes. As can be observed from Figs. 2.4*c*, 2.4*d*, and 2.4*e*, extreme changes in critical mass and geometry occur over the fissile material density ranges between about 0.1–2.0 g/cm^3.

The most recent and anticipated future operations involving ^{233}U are expected to involve nonreactor nuclear facility decontamination and decommissioning (D&D) and low-level waste (LLW) transportation and disposal. However, there is a limited, but promising, radiopharmaceutical future from retrieval of ^{213}Bi from the decay chain of ^{233}U. Such retrieval operations require the continued storage of ^{233}U in a safe and secure environment for periodic processing. Nearly all of these recent and anticipated future operations involving ^{233}U nuclear subcriticality and safety evaluations and analyses require conservative compensations for the lack of measured data (i.e., criticality experiments and neutron cross-section data) for ^{233}U fissile material systems predominantly influenced by intermediate-energy neutrons. Conservative compensations may be exercised through the simple use of criticality safety limits imposed for solution systems for which experiments and data do exist. Useful references to reports and documents regarding ^{233}U critical experiments and data my be examined on the web site:

http://ncsc.llnl.gov:8080/koponen/bibliography.html

by searching for the character string "uranium-233."

The *International Handbook of Evaluated Criticality Safety Benchmark Experiments*, published by the OECD and NEA, contains ^{233}U criticality safety benchmark specifications that have been derived from ^{233}U experiments performed at various nuclear critical facilities around the world. The benchmark specifications are intended for use by criticality safety engineers to validate calculational techniques used to establish minimum subcritical margins for operations with fissile material. The following ^{233}U experiments are in Vol. V of the handbook (OECD-NEA September 1998).

^{233}U Fast Metal Systems:

1. ^{233}U JEZEBEL: A Bare Sphere of Uranium-233 Metal (U233-MET-FAST-001)
2. Benchmark Critical Experiments of Uranium-233 Spheres Surrounded by Uranium-235 (U233-MET-FAST-002)
3. Benchmark Critical Experiments of Highly Enriched Uranium-233 Spheres Reflected by Normal Uranium (U233-MET-FAST-003)
4. Benchmark Critical Experiments of Highly Enriched Uranium-233 Spheres Reflected by Tungsten (U233-MET-FAST-004)
5. *Benchmark Critical Experiments of Highly Enriched Uranium-233 Spheres Reflected by* Beryllium (U233-MET-FAST-005)
6. Benchmark Critical Experiments of a Uranium-233 Sphere Reflected by Normal Uranium with Flat Top (U233-MET-FAST-006)

^{233}U Thermal Solution Systems:

1. Unreflected Spheres of ^{233}U Nitrate Solutions (U233-SOL-THERM-001)
2. Paraffin-Reflected 5-, 6-, and 7.5-Inch-Diameter Cylinders of ^{233}U Uranyl Nitrate Solutions (U233-SOL-THERM-004)
3. A 48-Inch-Diameter Unreflected Sphere of ^{233}U Nitrate Solution (U233-SOL-THERM-008)

2.4.3 Criticality Control of ^{233}U by Isotopic Dilution

Potentially, nuclear criticality problems in ^{233}U material systems can be avoided best by isotopic dilution of the ^{233}U material with the nonfissile neutron absorber ^{238}U. Because all uranium isotopes have the same chemical characteristics, the ^{238}U will not separate from the fissile uranium (either ^{233}U or ^{235}U) in any conventional chemical process, either before or after disposal. As shown in ORNL/TM-13524 (Elam et al. November 1997), about 188 kg of depleted uranium (DU) are needed for the criticality control of 1 kg of ^{233}U in all nuclear systems *except* those that have special nuclear moderators such as beryllium and heavy water. This is equal to 0.66 wt % ^{233}U in ^{238}U or 0.53 wt % ^{233}U in DU with an assay of 0.2 wt % ^{235}U. The basis for this result is a simple equation that has been developed to ensure the subcriticality of ^{233}U and uranium enriched in ^{235}U by dilution with DU, specifically 0.2 wt% ^{235}U. The mass of DU required is expressed in terms of the masses of ^{233}U and enriched U as follows:

$$\text{g DU} = 188 \cdot \text{g}\ ^{233}\text{U} + [(E - 1)/0.8] \cdot \text{g of enriched U},$$

where

g DU = mass (g) of DU (i.e., 0.2 wt % ^{235}U),
g ^{233}U = mass (g) of ^{233}U,
E = wt % of ^{235}U (measured with respect to total U), and
g of enriched U = mass (g) of (Total U – ^{233}U).

In this equation, the isotopes ^{234}U and ^{236}U may be considered to be ^{238}U, provided that the atom ratio ($^{234}U + ^{236}U$):^{235}U does not exceed 1.0. If the calculated quantity of g DU is negative, the uranium material already contains ^{238}U in sufficient quantity such that subcriticality would be ensured. Consequently, no additional DU is needed. A more general equation which applies to DU of assay other than 0.2 wt % ^{235}U is presented in Appendix A of Elam et al. (November 1997).

2.4.4 Nuclear Fuel Cycle

Criticality concerns are important considerations that must be incorporated into the design of nuclear fuel-cycle equipment containing ^{233}U materials. The use of ^{233}U from thorium fuel cycles introduces the possibility of dry criticality occurrences while presenting additional radiation hazards from the concentration of ^{232}U and its associated daughter products (Knief 1985). Uranium-232 also has a slight tendency to fission upon neutron capture, but its relatively dilute concentration, along with its association with the highly fissile ^{233}U, result in ^{232}U presenting an insignificant contribution to nuclear criticality.

2.4.5 Standards Affecting ^{233}U Criticality Control and Safety

The American National Standards Institute (ANSI) Inc. and the American Nuclear Society (ANS) have issued several nuclear criticality safety standards that impact the criticality requirements for ^{233}U. These include:

- ANS-8.1 Standard (ANSI/ANS 1998*a*), which provides single-parameter limits for operations with ^{233}U (as well as ^{235}U and ^{239}Pu), but it does not address their combinations. Tables 2.4*b*–2.4*d* (Clark 1981, 1982*a*, and 1982*b*) and Table 2.4*e* (ANSI/ANS 1998*b*) are based on this standard. Table 2.4*b* gives fissile mass and enrichment limits for ^{233}U, ^{235}U, and ^{239}Pu. These limits apply to a single piece of fissile material having no concave surfaces and may be extended to an assembly of pieces provided there is no interspersed moderation. Table 2.4*c* reports parameter subcritical limits for uniform aqueous solutions of ^{233}U, ^{235}U, and ^{239}Pu compounds. This implies that concentrations of the saturated solutions are not exceeded. Table 2.4*c* also gives subcritical limits of parameters for oxide compounds of ^{233}U, ^{235}U, and ^{239}Pu. The limits apply only if the oxide contains no more than 1.5 wt % water.
- ANS-8.7 Standard [the "storage guide" standard] (ANSI/ANS 1998*b*), which has been expanded in recent years to include enriched-uranium (^{233}U as well as ^{235}U) solutions as well as solids. Table 2.4*e* is based on this standard, which provides general storage criteria for ^{233}U. For purposes of interpreting this table, the following definitions apply:
    - — Storage unit (unit): a mass of fissile material (^{233}U) considered as an entity (may be any shape and consist of separate pieces);
    - — Storage cell (cell): a volume having defined boundaries within which a storage unit is positioned;
    - — Storage array (array): a regular arrangement of storage cells; and
    - — H:U ratio: hydrogen (H) to uranium (U) ratio, which is an expression of the composition of the stored material.
- ANS-8.9 Standard [the "pipe intersections" standard] (ANSI/ANS 1978), which includes ^{233}U solutions and could be expanded to include ^{233}U-Th solutions; and
- ANS-8.10 Standard (ANSI/ANS 1975), which gives criteria for nuclear criticality safety controls in operations where shielding protects personnel.

Other standards that pertain more to the safety considerations of nuclear criticality for storing ^{233}U-bearing materials are discussed in Sect. 4.6.

2.4.6 References for Sect. 2.4

Listed below are references cited in Sect. 2.4. This is followed by a list of additional sources that provide more information on ^{233}U nuclear criticality.

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2.4.6.2 Supplemental Resources

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ORNL DWG 98-8125

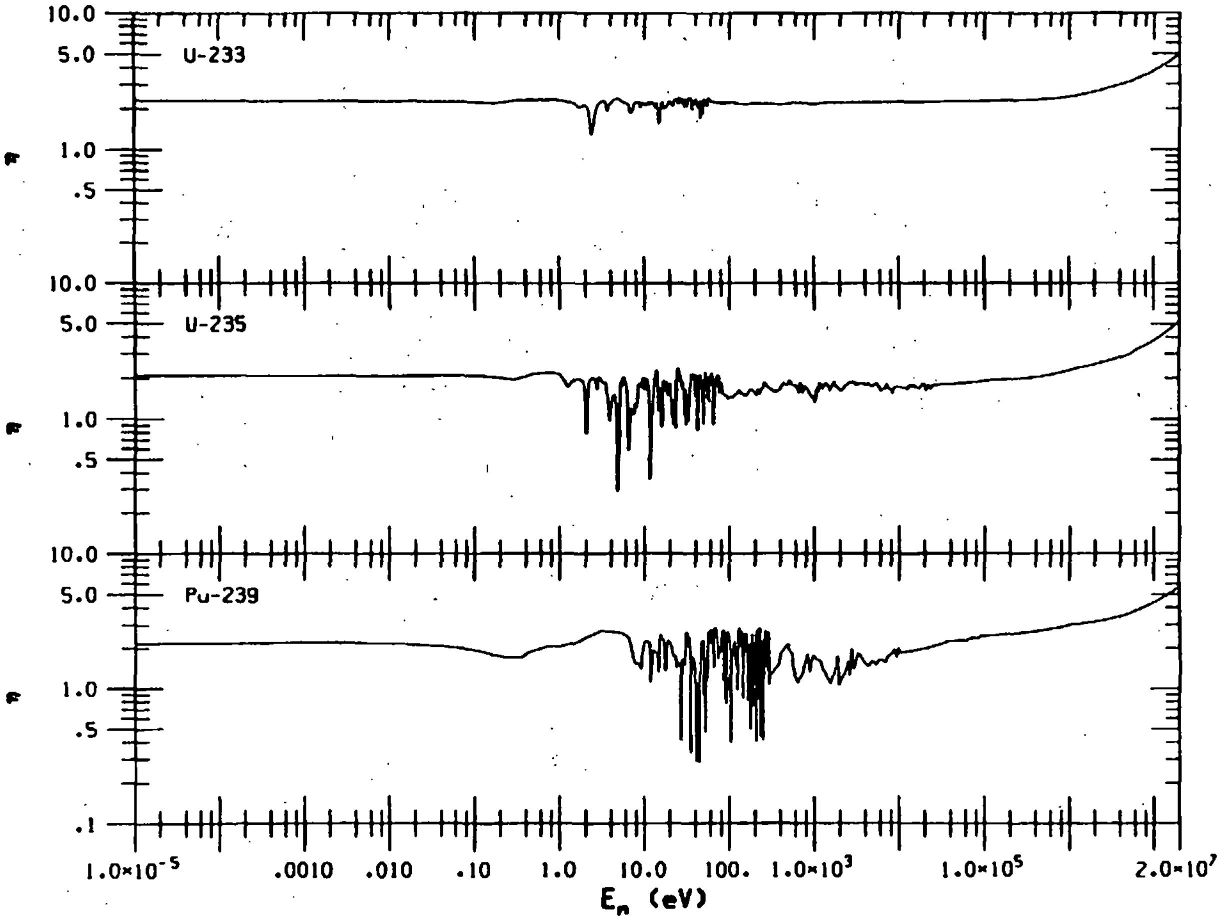

Fig. 2.4*a*. Energy-dependent neutron regeneration factors for ^{233}U, ^{235}U, and ^{239}Pu. *Copyright© 1982. Electric Power Research Institute. NP-2510. Guidebook for the ENDF/B-V Nuclear Data Files. Reprinted with permission.*

ORNL DWG 98-8126

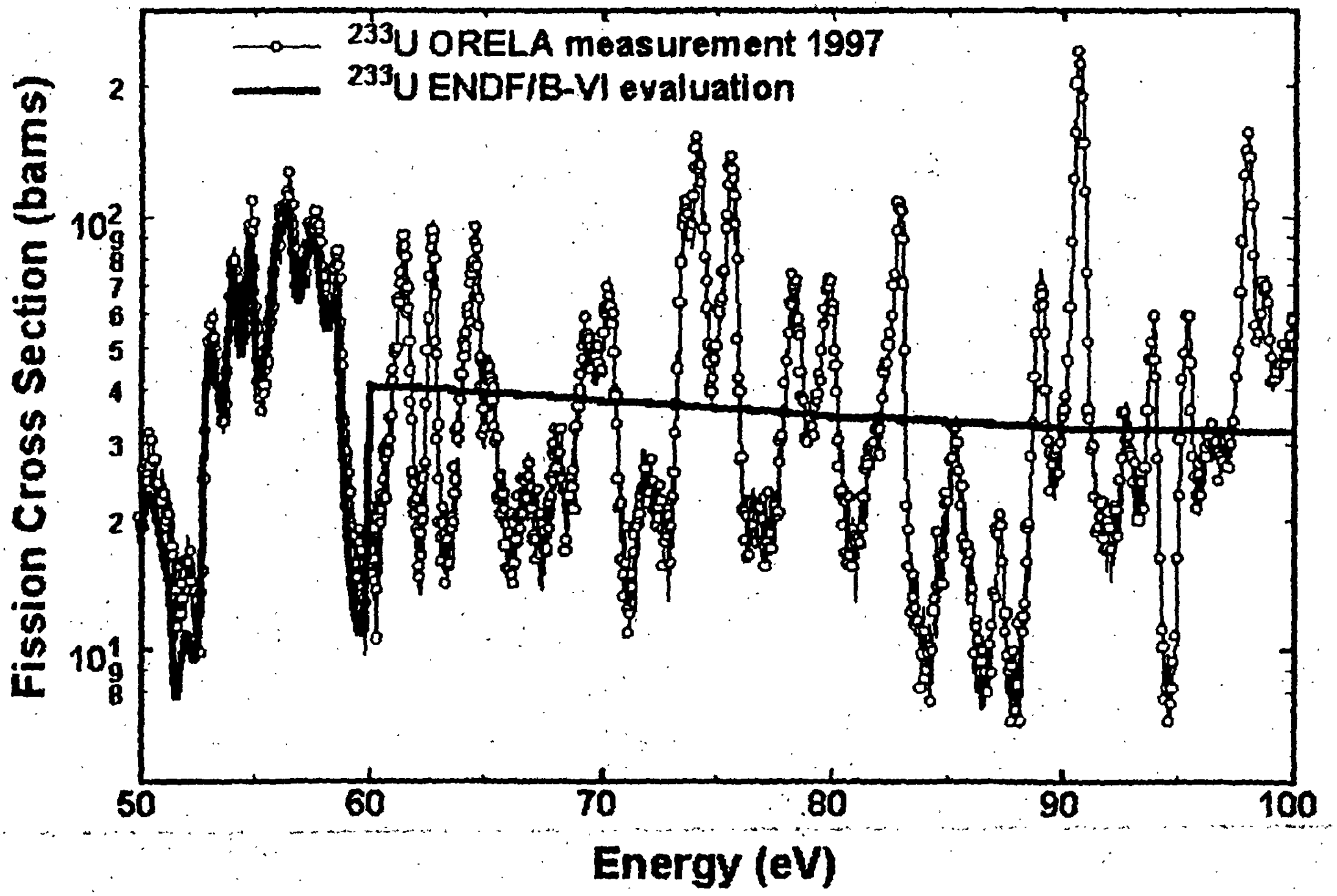

Fig. 2.4*b*. Comparison between ^{233}U fission cross-section data and recent 1997 ORELA measurements.

ORNL DWG 98-8127

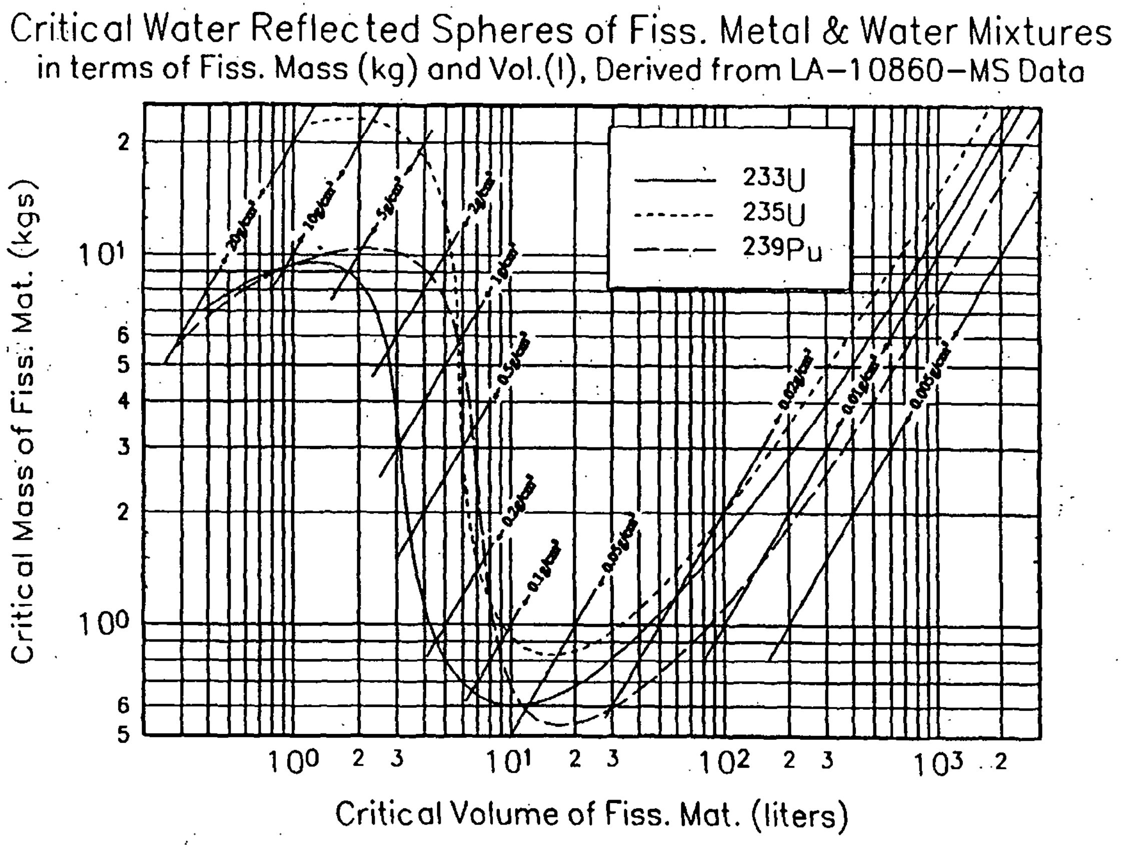

Fig. 2.4*c*. Water-reflected critical spherical masses vs critical spherical volumes.

ORNL DWG 98-8128

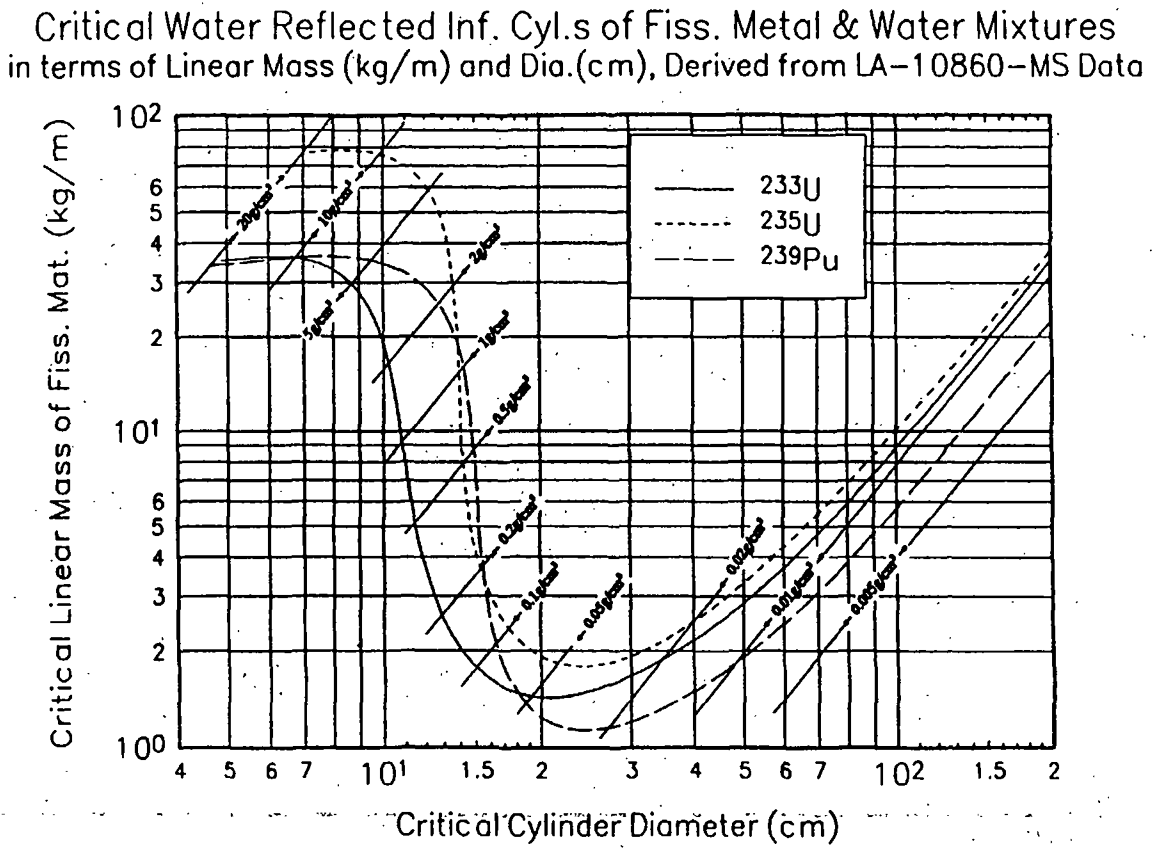

Fig. 2.4*d*. **Water-reflected critical infinite cylinder linear mass vs cylinder diameter.**

ORNL DWG 98- 8129

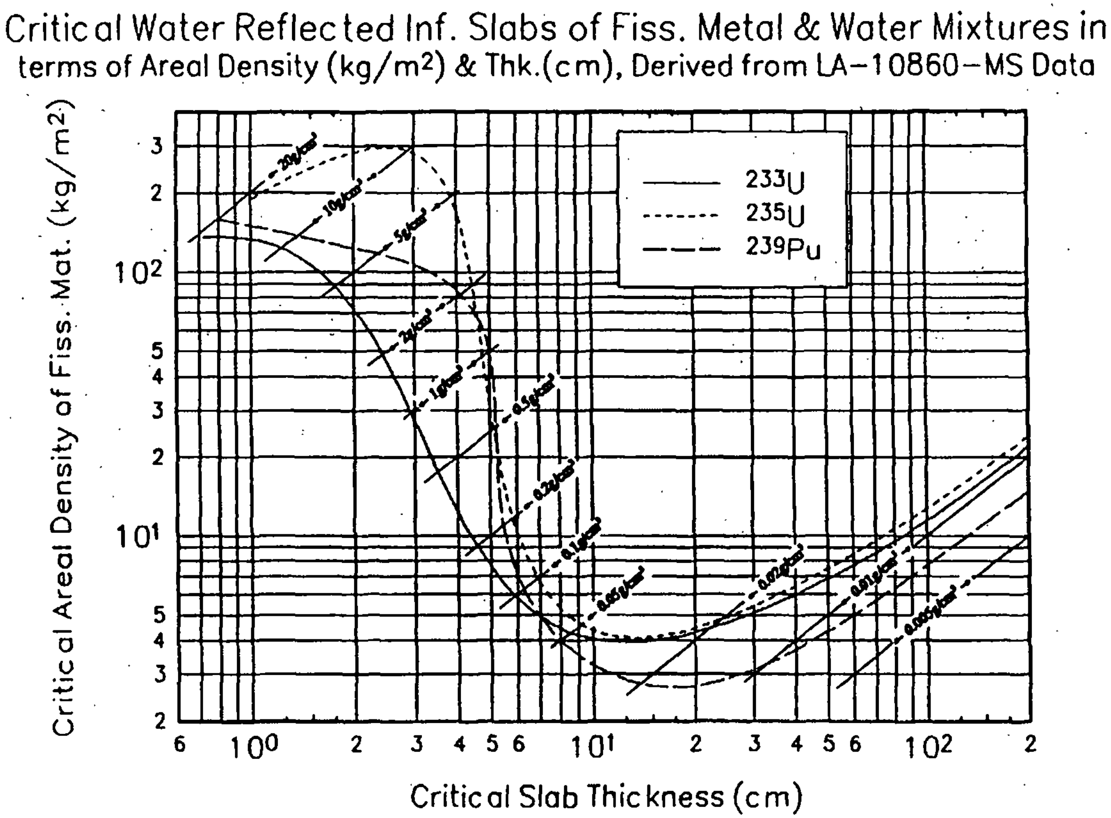

Fig. 2.4*e*. Water-reflected critical areal densities vs infinite slab thickness.

Table 2.4*a*. Rate of neutron emission per nuclide mass (neutrons/sec·g) from spontaneous fission

Nuclide	Material type	Neutron emission rate (neutron/s·g of nuclide)
^{232}Th	Fertile	1.2E−07
^{233}U	Fissile	5.4E−04
^{234}U	Nonfissile, fissionable	6.4E−03
^{235}U	Fissile	1.1E−05
^{238}U	Fertile	1.3E−02
^{237}Np	Nonfissile, fissionable	1.4E−04
^{238}Pu	Nonfissile, fissionable	3.6E+03
^{239}Pu	Fissile	1.5E−02
^{240}Pu	Nonfissile, fissionable	8.9E+02
^{241}Pu	Fissile	2.1E−03

Table 2.4*b*. Single-parameter limits of ^{233}U and other fissile nuclides for metal units

Parameter	Subcritical limit for		
	^{233}U[a]	^{235}U[b]	^{239}Pu[c]
Mass of fissile nuclide, kg	6.0	20.1	5.0
Cylinder diameter, cm	4.5	7.3	4.4
Slab thickness, cm	0.38	1.3	0.65
Maximum density for which mass and dimension limits are valid, g/cm^3	18.65	18.81	19.82

[a] Based on Clark 1982*a*.
[b] Based on Clark 1982*b*.
[c] Based on Clark 1981.

Table 2.4c. Single-parameter limits of ^{233}U and other fissile nuclides for uniform aqueous solutions

Parameter	Subcritical limit for fissile solute				
	$^{233}UO_2F_2$[a]	$^{233}UO_2(NO_3)_2$[a]	$^{235}UO_2F_2$[b]	$^{235}UO_2(NO_3)_2$[b]	$^{239}Pu(NO_3)_4$[c]
Mass of fissile nuclide, kg	0.54	0.55	0.76	0.78	0.48
Diameter of cylinder of solution, cm	10.5	11.7	13.7	14.4	15.4
Thickness of slab of solution, cm	2.5	3.1	4.4	4.9	5.5
Volume of solution, L	2.8	3.6	5.5	6.2	7.3
Concentration of fissile nuclide, g/L	10.8	10.8	11.6	11.6	7.3
Atomic ratio of hydrogen to fissile nuclide[d]	2390	2390	2250	2250	3630
Areal density of fissile nuclide, g/cm^2	0.35	0.35	0.40	0.40	0.25

[a] Based on Clark 1982*a*.

[b] Based on Clark 1982*b*.

[c] Based on Clark 1981. The ^{239}Pu limits apply to mixtures of plutonium isotopes provided the concentration of ^{240}Pu exceeds that of ^{241}Pu and provided ^{241}Pu is considered to be ^{239}Pu in computing mass or concentration.

[d] Lower limit.

Table 2.4*d*. Single-parameter limits for oxides of ^{233}U and other fissile nuclides containing no more than 1.5 wt % water at full density

Parameter	$^{233}UO_2$[a]	$^{233}U_3O_8$[a]	$^{233}UO_3$[a]	$^{235}UO_2$[b]	$^{235}U_3O_8$[b]	$^{235}UO_3$[b]	$^{239}PuO_2$[c]
Mass of fissile nuclide, kg	10.1	13.4	15.2	32.3	44.0	51.2	10.2
Mass of oxide,[d] kg	11.7	16.0	18.7	37.2	52.8	62.6	11.5
Cylinder diameter, cm	7.2	9.0	9.9	11.6	14.6	16.2	7.2
Slab thickness, cm	0.8	1.1	1.3	2.9	4.0	4.6	1.4
Maximum bulk density[e] for which limits are valid, g/cm³	$\frac{9.38}{1-0.085(1.5-W)}$	$\frac{7.36}{1-0.065(1.5-W)}$	$\frac{6.56}{1-0.056(1.5-W)}$	$\frac{9.44}{1-0.086(1.5-W)}$	$\frac{7.41}{1-0.065(1.5-W)}$	$\frac{6.60}{1-0.057(1.5-W)}$	$\frac{9.92}{1-0.091(1.5-W)}$

[a] Based on Clark 1982*a*.
[b] Based on Clark 1982*b*.
[c] Based on Clark 1981.
[d] These values include the mass of any associated moisture up to the limiting value of 1.5 wt %.
[e] W represents the quantity of water, in weight percent, in the oxide.

Table 2.4e. Unit mass limit in kilograms of ^{233}U per cell in water-reflected storage arrays[a]

Number of units in cubic storage arrays	Minimum dimension of cubic storage cell (mm)					
	254	305	381	457	508	610
Units: Uranium metal; H:U ≤ 0.01; 100 wt % ^{233}U						
64	4.2	5.3	6.7	7.8[b]	8.5[b]	9.4[b]
125	3.5	4.5	5.9	7.1[b]	7.7[b]	8.8[b]
216	3.1	4.0	5.3	6.4	7.1[b]	8.2[b]
343	2.7	3.5	4.8	5.9	6.6	7.7[b]
512	2.4	3.2	4.4	5.5	6.1	7.3[b]
729	2.2	2.9	4.0	5.1	5.8	6.9[b]
1000	2.0	2.7	3.7	4.8	5.4	6.6
Units: Oxides of uranium; H:U ≤ 0.4; 100 wt % ^{233}U						
64	4.9	6.6	9.1	11.5	12.9[b]	15.4[b]
125	4.0	5.4	7.7	9.9	11.2	13.7[b]
216	3.4	4.6	6.6	8.6	9.9	12.4
343	2.9	4.0	5.8	7.7	8.9	11.3
512	2.6	3.6	5.2	6.9	8.1	10.3
729	2.3	3.2	4.7	6.3	7.4	9.6
1000	2.1	2.9	4.3	5.8	6.8	8.9

[a] Based on ANSI/ANS-8.7-1998. Note that this standard is currently under revision; consequently, the data reported in this table are subject to possible future changes.

[b] Values are greater than 90% of critical spherical mass, water reflected.

2.5 PHYSICAL AND CHEMICAL CHARACTERISTICS

The domestic inventory of stored ^{233}U-bearing materials is found in a variety of physical and chemical compound forms. These include metals (and alloys), oxide powders, fluorides, and various other material forms and compositions. The major physical and chemical properties exhibited by ^{233}U materials are described in this section.

The physical and chemical properties of ^{233}U materials generally reflect those of compounds containing natural or HEU. Consequently, the same chemical processes used for natural uranium and HEU-bearing materials are generally applicable to ^{233}U. As previously shown in Table 2.1*a*, ^{233}U has a higher specific radioactivity than either natural uranium or HEU, which has greater than 20 wt % ^{235}U. This means that certain radiation-induced chemical reactions are faster in uranium-bearing materials that contain significant quantities of ^{233}U. The faster radiation-induced chemical reaction rates impact the long-term storage of ^{233}U by requiring that ^{233}U storage forms and containers be limited to exposure to water or any organic materials such as plastics, which degrade with higher radiation levels. (This is discussed further in Sect. 4.6).

Uranium is a radioactive element and, as found in nature, contains three radioactive isotopes [mostly ^{238}U (99.28 at. %), some trace amounts of ^{235}U (0.715 at. %), and ^{234}U (0.005 at. %)]. A significant number of other isotopes, including ^{232}U and ^{233}U, have been synthetically prepared.

Uranium has a toxicity similar to that of lead. When in the form of a solid or dust, uranium can be a dangerous fire hazard when it is exposed to heat or flame. Uranium dust can also be an explosion hazard when exposed to a flame in the presence of oxygen. (These properties are discussed further in Sect. 4.)

2.5.1 Uranium Valence States

In its purest state, uranium exists as a metal; and because it is strongly electropositive, it is highly reactive and readily forms compounds with all nonmetallic elements, except for the inert noble gases. It also forms intermetallic compounds with many metals, including iron, lead, mercury, and aluminum. Uranium has four oxidation states in aqueous media: 3+, 4+, 5+, and 6+. The U^{3+} state is chemically very unstable with respect to oxidation and has a red-wine color. U^{3+} reduces water, yielding U^{4+} and hydrogen. Known as the uranous ion, U^{4+} is metastable with respect to oxidation by nitrates and is dark green. The 5+ state, UO_2^{+}, is black-brown and tends to disproportionate U^{4+} and UO_2^{2+}. The 6+ state, UO_2^{+2} (uranyl ion), is yellow and is the most prevalent and significant aqueous state. It can be reduced to the 4+ state chemically, photochemically, or electrochemically.

2.5.2 Uranium Metal

Pure uranium is a heavy metal that exists as either silver-white or black crystals. In this form, uranium melts at 1132 °C, boils at 3818 °C, and has a density of 19.04 g/cm^3. By comparison, lead melts at 327 °C, boils at 1750 °C, and has a density of 11.35 g/cm^3. Other physical properties of uranium and some of its significant compounds (from a ^{233}U perspective) are listed in Table 2.5*a* (Linde 1998, Katz and Rabinowitch 1951, and Benedict, Pigford, and Levi 1981).

When uranium metal is in the form of solid chips, shavings, or dust, it can be a dangerous fire hazard if exposed to heat or flame in air. Because of uranium's rapid and exothermic reaction with oxygen, its condition as a finely divided metal is pyrophoric. Consequently, treatment of uranium at elevated temperatures must be carried out in an inert atmosphere or in a vacuum. Uranium metal can also react vigorously, evenly violently, with oxidizing agents. Solid pieces, larger than 1/16-in. diam will not spontaneously ignite (Peacock 1992), but their surfaces will corrode. The corrosion rate is a function of surface area, temperature, humidity, and oxygen. Corrosion of uranium metal has several consequences. First, it converts a cohesive metal solid to a dispersible oxide dust. Also, under wet conditions, uranium metal corrosion results in the formation of hydrides, which can lead to a fire, explosion hazard, or container pressurization from either the radiolytic decomposition of water or chemical reaction with water and the attendant evolution of hydrogen. Specific processes for uranium metal preparation are discussed in Sect. 3.6.

2.5.3 Uranium Oxides

The oxides are the most frequently found compounds of uranium with, perhaps, the exception of uranium hexafluoride (UF_6) (see discussion below). The uranium-oxygen phase diagram is complex. Many binary oxides and crystalline modifications have been reported. Three of the uranium oxides are common in ^{233}U processing and storage areas: uranium dioxide (UO_2), uranium trioxide (UO_3), and triuranium octaoxide (U_3O_8), or pitchblende, also commonly referred to as uranium oxide.

Uranium dioxide is the most common compound used in reactor fuels (in a compressed pellet form) and is a significant intermediate material used in uranium metal manufacture. It exists in the form of brown-black (sometimes green-black) crystals, which are fairly chemically stable. At high temperatures, nonstoichiometric forms exist with oxygen ratios ranging from $UO_{1.63}$ to $UO_{2.25}$. In a very finely divided form, UO_2 is potentially pyrophoric (i.e., is capable of igniting spontaneously in air). In the early 1970s, UO_2 powder was prepared in Building 3019 at ORNL for use in fabricating thoria-urania (ThO_2-UO_2) fuel pellets at the Bettis Atomic Power Laboratory [BAPL (West Mifflin, Pennsylvania)] for the light-water breeder reactor (LWBR) in Shippingport, Pennsylvania (see Sect. 3.5.1).

Uranium trioxide is another significant intermediate compound used in uranium metal manufacture. It is a yellow-red powder that is chemically stable, except for dihydrate formation. Uranium trioxide is routinely prepared by thermal decomposition of uranium nitrate, $UO_2(NO_3)_2 \bullet 6H_2O$, or uranium peroxide, $UO_4 \bullet 2H_2O$.

The most stable oxide is U_3O_8, which makes it best suited for long-term storage. It is the primary oxide formed by burning in excess air and by corrosion after extended air exposure, so it can be derived readily from the other uranium oxides. Triuranium octaoxide is an olive-green powder which is normally formed at high temperature from the other oxides. Because of the chemical stability of U_3O_8, it is the preferred form for storage of uranium, including HEU (Cox July 1995).

Specific processes that have been developed for the stabilization of ^{233}U-bearing materials in an oxide form are discussed in Sect. 3.5.

2.5.4 Hydrates of Uranium Oxides

The uranium oxides (UO_2, UO_3, and U_3O_8) react directly with water to form hydrates. A summary of the major characteristics and origination of these compounds [based on information reported in two sources (Harrington and Ruehle 1959 and Vdovenko 1960)] follows.

Hydrates of UO_2 and U_3O_8 are prepared by precipitation reaction in solution. Those of UO_2 result from hydrolyzing a solution of uranium chloride or uranium acetate. For such hydrolysis to occur, the aqueous solution must be heated with air excluded or neutralized chemically with a base such as ammonium hydroxide.

Hydrates of U_3O_8 are formed during photochemical decomposition of uranyl oxalate, $UO_2(C_2O_4)$, and from reactions of uranyl salt solutions with organic reducing agents such as glucose, alcohols, ethers, or acetaldehyde. The U_3O_8 hydrates dissolve in acids and form a mixture of quadrivalent (U^{+4}) and hexavalent (U^{+6}) uranium salts.

For UO_3, there are four known hydrates: $UO_3•2H_2O$, $UO_3•H_2O$, $UO_3•0.8H_2O$, and $UO_3•0.5H_2O$. The dihydrate $UO_3•2H_2O$ is yellow or green-yellow and exists in two different forms. It is formed by reacting saturated water vapor with the red form of UO_3 in the temperature range of 5 to 75°C. However, heating to above 300°C drives off the water and returns the UO_3 back to a stabilized form (Vdovenko 1960). The stabilized UO_3 will reform $UO_3·2H_2O$ at temperatures under 60°C (Harrington and Ruehle 1959). The dihydrate can also be formed by the action of water on the anhydrous UO_3 or the monohydrate of UO_3.

The monohydrate, $UO_3•H_2O$, is yellow or orange-yellow and crystallizes in the form of needles or plates. This compound exists either as one amorphous or four crystalline forms, all of which are stable at room temperature. The monohydrate can be prepared by hydrating UO_3 in moist air at 25°C for a period of 24 h.

The compound $UO_3•0.8H_2O$ is sometimes referred to as the alpha monohydrate. It is formed by dehydration of $UO_3•2H_2O$ in the temperature range 140 to 260°C and also results from combining amorphous UO_3 and water at 180°C.

The orange-colored hemihydrate $UO3•0.5H_2O$ is monoclinic and can be obtained at water vapor pressure of 15 mm within a temperature interval of 160 to 300°C. The hemihydrate is prepared by heating $UO_4•2H_2O$ in water at 310 to 350°C and by hydrating the unreactive, orange UO_3 at 350 to 380°C. When heated in air to 700°C, the hemihydrate goes to pure U_3O_8.

2.5.5 Uranium Fluorides

Uranium fluorides are used extensively in the ^{235}U fuel cycle to enrich natural uranium and, as UF_6, represent the largest amounts of uranium that are available. However, fluoride compounds have less significance for the synthetic ^{233}U. Uranium tetrafluoride (UF_4) is nonvolatile and was used, in a dilute solution of other moderator salts ($LiF-BeF_2-ZrF_4$), in the Molten Salt Reactor Experiment (MSRE) at ORNL. Also, UF_4 can be directly fluorinated to form UF_6, which is volatile. It was this process that was used to strip the ^{235}U from the fuel solvent and to refuel with ^{233}U in the form of a eutectic binary salt mixture of LiF and UF_4.

During the past 30 years that the MSRE has been shut down, radiolysis of the fuel salt by fission products dissolved therein (with the formation of fluorine gas), coupled by an annual "annealing" cycle (intended to recombine the radiolytically produced fluorine), has caused much of the uranium to migrate from the fuel salt into the off-gas system connecting the fuel drain tanks to charcoal beds. Currently, the MSRE Remediation Program is underway to remove the fuel charge of approximately 37 kg of uranium (now distributed from the fuel salt through the gas piping and in the charcoal beds, principally as ^{233}U) from the MSRE facility. This material will eventually be converted to U_3O_8 and stored in Building 3019 at ORNL. For a more complete discussion of this relevant subject, see Sect. 3.5.3.

Uranium hexafluoride is highly reactive with water and moist air, forming uranyl fluoride (UO_2F_2) and releasing HF, both of which are chemically toxic. Inhalation and ingestion of UF_6 result in acutely serious health threats. Consequently, UF_6 must be stored in gas-tight, corrosion-resistant canisters. It is therefore desirable to convert the vast amounts of stored UF_6 to the more stable U_3O_8 for long-term storage.

2.5.6 Uranyl Nitrate

Uranyl nitrate solution, $UO_2(NO_3)_2$, is an important compound in the purification of uranium and separation of its daughter products by solvent extraction (SX). It is formed by the aqueous reaction of nitric acid (HNO_3) and uranium oxides. When dried, this nitrate solution forms yellow crystals, which corrode tin cans and degrade some plastics. Uranyl nitrate solutions can be absorbed through the skin.

2.5.7 Solution Chemistry of Uranium and Related Actinides

The solution chemistry of uranium and the other actinides from which it is often separated are discussed. Specifically, the solution chemistry related to the recovery of ^{233}U from irradiated thorium targets and to the periodic requirement to purify ^{233}U from the decay products of its isotopic impurity, ^{232}U, are discussed. Because of the presence of the natural uranium impurity in thorium targets or the use of equipment previously used in plutonium-bearing fuels processing, it may become necessary to remove traces of plutonium, americium, and curium either by ion exchange or SX. Separations are based on differences in valences and/or in the ability of the actinide ions to form complex species. The information presented below does not presume to be comprehensive and includes only information relative to manufacture and purification of ^{233}U. More comprehensive information may be found elsewhere (Ahrland, Liljenzin, and Rydberg 1973; Katz, Seaborg, and Morss 1986; and Choppin and Rydberg 1980).

2.5.7.1 Actinide Valence

The valences exhibited by the actinide elements and the values for their ionic radii are shown in Tables 2.5*b* and 2.5*c* (Choppin and Rydberg 1980), respectively. The ionic radii of the actinide elements of the different valences decrease with increasing atomic number. Consequently, the charge density of the actinide ions increases with increasing atomic number and, therefore, the probability of the formation of complexes and of hydrolysis increases with atomic number. For example, the pattern of stability of the complexes—not to be confused with the stability of the uncomplexed ions—in the tetravalent state is:

$$Th^{4+} < U^{4+} < Np^{4+} < Pu^{4+}$$

Similarly, for the same element, the stability of the complexes varies with the oxidation state according to the following series:

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$$

The pentavalent state of the actinides is the less stable than the other states (except for protactinium and neptunium) and normally undergoes to disproportionation by the following reaction:

$$2\,MO_2^{+} \quad + \quad 4\,H^{+} \quad = \quad MO_2^{2+} \quad + \quad M^{4+} \quad + \quad 2\,H_2O$$

Pentavalent uranium and plutonium are relatively stable at $H^+ = 0.01\ M$ or less, whereas NpO_2^+ is relatively stable in 1 *M* acid. The most stable valence states of the actinides in aqueous solution in air are depicted in bold letters in Table 2.5*b*. Through the appropriate choice of acidity and redox agents, uranium valence can be adjusted and maintained as 4+ or 6+, plutonium as 3+, 4+, or 6+, and neptunium as either 4+, 5+, or 6+. The ions U^{3+}, Np^{3+}, and Pa^{4+} are unstable in air and oxidize to the next higher valence. In aqueous systems, thorium can exist only in the Th^{4+} state and actinium in the Ac^{3+} state. The 7+ state of neptunium is formed under very strong oxidizing conditions and is relatively unstable. The 5+ and 6+ states of americium are also relatively unstable except in the presence of very strong oxidizing agents such as sodium peroxodisulfate ($Na_2S_2O_8$) or ozone (O_3).

2.5.7.2 Complexes of the Actinides

Actinides form ionic and neutral complexes with inorganic and organic ligands, and this is the basis of separations and recovery of actinides from aqueous solution. Reactions of aqueous phase complexes of the actinides with organic species to form compounds or adducts that are highly soluble in an organic phase provide the basis for the separation of actinides from other elements and from each other by liquid-liquid extraction. Likewise, differences in the affinity of the various elements to form adducts with the organic constituents associated with solid sorbents (e.g., ion exchange) make separations possible by column chromatography methods. Only the complexes relevant to the recovery and purification of ^{233}U are discussed here. More comprehensive and in-depth discussions are reported elsewhere (Ahrland, Liljenzin, and Rydberg 1973; and Katz, Seaborg, and Morss 1986). In aqueous solution, the 3+, 4+, and 6+ valence actinides form cationic, anionic, and neutral complexes with a variety of inorganic ligands (nitrate, chloride, sulfate, etc.) and with a large number of organic species.

Of the complexes formed with organic ligands, only the complexes with carboxylate ions, such as acetate, find applications in ^{233}U separations. Other types of carboxylate ions (such as hydroxyisobutyrate and aminocarboxylate) are used in separations of higher actinides such as americium, curium, berkelium, and californium. Acetate complexation is employed in the purification of ^{233}U from ^{232}U radioactive daughter products by a cation exchange process (Rainey December 1972). Also see Sect. 3.5.1.2. Preferential sorbtion of the anionic nitrate complex of thorium on anion exchange resin serves to recover ^{229}Th from the ^{233}U parent in nitric acid solutions (Webb 1998*a*). Also see Sect. 3.3.2.

SX separation of macro quantities of thorium and uranium that are involved with the recovery of ^{233}U from irradiated thorium fuels or targets is based on the extractability of the tributylphosphate (TBP) complexes from nitric-acid solutions. This separation is called the Thorex process and is based on the difference in the extractability of the neutral complexes $UO_2(NO_3)_2{\bullet}2\ TBP$ and $Th(NO_3)_4{\bullet}2\ TBP$ into an immiscible organic phase of TBP dissolved in normal paraffin hydrocarbon. The reactions for complexation and extraction are as follows:

$$UO_2{}^{2+}{}_{(aq)} + 2\ NO_3{}^{-}{}_{(aq)} + 2\ TBP_{(org)} \leftrightarrow UO_2(NO_3)_2{\bullet}2\ TBP_{(org)}$$

$$Th^{4+}{}_{(aq)} + 4\ NO_3{}^{-}{}_{(aq)} + 2\ TBP_{(org)} \leftrightarrow Th(NO_3)_4{\bullet}2\ TBP_{(org)}$$

Relatively high concentrations of nitrate ions are used to promote extraction. The extracted uranium and thorium may be recovered from the loaded organic phase by back-extracting (stripping) it with an aqueous solution of relatively low nitrate concentration. Trivalent plutonium, americium, and curium are virtually inextractible in TBP except at low acidity and very high nitrate ion concentrations. Under normal conditions for the Thorex™ process, they are not extractible to a significant extent.

The process flowsheets and chemistry of the Thorex processing have been discussed by several authors (Bond 1990 and Gresky et al. 1952). The removal of radioactive daughters of ^{232}U from aged nitric acid solutions of ^{233}U has been accomplished with the extractant di-(sec-butyl)phenyl phosphonate (DSBPP) (Ferguson 1970), which also forms a neutral complex with uranyl nitrate. DSBPP has a higher extractability for uranium than does TBP. The Thorex process is discussed in more detail in Sect. 3.2.3.3.

2.5.8 Characteristics of Current ^{233}U Inventories

Summary chemical and physical characteristics of the inventories of ^{233}U-bearing materials at major sites are provided in Table 2.5*d* [Bereolos et al. June 1998 and DOE/Idaho (ID) and Idaho National Engineering and Environmental Laboratory (INEEL) December 1998]. More detailed ^{233}U inventory data are provided in Appendix C of this handbook and in other reports (in particular, Bereolos et al. June 1998, DOE/ID and INEEL December 1998, and Lewis and Wilkinson March 1998). Most of the domestic ^{233}U inventory is found in two major types of solid form material: unirradiated Shippingport LWBR fuel at INEEL and Consolidated Edison Uranium Solidification Program (CEUSP) material at ORNL.

2.5.9 References for Sect. 2.5

Listed below are references cited in Sect. 2.5. This is followed by a list of additional sources that provide more information on the physical and chemical characteristics of ^{233}U-bearing materials.

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Table 2.5*a*. Characteristics of uranium and some uranium compounds[a]

Characteristic	Natural U	UO_2	UO_3	U_3O_8	$UO_2(NO_3)_2 \cdot 6\ H_2O$	UF_4	UF_6
Boiling point, °C	3818	Decomposes	Decomposes[b]	Decomposes[c]	118	1457	57[d]
Crystalline form	Cubic	Rhombic cubic[e]	Multiple forms	Multiple forms	Rhombic	Triclinic	Monoclinic
Color	Silvery-white	Brown	Orange	Olive green-black	Yellow	Green	Colorless
Heat of fusion, cal/g	4700	67	NA[f]	NA			
Heat of vaporization, cal/g	106,700	NA	NA	NA			NA
Melting point, °C	1132	2878	*b*	*c*	60.2	960	64
Molecular weight	238.03	270.03	286.07	842.21	502.13	314.02	352.02
Specific gravity[g]	19.05	10.96	7.29	8.30	2.81	6.70	5.06
Specific heat,[g] cal/g/°C	6.57	0.056	0.071	0.0798			
Thermal conductivity,[g] cal/cm·sec·°C	0.071	0.02					1.60
Water solubility[h]	I	I	I	I	S	S[i]	*j*

[a] Based on Linde 1998; Katz and Rabinowitch 1951; and Benedict, Pigford, and Levi 1981.
[b] Decomposes at greater than 600°C at reduced pressures.
[c] Decomposes at greater than 1300°C at reduced pressures.
[d] Sublimes at 1 atm.
[e] Face-centered cubic lattice.
[f] NA = not applicable.
[g] Measured at 25°C.
[h] I = insoluble; S = soluble.
[i] Very slightly soluble in cold water.
[j] Decomposes in cold water.

Table 2.5*b*. Oxidation states of the actinides in aqueous solution[a]

(The most stable oxidation states are shown in parentheses.)

Atomic No.	89	90	91	92	93	94	95	96
Element	Ac	Th	Pa	U	Np	Pu	Am	Cm
	(3)			3	3	3	(3)	(3)
		(4)	4	4	4	(4)		
			(5)	5	(5)	5	5	
				(6)	6	6	6	
					7	7		

[a] Actinides of atomic number 97 and higher are omitted because of their short half-lives and because they are not formed in significant amounts in ^{233}U production.

Table 2.5*c*. Ionic radii of the actinides (Å)[a]

Element	M^{3+}	M^{4+}	M^{5+}	M^{6+}
Ac	1.076			
Th		0.984		
Pa		0.944	0.90	
U	1.005	0.929	0.88	0.83
Np	0.986	0.913	0.87	0.82
Pu	0.974	0.896	0.87	0.81
Am	0.962	0.888	0.86	0.80
Cm	0.946	0.886		
Bk	0.935	0.870		

[a] Adapted from Choppin and Rydberg 1980.

Table 2.5*d*. Summary chemical and physical characteristics of major components of the current inventory of ^{233}U-bearing materials[a]

Site	Material description	Chemical/physical form	CY(s)[b] of generation	Total U (kg)	^{233}U content (kg)
INEEL	Containers of unirradiated LWBR fuel	UO_2–ThO_2 pellets in fuel and blanket rods	1976–77	306.64	300.80
	Unirradiated assembled LWBR seed module	UO_2–ThO_2 pellets in rods	1976–77	16.84	16.56
	55-gal and 110-gal 6M containers of unirradiated LWBR fuel	UO_2–ThO_2 pellets in fuel and blanket rods	1976–77	35.42	34.20
	LWBR fuel fabrication scrap	Clothing, grinding sludge, rags, polyethylene, gloves, processing equipment components	1976–77	61.86	60.0[c]
INEEL total				420.76	411.56
LANL	Various compounds	Carbides, oxides, nitrates, tetrafluoride, and U_3O_8		4.09	4.00
	Metals	Encapsulated, turnings, and special alloys		2.82	2.78
	Noncombustibles	Graphite, nonactinide, and plastics		0.13	0.13
	Process residues	Hydroxide precipitates, sweepings, and screenings		0.20	0.19
	Other	Combustibles (rags) and nitrate solutions		0.01	0.01
LANL total				7.25	7.11
ORNL	Savannah River (165 ppm ^{232}U)	UO_x powder	1964–65	67.4	61.6
	MSRE salt (excess feed material)	UF_4 with LiF	1965–69	3.2	2.9
	CEUSP material	U_3O_8 monolith (with CdO)	1985–86	1042.6	101.1

Table 2.5*d* (continued)

Site	Material description	Chemical/physical form	CY(s)[b] of generation	Total U (kg)	^{233}U content (kg)
ORNL (contd.)	Mound Plant material	UO_x powder	1967	3.6	3.5
	Uranium metals	Uranium metal and alloys		17.3	17.0
	RCP-06[d]	U_3O_8 monolith (with CdO)	1986	65.2	60.3
	BAPL[e]	UO_2 powder	1976	15.4	15.0
	Savannah River (35 ppm ^{232}U)	UO_3 powder	1964–65	11.1	10.7
	Oxide lots	U_3O_8 powder	1980–88	96.5	91.2
	Zero-Power Reactor packets	U_3O_8 powder	1978–79	45.7	44.8
	Miscellaneous	Oxide powders		10.4	10.2
	Other	Miscellaneous forms		9.2	9.0
ORNL total				1387.5	427.2
Other sites[f]	Miscellaneous			>83.7	>5.1

[a] Based on Bereolos et al. June 1998 and U.S. DOE-ID and INEEL December 1998.

[b] CY = calendar year.

[c] This is LWBR scrap material which has a fissile (^{233}U) content of 97 wt % (of total uranium) and a ^{232}U content of 9 ppm (of total uranium).

[d] This is an arbitrary designation related to the history of the material.

[e] Bettis Atomic Power Laboratory.

[f] Includes contributions from 19 sites.

2.6 WASTE THRESHOLD CRITERIA

The requirements for storage, transport, and disposal of radioactive wastes are significantly different from those for fissile materials. Consequently, a proposed basis for defining and managing different classes of the current inventory of ^{233}U-bearing materials was recently developed and documented (Forsberg, Storch, and Lewis July 7, 1998). A summary of the major results from that investigation is provided below.

2.6.1 Introduction

Three categories that pertain to the current inventory of ^{233}U-bearing materials have been defined to establish separate and appropriate sets of criteria for storage, transport, and disposition or disposal. These are wastes, exception-case materials, and concentrated fissile materials (nonwastes).

Each of these material categories has a unique set of features relating to concerns regarding economic value, nuclear criticality, and nuclear safeguards (including arms control). The safeguards requirements for ^{233}U are similar to those of plutonium. Current domestic inventories of the above three categories of ^{233}U-bearing materials are documented in the report *Uranium-233 Waste Definition: Disposal Options, Safeguards, Criticality Control, and Arms Control*, ORNL/TM-13591 (Forsberg, Storch, and Lewis July 7, 1998).

2.6.2 Wastes

Wastes containing ^{233}U-bearing materials are defined as materials containing sufficiently small masses or concentrations of fissile materials (^{235}U as well as ^{233}U) such that they can be managed as typical radioactive waste.

Uranium-233-containing material is waste if three conditions are met:

1. There is no existing, planned, or proposed use for the material.
2. The ^{233}U in the material is such that either:
   a. The actual ^{233}U concentration is <1 kg/m^3, or
   b. The enrichment level is <0.66 wt % ^{233}U in ^{238}U.
3. The ^{233}U in the material is such that either:
   a. The approximate ^{233}U homogeneous concentration is <1 kg/m^3, or
   b. The enrichment level is <12 wt % ^{233}U in ^{238}U.

This definition covers three requirements that must be met (in the areas of economics, criticality control, and safeguards and arms control) to allow the ^{233}U-bearing material to be handled as any other radioactive waste. This definition assumes that the wastes will be managed in a manner similar to transuranic (TRU) (alpha emitting) waste. The hazards and characteristics of TRU and ^{233}U wastes are similar. Consequently, most sites with ^{233}U wastes manage those wastes like TRU wastes. The definition also assumes that, for safeguards purposes, the concentration of ^{233}U in the waste does not exceed 0.15 wt %. More restrictive conditions apply if highly concentrated ^{233}U exists in a batch of waste (Forsberg, Storch, and Lewis July 7, 1998).

Wastes containing ^{233}U-bearing materials at various sites contain materials from contaminated areas, glove boxes, and hot cells; construction debris; personal protective equipment; piping; and used standard equipment for either laboratory analysis or material processing and handling. The waste forms include metals, wood, plastic, glass, and cardboard.

2.6.3 Exception-Case Materials

It has been proposed that exception-case materials be defined as materials that should be examined on a case-by-case basis to determine if they are wastes. They include materials not covered in the definition of wastes as described above, and are chemically contaminated up to 12 wt % ^{233}U in non-^{238}U-containing materials. As a result, such materials have a ^{233}U mass concentration that exceeds 1 kg/m^3 or about 200 g per 55-gal drum. Some of these materials may be economically considered wastes, but they currently have properties that may impact how they would be managed depending upon future decisions regarding criticality, safeguards, and arms-control.

The DOE (U.S. DOE Feb. 11, 1999) has decided that certain plutonium residues containing up to 10 wt % plutonium may be treated as wastes. No decision has been made for ^{233}U. However, this precedent indicates the potential option to classify similar ^{233}U materials as wastes with limited safeguards and security requirements.

Most of the domestic inventory of exception-case materials are currently found at INEEL. This material is a mixture of 2 to 12 wt % $^{233}UO_2$ in ThO_2, which is stored in dry storage vaults and 6M transport drums. Most of the material is in the form of unirradiated LWBR fuel rods stored in canisters in dry storage vaults. The canisters contain a variety of LWBR fuel forms—pellets, rods and tubes. Overall, these materials are chemically stable and have a relatively uniform composition.

Other exception-case materials at INEEL are in storage at the Radioactive Waste Management Complex (RWMC). These materials reside in two major types of storage buildings: a building for above-ground retrievable storage and earthen-cover berms inside a building. The building contains exception-case material regarded as "accessible" in 11 overpack boxes, each of which contains 5 to 6 bbl, each having 55- or 110-gal capacity. Each overpack box has 3/4-in.-thick lead shielding. Earthen-cover berms contain barrels of ^{233}U exception-case material that are stacked on asphalt pads. The barrels are separated by layers of plywood and plastic and backfilled under an earthen cover. A total of 1804 barrels, 107 of which contain exception-case material, are regarded as "unaccessible" and are found in the earthen-cover berms.

2.6.4 Concentrated Fissile Materials

It has been proposed that concentrated fissile materials be defined as materials of sufficient fissile material content such as to require special handling to address nuclear criticality, safeguards, and arms-control concerns. These materials exclude spent nuclear fuel (SNF), but they essentially include all other ^{233}U-bearing materials. Concentrated ^{233}U fissile materials contain >12 wt % ^{233}U equivalent.

Examples of concentrated fissile materials stored at ORNL include packages containing $^{233}UO_3$ powder received from the Savannah River Site (SRS) and stainless steel cans containing stabilized uranium in the form of solidified U_3O_8. The latter material was generated as part of the CEUSP. The CEUSP material originated from Consolidated Edison reactor fuel uranium that was recovered by the West Valley Nuclear Services (WVNS) plant at West Valley, New York, and later sent to ORNL for storage.

2.6.5 Future Wastes and Wastes That Are Repackaged

The categorization scheme previously described for the current ^{233}U material inventory does not necessarily imply that any ^{233}U-containing materials will be treated differently from those in the past. The previously described categorization scheme defines different levels of ^{233}U wastes and flags some materials as exception case. As new policies are developed in the future, the requirements for the management of exception-case materials may change significantly and result in these materials being managed as either wastes or concentrated fissile materials.

Potentially significant quantities of new ^{233}U wastes may be generated in the future from repackaging and from future processing of fissile materials. Some of the ^{233}U waste inventory (including some exception-case material) will need to be repackaged to meet repository [Waste Isolation Pilot Plant (WIPP) and Yucca Mountain (YM)] waste acceptance criteria (WAC). Future processing of ^{233}U fissile materials will be needed to extract ^{233}U for medical and other beneficial purposes and to stabilize ^{233}U-bearing materials for either long-term storage or final disposition.

A recent study (Forsberg, Storch, and Lewis July 7, 1998) conducted for the DOE Office of Fissile Materials Disposition (MD) recommends that, where feasible, sufficient DU (i.e., ^{238}U) be added to any future generated ^{233}U wastes to isotopically dilute the ^{233}U to a concentration level of <0.66 wt % ^{233}U in ^{238}U.

Implementing this recommendation has the major advantage of minimizing major ^{233}U waste concerns and issues associated with nuclear criticality, domestic safeguards, and arms control. In addition, there is no shortage of DU to meet this recommendation. The addition of DU to ^{233}U waste streams is a beneficial use of DU.

2.6.6 References for Sect. 2.6

A full citation of the major reference that provides the basis for the ^{233}U waste threshold criteria previously discussed is given below. This is followed by a list of sources that provide additional information on this topic.

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2.7 BIOCHEMISTRY AND METABOLIC PATHWAYS

2.7.1 Biological Properties and Hazards

All isotopes of uranium (including ^{233}U) and their compounds present biological hazards through ingestion and inhalation. The DOE and NRC permissible levels for soluble uranium compounds are based on chemical toxicity, whereas the permissible body level for insoluble compounds is based on radiotoxicity. Following acute and chronic exposures, chemical toxicity often appears as irreversible kidney damage and acute arterial lesions (Lewis 1996). Uranium is a heavy metal and has characteristics of other heavy metals like lead. Soluble uranium compounds may be absorbed through the skin, especially through open wounds. Insoluble uranium compounds have a detrimental effect on the lungs as a result of irradiation by the radioactive decay of the inhaled particles. This material is transferred from the lungs very slowly. Regarding the inhalation of moderately soluble and soluble forms of uranium, the radiation dose generally decreases with increasing solubility of the inhaled compounds, but the kidney burden generally increases. Some compounds associated with certain forms of uranium can also be toxic (e.g., HF, which is often absorbed on UF_4 and is often a chemical reaction product between UF_6 and water). Table 2.7*a* (Lewis 1996) lists groups of uranium compounds according to their varying degrees of solubility.

Unlike the long-lived (7340-year half-life) ^{229}Th in the decay of ^{233}U, the ^{232}U decay chain has no long-lived "stopper" isotope that can be used to "break" the decay chain by chemical separation. This property implies that the effective absorbed energy per disintegration of ^{232}U and its decay products will be much higher than that for ^{233}U. This is a significant point in the consideration of biological hazards. The lack of a "stopper" isotope in the ^{232}U decay chain leads to an approximately four times greater effective energy per disintegration to bone than from the ^{233}U decay chain.

Biological half-life and rate of absorption into the body are also factors affecting internal doses from the decay of ^{233}U and ^{232}U. The biological half-life indicates the time required for the body to eliminate half of an administered dose of a radioactive substance by the regular (natural) processes of elimination. For a particular radionuclide, the biological half-life varies with the organ of the body under consideration. Table 2.7*b* (ICRP 1979) lists the half-lives and critical organs for ^{232}U, ^{233}U, and other fissile nuclides. The retention of uranium in various tissues of the body is no longer described by a single biological half-life. Table 2.7*b* is based on ICRP Publication 30 (ICRP 1979), which describes the retention of uranium in all tissues by a sum of two exponential functions. This means that for each uranium isotope there are two biological half-lives, each of which applies to a certain fraction of the material deposited in the tissues of concern. Thus, for each uranium isotope and organ listed, Table 2.7*b* reports two biological half-lives and the percentage of the activity deposited in that organ to which each half-life applies.

The biological half-life of all uranium isotopes is the same, and the half-life of ^{232}U is not so short that it greatly shortens the residence time in the body compared with other uranium isotopes with much longer half-lives. The dose from ingestion and inhalation of radionuclides depends on the amount (activity) taken into the body, and the dose per unit activity of ^{232}U ingested or inhaled is higher than the dose from the same activity intake of any longer-lived isotopes, due to rapid buildup and decay of the ^{232}U decay products in the body.

2.7.2 Metabolic Pathways

In general, external exposure to alpha radiation from actinide contamination is not a concern because of the protection afforded by the outer layer of skin. However, inhalation of the more radioactive actinides such as ^{233}U and ^{232}U, even in microgram quantities, delivers significant internal radiation doses to the body. Absorption of actinides through contamination of open wounds also delivers an internal dose. Ingestion of actinides generally results in substantially lower radiation doses than inhalation.

When an actinide such as ^{233}U and ^{232}U enters the body through inhalation, ingestion, or an open wound, its biologic behavior is determined by its physical and chemical characteristics. When larger insoluble particles are inhaled, they are efficiently removed from the upper airways by ciliary action, ingested and then excreted in the feces. Inhaled small actinide particles, less than a few microns in diameter, penetrate deeper into the lungs, where they are aggregated in place by cellular encapsulation or are translocated to lymph nodes and the liver. Massive inhalation doses from smaller particles can cause pulmonary injury, fibrosis, and even death, while intermediate doses pose a potential for delayed lung cancer. Very small actinide particles and ionic forms are complexed in the blood serum and then deposited in the liver and on bone surfaces. These deposits are metabolized very slowly. A fraction of the actinide being translocated is excreted in urine; therefore, the urinary actinide level can provide an estimate of the total body actinide content. An actinide's potential long-term radiological consequences, i.e., cancer, are proportional to the local absorbed dose from short-range alpha particles, and the consequences are confined to the organs of concentration: lung, liver, and bone (Cantey June 1995).

2.7.3 Regulatory Exposure Limits, Concentration Limits, and Permissible Intakes

Federal regulations specified by the U.S. Nuclear Regulatory Commission (NRC) in tables of Appendix B of 10 CFR Part 20 (U.S. NRC Jan. 1, 1999) indicate the maximum permissible limits of ^{233}U (and ^{232}U) for workers and occupational exposure, for concentrations in airborne and liquid effluents released to the environment, and for concentrations in discharges to sanitary sewer systems. These regulations serve as radiation protection standards for the general public. Table 2.7*c* (U.S. NRC Jan. 1, 1999) lists the occupational exposure limits for ^{233}U, ^{232}U, other uranium radionuclides, and natural uranium. The annual limit on intake (ALI) and derived air concentration (DAC) for inhalation are given for an aerosol that has an average particle diameter of 1 μm and for three classes (D, W, Y) of radioactive materials, which refer to their retention period (approximately days, weeks, or years) in the pulmonary region of the lung. This classification refers to a range of nuclide clearance half-times as follows:

D: < 10 d.
W: ≥ 10 d and < 100 d.
Y: ≥ 100 d.

For uranium radionuclides, this classification also refers to the following groups of compounds:

D: UF_6, UO_2F_2, and $UO_2(NO_3)_2$.
W: UO_3, UF_4, and UCl_4.
Y: UO_2 and U_3O_8.

It should be noted that the classification of a compound as Class D, W, or Y is based on the chemical form of the compound and not on the radiological half-life.

In Table 2.7*c*, the ALI values are the annual activity intakes of a given radionuclide which would result in either a committed effective dose equivalent of 5 rem or a committed dose equivalent of 50 rem to any organ or tissue. The DAC values in Table 2.7*c* are derived limits intended to control chronic occupational exposures. Further discussion of the relationship between the ALI and DAC values is provided in Appendix B of 10 CFR Part 20.

Table 2.7*d* (U.S. NRC Jan. 1, 1999) lists the maximum permissible concentrations of ^{233}U, ^{232}U, and other uranium nuclides in airborne and liquid effluents released to the environment. This is followed by Table 2.7*e* (U.S. NRC Jan. 1, 1999), which reports the maximum permissible concentrations of ^{233}U, ^{232}U, and other uranium nuclides in monthly and annual discharges to sanitary sewer systems. In Table 2.7*d*, the limits on activity concentrations in air and water for releases to unrestricted areas that may be accessed by the public are based on an annual committed effective dose equivalent of 50 mrem (0.5 mSv) from inhalation and ingestion, respectively. The effective dose equivalent is a weighted sum of dose equivalents to different organs or tissues defined by the ICRP (1977), and the committed dose is the dose received over 50 years following an acute intake of a radionuclide. For any radionuclide, the committed dose includes the contributions from any radioactive decay products arising from decay of the radionuclide in the body. For inhaled materials, concentration limits for different lung clearance classes (solubilities in the lung, described above) are given.

The concentration limits for air and water presented in Table 2.7*d* are inversely proportional to the internal doses per unit activity intake by way of inhalation and ingestion, respectively. The dose per unit intake of a radionuclide provides a measure of its radiotoxicity. Thus, the data of Table 2.7*d* indicate that longer-lived uranium isotopes such as ^{235}U and ^{238}U are less radiotoxic than ^{233}U and especially ^{232}U.

Table 2.7*f* (U.S. NRC Jan. 1, 1999 and ICRP 1979) gives the maximum permissible quarterly intakes (oral and inhalation) of ^{233}U, ^{232}U, and other uranium nuclides for critical body organs. The levels reported in Table 2.7*f* are those recommended for occupational exposure by the NCRP. However, Table 2.7*f* does not represent the annual limits on intake (ALIs) currently used by the NRC and DOE. The ALIs in NRC and DOE regulations are reported in Table 2.7*g* (ICRP 1994) and are based on the models in ICRP Publication 30 and a limit on annual effective dose equivalent for workers of 5 rem. By contrast, the ICRP's latest ALIs for workers are based on revised models and a limit on annual effective dose for workers of 2 rem. (It should be noted that an effective dose is not the same as an effective dose equivalent.)

2.7.4 Protection and Radiation Exposure

The penetrating radiation field from a source of ^{233}U and ^{232}U depends upon many factors. These factors are discussed further in Sect. 4 and include:

- surface area of the radioactive source,
- distance from the source,
- self-shielding due to density and geometry of source material, and
- external shielding used to reduce the radiation field from the source.

The most important factor specific to the penetrating radiation field for ^{233}U is the quantity of ^{232}U. Because of the high-energy gamma radiation given off by the ^{232}U daughter, ^{208}Tl, the quantity of ^{232}U is the determining factor in the ^{233}U radiation field. External exposure is a much greater concern for ^{232}U and its short-lived decay products than for ^{233}U, primarily because the ^{212}Bi and ^{208}Tl decay products of ^{232}U emit high intensities of high-energy photons but ^{233}U and its decay products emit only low intensities of lower-energy photons. Figure 2.7*a* shows the calculated gamma radiation levels over time for material with varying concentrations of ^{232}U. These calculations were made for exposures 1 ft away from a 10-kg UO_3 source packed in a cylindrical can with a 6-cm radius, 12-cm height and a thickness of 12 mil (0.03 cm). After the initial increase as the gamma daughters are produced, the radiation levels are linear with ^{232}U concentration. Maximum gamma exposure levels are reached after about 3800 d (10.3 years) (Bereolos et al. April 1998).

Uranium-233 compounds are handled in sealed containers or in high-quality enclosures (shielded cells, glove boxes, and ventilated tanks) because of the high radiation hazard (Horton 1972). Additional countermeasures to protect workers, discussed in Sect. 4.6, include ventilation control, personal hygiene, first aid, and shipping regulations (Lewis 1996).

2.7.5 References for Sect. 2.7

Listed below are the specific references cited in Sect. 2.7. This is followed by a list of additional sources providing more detailed information on ^{233}U biochemistry and metabolic pathways.

2.7.5.1 References Cited

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2.7.5.2 Supplemental Resources

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ORNL DWG 98-3896

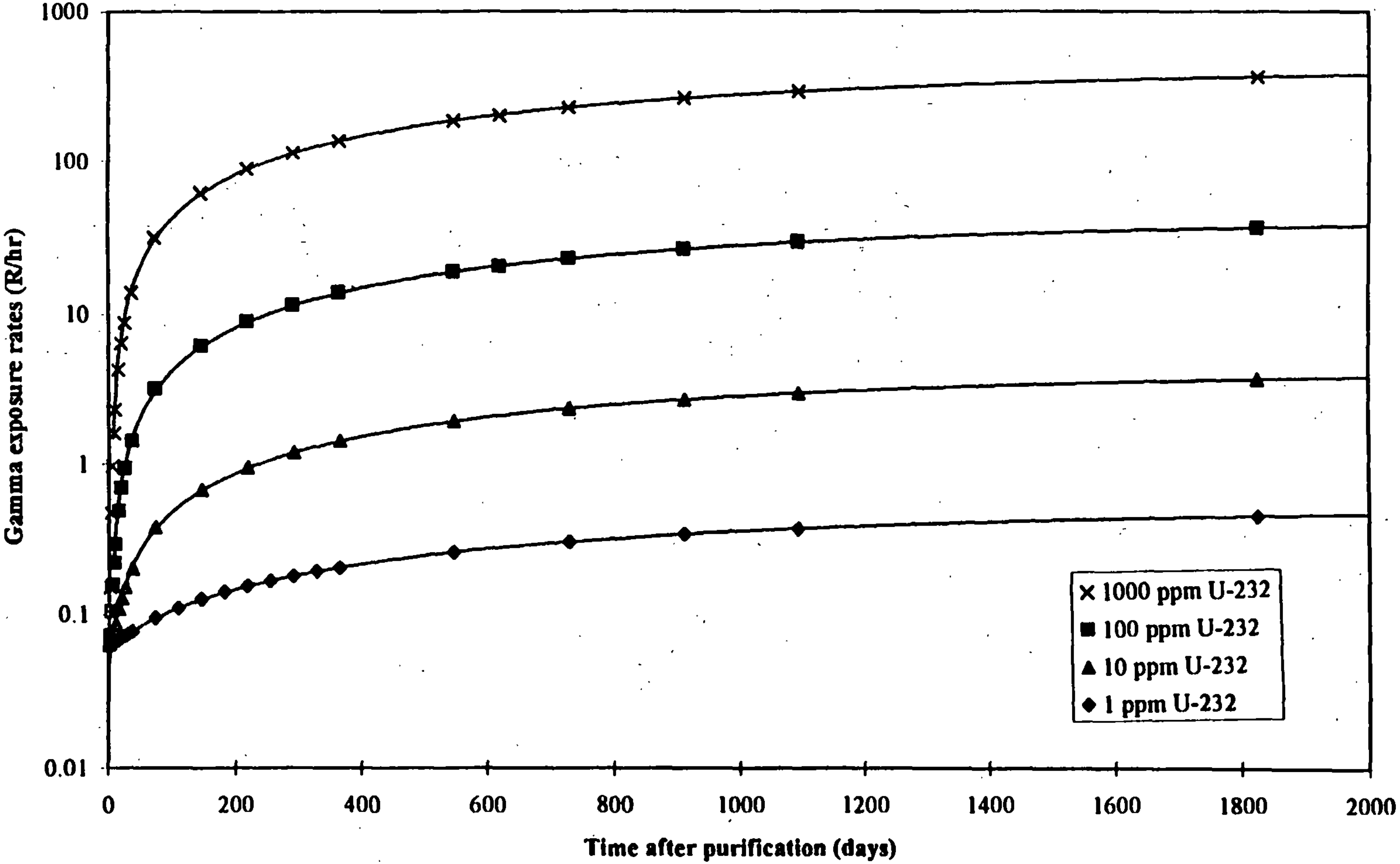

Fig. 2.7*a*. Gamma exposures at 1 ft from 10 kg of UO_3 with varying amounts of ^{232}U.

Table 2.7*a*. Solubility of uranium compounds[a]

Relative degree of solubility	Compound(s)
Most soluble	UF_6 $UO_2(NO_3)_2$ UO_2Cl_2 UO_2F_2 Uranyl acetates Uranyl carbonates Uranyl sulfates
Moderately soluble	UF_4 UO_2 UO_3 UO_4 $(NH_4)_2U_2O_7$
Least soluble	UO_2 (high fired) U_3O_8 Uranium hydrides Uranium carbides

[a] Based on Lewis 1996.

Table 2.7*b*. Comparison of half-lives and critical organs for selected isotopes of uranium and plutonium[a]						
Characteristic	^{232}U	^{233}U	^{235}U	^{238}U	^{239}Pu	^{241}Pu
Half-lives						
Physical (y)	6.89E+01	1.592E+05	7.037E+08	4.468E+09	2.44E+04	1.32E+01
Biological (d)						
Bone	20 (90%) 5,000 (10%)	20 (90%) 5,000 (10%)	20 (90%) 5,000 (10%)	20 (90%) 5,000 (10%)	36,500	36,500
Kidney[b]	6 (99.6%) 1,500 (0.4%)	6 (99.6%) 1,500 (0.4%)	6 (99.6%) 1,500 (0.4%)	6 (99.6%) 1,500 (0.4%)		
Liver					14,600	14,600
Gonads					*c*	*c*
Effective (d)[d]						
Bone	20 (90%) 5,000 (10%)	20 (90%) 5,000 (10%)	20 (90%) 5,000 (10%)	20 (90%) 5,000 (10%)	36,500	4,300
Kidney[b]	6 (99.6%) 1,500 (0.4%)	6 (99.6%) 1,500 (0.4%)	6 (99.6%) 1,500 (0.4%)	6 (99.6%) 1,500 (0.4%)		
Liver					14,600	3,600
Gonads					*c*	4,800
Critical organs[e]	Bone Kidneys GI[f] tract Red marrow Lungs	Bone Kidneys GI[f] tract Red marrow Lungs	Bone Kidneys GI[f] tract Red marrow Lungs	Bone Kidneys GI[f] tract Red marrow Lungs	Bone Liver Red marrow Gonads GI[f] Tract Lungs	Bone Liver Red marrow Gonads GI[f] Tract Lungs

[a] Based on information in ICRP 1979. This reference describes the retention of uranium in all tissues by a sum of two exponential functions. This means that for each uranium isotope there are two biological half-lives, each of which applies to a certain fraction of the material deposited in the tissues of concern. Thus, for each uranium isotope and organ listed, there are two biological half-lives and the percentage of the activity deposited in that organ to which each half-life applies. This approach does not apply to the isotopes of plutonium, for which only one biological half-life needs to be specified for each organ.

[b] Biological half-lives for kidneys also apply to all other soft tissues.

[c] Plutonium deposited in gonadal tissues is assumed to be permanently retained there.

[d] Effective half-life takes into account radioactive decay and biological removal.

[e] Critical organs depend on route of intake (ingestion or inhalation), and critical organs for particular route of intake depend on solubility of chemical form.

[f] GI = gastrointestinal; critical tissues include walls of upper and lower large intestines.

Table 2.7c. Occupational exposure limits for ^{232}U, ^{233}U, and other uranium radionuclides[a]

Radionuclide	Retention class[b]	Annual limit on intake (μCi)		Derived air concentration for inhalation (μCi/cm^3)
		Oral ingestion	Inhalation	
^{232}U	D	2E+0	2E-1	9E-11
	W		4E-1	2E-10
	Y		8E-3	3E-12
^{233}U	D	1E+0	1E+0	5E-10
	W		7E-1	3E-10
	Y		4E-2	2E-11
^{234}U	D	1E+1	1E+0	5E-10
	W		7E-1	3E-10
	Y		4E-2	2E-11
^{235}U	D	1E+1	1E+0	6E-10
	W		8E-1	3E-10
	Y		4E-2	2E-11
^{238}U	D	1E+1	1E+0	6E-10
	W		8E-1	3E-10
	Y		4E-2	2E-11
Nat. U[c]	D	1E+1	1E+0	5E-10
	W		8E-1	3E-10
	Y		5E-2	2E-11

[a] Specified by the NRC in Table 1, Appendix B of 10 CFR Part 20. Values listed give limits in air and water for releases to unrestricted areas accessible to the public. Concentration limits are inversely proportional to radiation doses per unit activity intake by way of either inhalation (air) or ingestion (water).

[b] Clearance of inhaled radionuclides from respiratory tract in a matter of days (D) for soluble chemical forms, weeks (W) for chemical forms with intermediate solubility, and years (Y) for insoluble chemical forms. Uranium (or thorium) in insoluble oxide forms should be Class Y. Reflects the following clearance half-times and groups of uranium compounds:

D (< 10 d): UF_6, UO_2F_2, and $UO_2(NO_3)_2$.
W (≥ 10 d and < 100 d): UO_3, UF_4, and UCl_4.
Y (≥ 100 d): UO_2 and U_3O_8.

[c] Natural uranium is comprised of ^{234}U (0.0055 at. %), ^{235}U (0.720 at. %), and ^{238}U (99.2745 at. %).

Table 2.7d. Concentration limits of uranium radionuclides in airborne and liquid effluents released to the general environment[a]

Radionuclide	Retention class[b]	Maximum effluent concentration (µCi/cm^3)		Maximum effluent concentration (µg/cm^3)	
		Air	Water	Air	Water
^{232}U	D	6E-13	6E-8	3E-14	3E-9
	W	5E-13		2E-14	
	Y	1E-14		5E-16	
^{233}U	D	3E-12	3E-7	3E-10	3E-5
	W	1E-12		1E-10	
	Y	5E-14		5E-12	
^{234}U	D	1E-12	3E-7	2E-10	5E-5
	W	5E-14		8E-12	
	Y	3E-12		5E-10	
^{235}U	D	3E-12	3E-7	1E-6	1E-1
	W	1E-12		5E-7	
	Y	6E-14		3E-8	
^{238}U	D	3E-12	3E-7	9E-6	9E-1
	W	1E-12		3E-6	
	Y	6E-14		2E-7	
Nat. U[c]	D	3E-12	3E-7	4E-6	4E-1
	W	9E-13		1E-6	
	Y	9E-14		1E-7	

[a] Specified by the NRC in Table 2 of Appendix B of 10 CFR Part 20. Values listed give limits in air and water for releases to unrestricted areas accessible to the public. Concentration limits are inversely proportional to radiation doses per unit activity intake by way of either inhalation (air) or ingestion (water).

[b] Clearance of inhaled radionuclides from respiratory tract in a matter of days (D) for soluble chemical forms, weeks (W) for chemical forms with intermediate solubility, and years (Y) for insoluble chemical forms. Uranium (or thorium) in insoluble oxide forms should be Class Y. Reflects the following clearance half-times and groups of uranium compounds:

D (< 10 d): UF_6, UO_2F_2, and $UO_2(NO_3)_2$.
W (≥ 10 d and < 100 d): UO_3, UF_4, and UCl_4.
Y (≥ 100 d): UO_2 and U_3O_8.

[c] Natural uranium is comprised of ^{234}U (0.0055 at. %), ^{235}U (0.720 at. %), and ^{238}U (99.2745 at. %).

Table 2.7*e*. Concentration limits of uranium radionuclides for discharges to sanitary sewer systems

Radionuclide	Maximum discharge concentration (μCi/cm^3)		Maximum discharge concentration (μg/cm^3)	
	Monthly average[a]	Annual (calculated)	Monthly average[a]	Annual (calculated)
^{232}U	6E-7	7.2E-6	3E-8	3.4E-7
^{233}U	3E-6	3.6E-5	3E-4	3.7E-3
^{234}U	3E-6	3.6E-5	5E-4	5.8E-3
^{235}U	3E-6	3.6E-5	1E+0	1.7E+1
^{238}U	3E-6	3.6E-5	9E+0	1.1E+2
Nat. U[b]	3E-6	3.6E-5	4E+0	5.2E+1

[a] Specified by the NRC in Table 3 of Appendix B of 10 CFR Part 20. Values listed give limits in air and water for releases to unrestricted areas accessible to the public. Concentration limits are inversely proportional to radiation doses per unit activity intake by way of either inhalation (air) or ingestion (water).

[b] Clearance of inhaled radionuclides from respiratory tract in a matter of days (D) for soluble chemical forms, weeks (W) for chemical forms with intermediate solubility, and years (Y) for insoluble chemical forms. Uranium (or thorium) in insoluble oxide forms should be Class Y. Reflects the following clearance half-times and groups of uranium compounds:

D (< 10 d): UF_6, UO_2F_2, and $UO_2(NO_3)_2$.
W (≥ 10 d and < 100 d): UO_3, UF_4, and UCl_4.
Y (≥ 100 d): UO_2 and U_3O_8.

[c] Natural uranium is comprised of ^{234}U (0.0055 at. %), ^{235}U (0.720 at. %), and ^{238}U (99.2745 at. %).

Table 2.7*f*. Annual limits on intake of selected uranium isotopes by workers in current NRC regulations[a]

Radionuclide	Inhalation intake		Oral intake	
	Solubility class[b]	ALI (μCi)	f_1[c]	ALI (μCi)[d]
^{232}U	D	2E-1[e]	5E-2	2E+0[e]
	W	4E-1	2E-3	5E+1[e]
	Y	8E-3		
^{233}U	D	1E+0[e]	5E-2	1E+1[e]
	W	7E-1	2E-3	2E+2
	Y	4E-2		
^{234}U	D	1E+0[e]	5E-2	1E+1[e]
	W	7E-1	2E-3	2E+2
	Y	4E-2		
^{235}U	D	1E+0[e]	5E-2	1E+1[e]
	W	8E-1	2E-3	2E+2
	Y	4E-2		
^{238}U	D	1E+0[e]	5E-2	1E+1[e]
	W	8E-1	2E-3	2E+2
	Y	4E-2		
U-natural	D	1E+0[e]	5E-2	1E+1[e]
	W	8E-1	2E-3	2E+2
	Y	4E-2		

[a] Annual limits on intake (ALIs) are obtained from Table 1 of 10 CFR Part 20 and are based on limit on annual effective dose equivalent of 5 rem, unless otherwise noted.

[b] Compounds that are cleared from respiratory tract in a matter of days (D), weeks (W), or years (Y). Class D applies to soluble compounds including UF_6, UO_2F_2, and $UO_2(NO_3)_2$; Class W applies to less soluble compounds including UO_3, UF_4, and UCl_4; Class Y applies to insoluble compounds including UO_2 and U_3O_8.

[c] Fraction of ingested activity absorbed into blood from the GI tract. Higher value applies to soluble hexavalent compounds of uranium, and lower value applies to relatively insoluble compounds in which uranium is usually tetravalent.

[d] Values for oral intakes of insoluble compounds are obtained from ICRP 1979.

[e] Value is based on limit on annual dose equivalent to bone surfaces of 50 rem.

Table 2.7*g*. Annual limits on intake of selected uranium isotopes by workers based on current ICRP recommendations[a]

Radionuclide	Inhalation intake		Oral intake	
	Solubility class[b]	ALI (μCi)	f_1[c]	ALI (μCi)
^{232}U	F	1E-1	2E-2	2E+0
	M	8E-2	2E-3	1E+1
	S	2E-2		
^{233}U	F	9E-1	2E-2	1E+1
	M	2E-1	2E-3	6E+1
	S	6E-2		
^{234}U	F	1E+0	2E-2	1E+1
	M	2E-1	2E-3	7E+1
	S	6E-2		
^{235}U	F	1E+0	2E-2	1E+1
	M	2E-1	2E-3	7E+1
	S	7E-2		
^{238}U	F	1E+0	2E-2	1E+1
	M	2E-1	2E-3	7E+1
	S	7E-2		
U-natural	F	1E+0	2E-2	1E+1
	M	2E-1	2E-3	7E+1
	S	7E-2		

[a] Annual limits on intake (ALIs) are based on effective dose coefficients (Sv/Bq) for inhalation or ingestion in Table B.1 of ICRP 1994 and limit on annual effective dose of 2 rem.

[b] Compounds that are cleared from respiratory tract in times that are fast (F), moderate (M), or slow (S). Class F applies to soluble compounds including UF_6, UO_2F_2, and $UO_2(NO_3)_2$; Class M applies to less soluble compounds including UO_3, UF_4, UCl_4, and most other hexavalent compounds; Class S applies to insoluble compounds including UO_2 and U_3O_8.

[c] Fraction of ingested activity absorbed into blood from the GI tract. Higher value applies to soluble hexavalent compounds of uranium, and lower value applies to relatively insoluble compounds in which uranium is usually tetravalent.

3. PROCESSING OF ^{233}U

This section is a brief summary of the processing history of ^{233}U materials. The radiological and chemical characteristics of specific ^{233}U materials processes are also discussed. For the most part, Sect. 3 discusses activities associated with the processing of ^{233}U in the United States. Other international efforts associated with the processing of ^{233}U-bearing materials are exemplified and discussed in International Atomic Energy Agency (IAEA) publication IAEA Technical Report No. 52, *Utilization of Thorium in Power Reactors* (IAEA 1966). (This reference is listed in Sect. 3.1.3.1.)

3.1 HISTORY OF ^{233}U PROCESSING

3.1.1 Background

Since 1947, several federally sponsored programs have either produced or stabilized ^{233}U-bearing materials at government sites, most notably (in chronological order) at ORNL, SRS, and the Hanford Site. A historical list of these programs is provided in Table 3.1*a*. This section describes the major features associated with each of these ^{233}U processing activities, including the program and process objectives and process description (with basic flowsheet, as appropriate), and major results associated with the process performance. Further information on each process is available in the references cited and in the supplemental resources listed.

3.1.2 Nuclear Power Reactors Using ^{233}U Fuel

A major application of ^{233}U materials has been the use as a fuel in nuclear power reactors. Table 3.1*b* (U.S. DOE September 1995 and *Nuclear Engineering International* May 1975) lists the major features of those civilian power reactors that have used fuel containing ^{233}U with natural uranium. Collectively, these eight reactors generated over 4800 MW(e)-years of energy during their operating lifetimes.

As indicated in Table 3.1*b*, eight nuclear power reactors have used ^{233}U fuel in their operation, and most of these used ^{233}U only for a single core. Major features of these reactors and their ^{233}U fuel characteristics are described below. This description is followed by a description of the major features of a new reactor design that is being proposed for the ^{233}U-Th fuel cycle.

3.1.2.1 Dresden Unit 1 Reactor

The Dresden Unit 1 Nuclear Power Station was a 200-MW(e) BWR in northeastern Illinois. This plant was operated for 18 years by the Commonwealth Edison Company before it was permanently shut down in 1978.

The nuclear core of Dresden Unit 1 had space for 488 fuel assemblies, although it was never loaded in excess of 464 (Commonwealth Edison Company March 1988). The ^{233}U fuel assemblies were manufactured by General Electric and consisted of conventional U-Th fuel elements (UO_2-ThO_2) clad in stainless steel. Each fuel assembly consisted of a 10.9-cm^2 zirconium channel surrounding 36 fuel rods, 1.4 cm in diam (Kramer 1958). Most of the Dresden ^{233}U fuel was reprocessed at the West Valley site, except for the corner rods, which were shipped for storage to the SRS.

To demonstrate application of the ^{233}U-Th fuel cycle in a large BWR, thorium fuel was loaded into the core of Dresden Unit 1 and used to generate ^{233}U.

3.1.2.2 Elk River Reactor (ERR)

Located near Minneapolis, Minnesota, the Elk River Reactor (ERR) was a 24-MW(e) BWR, which was built by Allis-Chalmers. This facility was operated for 5 years by the United Power Association for the U.S. Atomic Energy Commission (AEC) before it was permanently shut down in 1968. The reactor was fully dismantled during 1971–1974.

The ERR supported 148 fuel-element assemblies in a complete core loading. Each fuel assembly was about 8.9 cm^2 by 2.1 m long and had 25 fuel pins of $^{235}UO_2$-ThO_2 clad with stainless steel. One of the major objectives of the ERR was to demonstrate the thorium fuel cycle (Fisher and Kendrick February 1968). The ^{233}U in the discharged ERR SNF resulted from the absorption of neutrons in the thorium of the initial fuel. Currently, 188 assemblies of ERR SNF are stored at the SRS (U.S. DOE December 1994).

In the late 1960's, a cooperative project was established between Italy's Comissao Nacional de Energia Nuclear (CNEN) and Allis Chalmers, leading to 3 shipments (28 assemblies per shipment) of ERR fuel to a reprocessing facility [Italian Reprocessing Corporation (ITREC)] in southern Italy during 1968–1970. Of the 84 ERR assemblies shipped to ITREC, 20 were reprocessed, and the remaining 64 were placed in stainless steel cans and stored at ITREC in a fuel storage pool (Nichols Mar. 8, 1996).

3.1.2.3 Fort St. Vrain Reactor (FSVR)

The Fort St. Vrain Reactor (FSVR) station was a 330-MW(e) HTGR in east central Colorado. Serving as a full-scale HTGR for the U-Th fuel cycle, the FSVR was operated by Public Service of Colorado for 10 years before it was permanently shut down in 1989.

The Fort St. Vrain reactor fuel is a carbide-based fuel consisting of a 0.5-in.-diam by 2-in.-long graphite-based compact containing a homogeneous mixture of fissile and fertile TRISO-coated particles. The coated fissile particles consist of a 1:4 mixture of 93 wt % enriched, ^{235}U carbide and thorium carbide that range in size from 380–485 μm in diam. The coated, fertile particles are 100% thorium carbide which range in size from 635–805 μm. The coatings consist of an inner- buffer layer of porous pyrolitic carbon followed by a layer of high-density, isotropic pyrolitic carbon. The next layer consists of silicon carbide to provide fission product containment and physical protection to the particle. The final layer is another layer of high-density, isotropic pyrolitic carbon. The mixture of particles were blended into powdered graphite and processed into cylindrical shapes, which were then sintered. The cylindrical compacts were placed in holes drilled in the fuel block. Each block had 210 fuel holes approximately 30 in. long by 0.5 in. diam (Bendixsen et al. September 1992).

3.1.2.4 Indian Point Unit 1 (IP-1) Reactor

Located near New York City, Indian Point Unit 1 (IP-1) was a 265-MW(e) pressurized-water reactor (PWR) designed by Babcock & Wilcox. The reactor was operated by Consolidated Edison of New York for 12 years before it was permanently shut down in 1974. In the early 1960s, the AEC sponsored a test irradiation of IP-1's initial core to check the feasibility of using the thorium fuel cycle. This gave the IP-1 reactor a distinction of having the only UO_2-ThO_2 core to operate in a commercial U.S. PWR [Electric Power Research Institute (EPRI) July 1981].

For its initial core, IP-1 used Babcock & Wilcox manufactured U-Th fuel elements ($^{235}UO_2$-ThO_2). The core was comprised of 120 fuel assemblies, each measuring 14.1 cm^2. Each assembly contained 195 fuel pins clad with Zircaloy-2 and arranged in a square at a pitch of 0.95 cm (EPRI July 1981).

During reactor operation, some ^{233}U was produced in the IP-1 fuel from neutron irradiation of the thorium. After permanent discharge, all of these assemblies were reprocessed (November 1968 through January 1969) at the West Valley Nuclear Fuel Services (NFS) plant in West Valley, New York, to separate the uranium (mostly ^{235}U and ^{233}U). This material was shipped in nitrate solution for storage at ORNL. As described in Sect. 3.5.2, this reprocessed uranium solution was converted to a stable oxide and stored in the cells of ORNL Building 3019. It is often referred to as the CEUSP material.

3.1.2.5 Molten Salt Reactor Experiment (MSRE)

The MSRE was constructed at ORNL in the early 1960s as part of a larger program to develop a molten salt thermal breeder power reactor using the thorium fuel cycle. The Molten Salt Breeder Reactor program focused on the development of both converter and breeder reactor concepts using uranium and thorium fluoride salts dissolved in a carrier salt mixture consisting of LiF, BeF_2, and ZrF_4. These salts are molten and stable at high temperatures, allowing the design of reactors that operate at high thermal efficiency at essentially atmospheric pressures (Rosenthal, Haubenreich, and Briggs August 1972). Although many desirable features of the molten salt reactor were identified, its development ceased in the mid-1970s in favor of development of the liquid metal fast breeder reactor (LMFBR).

Prior to the thermal power reactor program, molten-salt fuels were considered for aircraft reactor applications. In the early 1950s, a small Aircraft Reactor Experiment was constructed and operated using UF_4 dissolved in a NaF-ZrF_4 salt mixture. Construction of a larger Aircraft Reactor Test was then begun, but stopped when the overall aircraft reactor program ceased. The MSRE was constructed as an inexpensive test of the molten salt breeder concept using the facility left over from the aircraft reactor program. The objectives of MSRE were to demonstrate the stability and compatibility of the LiF-BeF_2 salt with nickel-based alloys and graphite moderator materials, and to demonstrate the continued operation of a molten salt reactor. It produced no electric power, and did not irradiate thorium. Initial operation was with ^{235}U, but later that uranium was replaced with ^{233}U. The MSRE then became the first reactor to operate solely on ^{233}U fuel. MSRE achieved initial criticality in 1965, and operated successfully until the experiment was terminated at the end of 1969 to focus on other aspects of molten salt breeder reactor technology.

The MSRE circulated a LiF-BeF_2-ZrF_4-UF_4 fuel salt through a graphite-moderated reactor vessel, a centrifugal circulating pump, and a shell and tube heat exchanger that transferred heat to a secondary LiF-BeF_2 coolant salt. The coolant salt, in turn, was pumped through an air-cooled radiator that discharged heat into a coolant salt. The reactor operated at 8 MW (Robertson January 1965).

Extensive references document the preparation of the salt mixtures used in the MSRE (Shaffer January 1971), the processing of salts in preparation for reactor operation and as part of the change to ^{233}U operation (Lindauer August 1969) and the preparation of the LiF-^{233}UF$_4$ enriching salt used during ^{233}U operations (Chandler and Bolt March 1969). An excellent compendium of all chemical aspects of MSRE operation was prepared by Thoma (December 1971). Specific technologies generally applicable to the use of ^{233}U include:

- demonstration of the use of ^{233}U to fuel a reactor for extended periods of time;
- fluoride fuel and carrier salt behavior, in contact with nickel alloys and graphite moderator;
- control of corrosion rates by adjustment of the UF_3/UF_4 ratio;
- separation of UF_4 from fluoride salt by sparging with fluorine (fluorination process);
- preparation of $^{233}UF_4$ salt for use as fuel; and
- the general handling of the salts and maintenance of equipment containing the salt.

Other test loops associated with the MSBR program evaluated breeding ratios with various ^{233}U and thorium fuel and blanket concepts, including a simplified single-fluid reactor concept, evaluated alternative secondary coolant salts for tritium control, and demonstrated various aspects of chemical flowsheets to separate uranium and protactinium from the fuel and blanket salts. Processes for the latter include the extraction of uranium from molten fluoride salt into liquid bismuth.

The MSRE fuel salt, a separate flush salt used during maintenance of the reactor circuit, and coolant salt were allowed to freeze in their respective drain tanks at the conclusion of MSRE operation. Recovery and disposition of the salts and the uranium left in the fuel salt is addressed in Sect. 3.5.3.

3.1.2.6 Peach Bottom Reactor (PBR)

The 40-MW(e) PBR was a prototype HTGR in southern Pennsylvania that the Philadelphia Electric Company operated for 8 years before the plant was permanently shut down in 1974. As an HTGR, the PBR was designed to operate on the thorium fuel cycle. In the reactor, ^{233}U was generated from the neutron irradiation of ^{232}Th in the fuel. Following permanent discharge, most of the PBR SNF was shipped to Idaho (INEEL). Some test fuel was shipped to ORNL.

The PBR fuel was a graphite-based fuel element in which the fueled portion is in a stack of annular fuel compacts 2.7 in. OD by 1 in. ID and 3 in. long. The compacts were stacked on a 1-in.-diam high-density, graphite rod and enclosed inside a graphite sleeve 3.5 in. OD. The compacts were made up of particles of 93% enriched ^{235}U carbide and thorium carbide in a graphite matrix which has been sintered at 1800°C. The particles are the carbides of an intimate mixture of uranium and thorium that are 200–600 μm in diam. Each particle had been coated with a layer of pyrolitic carbon. The core 1 particles, which had suffered significant degradation during reactor operation, were coated with a layer of laminar, monolithic pyrolitic carbon. In order to improve the performance of the particle coating, the core 2 particles were coated with isotropic pyrolitic carbon (Morissette, Tomsio, and Razvi October 1986).

3.1.2.7 Shippingport Light-Water Breeder Reactor (LWBR)

Operated by the Duquesne Light Company for the AEC (and later DOE), the Shippingport reactor began power operations in 1957. Located near Pittsburgh, this reactor was the first commercial nuclear power station in the United States. During its operating life, the Shippingport reactor had three different cores, the last being a seed-blanket, LWBR-type core, which operated from 1977 until 1982, when the reactor was permanently shut down. The reactor was fully dismantled during 1985–1989.

The Shippingport LWBR core was developed as part of a research and development (R&D) program whose objective was to use the well-established LWR technology to demonstrate the potential of the ^{233}U-Th fuel cycle. (Use of a nuclear fuel cycle based on thorium, which is more naturally abundant than uranium and offers the potential for better use of the nation's nuclear fuel resources.) During its 5 years of operation, the LWBR core generated a gross electrical output of 2.13 million MWh (Atherton et al. October 1987).

The LWBR core consisted of 12 "seed" fuel assemblies—hexagonal modules arranged in a symmetrical array, surrounded by a reflector-blanket region. Each module contained an axially movable "seed" region [which had a multiplication factor (k) greater than unity], and a stationary, annular hexagonal blanket (which had $k < 1$). Each of these regions, in turn, consisted of arrays of tightly packed, but not touching, fuel rods, which contained pellets of ThO_2 (thoria) and UO_2 (urania), the latter in amounts that range from 0 to 6 wt % in the seed and from 0 to 3 wt % in the blanket region (Lamarsh 1975).

Most of the fuel fabricated for the Shippingport LWBR was shipped to the ICPP [now called the Idaho Nuclear Technology and Engineering Center (INTEC)]. This included about 317 kg of unirradiated LWBR fuel and all of the irradiated LWBR fuel. In addition, about 34 kg of LWBR fuel rods and pellets were shipped for storage to the RWMC at INEEL.

3.1.2.8 Sodium Reactor Experiment (SRE)

Located northwest of Los Angeles, California, the Sodium Reactor Experiment (SRE) was a 10-MW(e) sodium-cooled, graphite-moderated reactor that was designed by Atomics International (a subsidiary of Rockwell International Corporation) and operated by Southern California Edison for the AEC for 7 years before being permanently shut down in 1964. The plant was decommissioned from 1974–1983, during which time the reactor was fully dismantled.

The SRE system was initially operated as a graphite-moderated, sodium-cooled reactor. Later it was modified to operate as a thermal power breeder reactor using ^{233}U fuel and thorium, respectively, as the fissionable and fertile components of the fuel. The SRE ^{233}U-Th core was comprised of uranium and thorium rods clad in stainless steel. Investigations made with this type of core in the SRE included the feasibility of the ^{233}U fuel and evaluations of the fuel element design, coolant, structural temperatures, fuel burnup, and corrosion (Glasstone 1955 and *Nuclear Engineering* February 1957).

The ^{233}U fuel discharged from the SRE was shipped to SRS for storage.

3.1.2.9 New Developments

In recent years, a seed-blanket reactor core design utilizing a thorium-based fuel element (rod) has been proposed by Alvin Radkowsky (Galperin, Reichert, and Radkowsky 1997). Called the Radkowsky Thorium Reactor (RTR), the major advantage of this design is the potential safety it offers against proliferation risks while burning excess plutonium. The RTR core produces almost no plutonium and can be configured to dispose of HEU or weapons-grade plutonium (WGP). This core uses uranium enriched to just under 20 wt % (^{235}U), the threshold considered by the IAEA to be unsuitable for nuclear weapons production (*Nukem Market Report* June 1996).

It has been proposed that by replacing the bulk of the ^{238}U present in a conventional LWR core with either ^{235}U or thorium, plutonium production can be reduced by as much as 80 to 90%. In addition, by the time the RTR thorium fuel blankets are removed (scheduled once every 10 years), the total plutonium itself is estimated to contain enough ^{238}Pu and other nonfissile Pu isotopes that it would not be suitable for weapon applications (*Nukem Market Report* June 1996).

The basics of the RTR core design is a "seed" and "blanket" fuel design. A conceptual design for the RTR includes an implementation of a RTR fuel reload for a standard Russian VVER (a pressurized-water type reactor) having a capacity of 1000 MW(e). The RTR core for this reactor has 163 fuel assemblies, each of which is comprised of a hexagonal "seed" and surrounding "blanket." Each seed and blanket is comprised of a set of fuel elements of 1.5 cm diam. Bundles of these elements could be assembled to form a replacement core for an LWR.

The basic fuel management concept for an RTR includes replacing the seeds on a schedule similar to that for conventional LWR fuels, but leaving the uranium-thorium blankets in the core for 10 years at a time. As burnup in the RTR proceeds, the newly generated ^{233}U assumes an increasingly greater share of the fission load. Since any ^{233}U produced from thorium irradiation would also be irradiated in the core (i.e., in situ), the ^{233}U would not become a proliferation risk. Even when an assembly blanket is removed, any ^{233}U would be mixed in with other nonfissile uranium isotopes to the extent that separating it would be significantly harder than simply fabricating fresh weapons grade ^{235}U (Friedman September 1997 and *Nukem Market Report* June 1996).

However, there are questions (Friedman September 1997) about the current feasibility of the RTR design. These include concerns regarding the present lack of economic incentive as a result of the current low price for conventional uranium fuel. Largely for that reason, it has been difficult to convince utilities that significant financial savings will result from either a new RTR or retrofitted core before they put up capital for licensing and technical development work in making the transition to the RTR design (Friedman September 1997).

Private investors in the Radkowsky Thorium Power Corporation (New York, New York) and government organizations in the United States and Russia are currently promoting the RTR design. These proponents acknowledge that for economic reasons, the near future will not see construction of many new RTRs. Rather, they anticipate a number of existing LWR-type facilities being retrofitted (i.e., recored) in the near future to accommodate RTR assemblies and achieve lower fuel cycle costs (*Nukem Market Report* June 1996).

3.1.3 References for Sect. 3.1

A list of cited references documenting both the background of past major ^{233}U government-sponsored programs and the use of ^{233}U in nuclear power reactors is provided below. This is followed by a list of sources providing additional information on these topics.

3.1.3.1 References Cited

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The work conducted as part of the Molten Salt Breeder Reactor Program at ORNL (Sect. 3.1.2.5) is well documented, covering reactor design and operating history, salt preparation and experience, fission product migration, tritium migration, salt and uranium processing, and other aspects of the project. In addition to the key references cited in Sect. 3.1.2.5, the series of semiannual reports generated throughout the life of the program is particularly useful.

Table 3.1*a*. Historical summary of major ^{233}U reprocessing and stabilization programs					
Year(s)	Site(s)	Facility	Program/process	Major objective(s)/result(s)	Major reference(s)[a]
1947–50	ORNL	Bldg. 3019	Hexone-23	Solvent extraction for Th/^{233}U from metal slugs	Brooksbank, Patton, and Krichinsky (ORNL/TM-12720, August 1994)
1952	ORNL	Bldg. 3019	TBP-Interim 23	Solvent extraction for ^{233}U recovery	Brooksbank, Patton, and Krichinsky (ORNL/TM-12720, August 1994)
1952–59	ORNL, Hanford, SRS	Bldg. 3019	Thorex campaigns	60 kg of ^{233}U recovered for experiments testing the ^{233}U fuel cycle	Brooksbank, Patton, and Krichinsky (ORNL/TM-12720, August 1994)
1960–64	ORNL	Bldg. 3019	Kilorod Facility	Pilot facility for ^{233}U/Th reactor fuel fabrication	Brooksbank, Nichols, and Lotts (February 1968) Haws et al. (ORNL-3681, August 1965)
1964–66, 1968, 1969	SRS	Purex Plant	^{233}U production campaign	564 kg of ^{233}U produced from 240 t of irradiated ThO_2 (for research and for LWBR program)[b]	Orth (April 1979)
1966, 1970	Hanford	Purex Plant	^{233}U production campaign	863 kg of ^{233}U produced from 635 t of irradiated ThO_2 (for confirming the suitability of the Purex process for processing Th on a campaign basis)[c]	Atlantic Richfield Hanford Co. (ISO-440RD, March 1968) Jackson and Walser (ARH-2127, March 1977)
1965–76	ORNL	Bldg. 3019	LWBR/Sol-gel	Preparation of 1500 kg of ^{233}U as dioxide powder for Shippingport LWBR	Leitnaker et al. (ORNL-4755, April 1972)
1985–86	ORNL	Bldg. 3019	CEUSP	Conversion of hazardous liquid uranium nitrate to a stable oxide form for safe storage	McGinnis et al. (1986)

[a] Major reports that document the activities and results of a particular ^{233}U program. These are listed in Sect. 3.1.3.2.

[b] No information is available to indicate how much, if any, of the reported SRS production was discharged to waste tanks.

[c] About 45 kg of ^{233}U produced at Hanford was discharged to waste tanks.

Table 3.1*b*. Operational experience of reactors using ^{233}U fuel[a]

Reactor (location)	Type[b]	Period of operation	Capacity rating[c]		Lifetime energy generation [MW(e)–years]
			MW(e)	MW(th)	
Dresden Nuclear Power Station Unit 1 (Morris, IL)	BWR	1960–1978	200	700	1800
Elk River Power Station (Elk River, MN)	BWR	1963–1968	22	58	58
Fort St. Vrain Reactor (FSVR) (Platteville, CO)	HTGR	1979–1989	330	842	490
Indian Point Station–Unit 1 (Buchanan, NY)	PWR	1962–1974	265	615	1440
Molten Salt Reactor Experiment (MSRE) (Oak Ridge, TN)	MSR	1965–1969	NA[d]	8	12
Peach Bottom Power Station–Unit 1 (Peach Bottom, PA)	HTGR	1966–1974	40	115	157
Shippingport Nuclear Power Station (Shippingport, PA)	LWBR[e]	1957–1982	72	236	842
Sodium Reactor Experiment (SRE) (Santa Susana, CA)	SCGM	1957–1964	10	30	4

[a] Based on U.S. DOE September 1995 and *Nuclear Engineering International* May 1975.

[b] BWR = boiling-water reactor; HTGR = high-temperature, gas-cooled reactor; PWR = pressurized-water reactor; LWBR = light-water breeder reactor, MSR = molten-salt reactor, and SCGM = sodium-cooled, graphite-moderated reactor.

[c] Two ratings are reported: MW(e), the rate of electrical energy output in megawatts, and MW(th), the rate of thermal energy output.

[d] NA = not applicable.

[e] During its history, the Shippingport reactor operated with three different cores. Two of these were light-water cooled, seed-blanket, PWR-type cores. The third and last core in the reactor (during 1977–1982) was a seed-blanket LWBR type.

3.2 URANIUM-233 SEPARATION FROM THORIUM

3.2.1 Savannah River Campaigns

This section provides a summary of the ^{233}U production campaigns at Savannah River based on Orth (April 1979) and Rathvon et al. (February 1968). Additional information is provided in the references listed in Sect. 3.2.1.4.2.

3.2.1.1 Process Objective(s)

To produce ^{233}U for research purposes, the chemical reprocessing facilities at the Savannah River Plant (SRP) (now called the SRS) were used to separate and recover ^{233}U from irradiated thorium oxide (thoria) and thorium-metal targets. To use the reprocessing facilities at SRP, the existing reprocessing facilities (which were originally used for uranium and plutonium recovery with the PUREX™ process) were adapted to the Thorex™ process for the recovery of uranium and thorium.

Five separate campaigns were undertaken at SRP between 1966 and 1969. In the first two campaigns, thorium metal was used as the feed, and only uranium was recovered while the thorium was discarded as waste. For the last three campaigns, a new process also recovered thorium. In the first of these three campaigns, both thorium metal and thoria were used as feed while in the last two campaigns the feed consisted of only thoria.

3.2.1.2 Process Description and Basic Flowsheet

The five campaigns undertaken at SRP were based on two different flowsheets. In the first two campaigns where only ^{233}U was recovered, a 3.5 wt % TBP [$(C_4H_9O)_3PO$] flowsheet was used (Fig. 3.2.1*a*). In the final three campaigns, the flowsheet was changed to use 30 wt % TBP to extract and recover the thorium (Fig. 3.2.1*b*).

3.2.1.2.1 Dilute TBP Flowsheet

In the campaign that used the dilute TBP flowsheet, the initial feed was aluminum-clad thorium slugs. The slugs were put into a dissolver. Then a boiling sodium hydroxide-sodium nitrate ($NaOH$-$NaNO_3$) mixture was used to dissolve the aluminum cladding, which was then transferred out as a waste for storage. The remaining irradiated thorium metal was then dissolved by adding a solution of nitric acid, potassium fluoride, and aluminum nitrate [specifically, 12 *M* HNO_3 - 0.05 *M* KF - 0.2 *M* $Al(NO_3)_3$]. The dissolver product was then centrifuged to remove undissolved fines, which were then fed back into the dissolver.

Manganese nitrate [$Mn(NO_3)_2$] and potassium permanganate ($KMnO_4$) were then added to the solution to form a precipitate, manganese dioxide (MnO_2). The MnO_2 precipitate carried a major fraction of the ^{233}Pa and Zr-Nb fission products. The solution was then fed to a second centrifuge to separate the precipitate and to reduce significantly the radiation level of the solution. The precipitate was stored for recovery of the ^{233}U produced by the decay of the ^{233}Pa. The clarified solution was then adjusted with either acid or water (or both) for feed to the first cycle SX system (1A–C) (Fig. 3.2.1*a*).

In SX, mixer-settlers of 12 to 16 stages were used as the contactors. The first SX cycle used three mixer-settler banks. The uranium-thorium solution was fed to the 1A mixer-settler bank, where the uranium was extracted with 3.5 wt % TBP in Ultrasene™ (a high-grade kerosene). The extracted uranium solution was sent to the next mixer-settler (1B), and the thorium was discarded in a waste stream. In the second bank (1B), the uranium solution was then scrubbed with an acidic solution of sodium phosphate (Na_3PO_4), which was added to remove ^{233}Pa for recycle and improve the decontamination from zirconium-niobium (Zr-Nb). The uranium solution was then sent to the third stage (1C), where the uranium was stripped with a dilute 0.01 *M* HNO_3 solution. The uranium product from this first cycle extraction cycle was then washed with Ultrasene™, evaporated, and acid adjusted for feed to the second SX cycle (1D–E).

The second SX cycle consisted of two mixer-settler banks and was used for additional decontamination from fission products. In the first bank (1D), the uranium was extracted by a 7.5 wt % TBP solution and then stripped in the 1E bank with 0.01 *M* HNO_3 to produce a dilute uranium nitrate product solution. The uranium was absorbed on Dowex™ 50W-X12 cation exchange resin and then eluted with a mixture of 1 *M* HNO_3 and 2 *M* NH_4NO_3. The uranium was then precipitated as ammonium diuranate [$(NH_4)_2U_2O_7$] using ammonium hydroxide (NH_4OH). The precipitate was then calcined by heating at 550°C for 30 min to produce the final UO_3 product.

3.2.1.2.2 Thorex Flowsheet

The final three campaigns used a 30 wt % TBP flowsheet to recover thorium as well as uranium. The flowsheet (Fig. 3.2.1*b*) involved the addition of a third SX cycle for decontamination.

In the final three campaigns, the feed was both irradiated thorium metal (as in the first two campaigns) and (primarily) irradiated thorium oxide. The thoria (ThO_2) targets that were processed were aluminum cans filled with 3.6 kg of thoria particles. The thorium metal targets were treated to remove the aluminum cladding as described in the first flowsheet. For the thoria feed and aluminum cans, a two-step dissolving process was used. First, concentrated acid (12 *M* HNO_3, 0.05 *M* KF) was added to the dissolver to dissolve the thoria heel left in the dissolver from the previous charge. Then, fresh targets were added to the solution, the acid was diluted, and mercuric nitrate [$Hg(NO_3)_2$] was added to catalyze the dissolution of the aluminum. This reaction led to the dissolution of the aluminum and some of the thoria and left a heal of thoria. The solution was then sent through the centrifuge and MnO_2 precipitation steps as described in the previous flowsheet to recover the protactinium. The clarified solution was then sent to the first SX cycle (1A–C).

The first SX cycle used three mixer-settler banks. The first bank (1A) coextracted uranium and thorium using a 30 wt % TBP in Ultrasene™ solution. The extracted thorium and uranium were then sent to the second mixer-settler bank where thorium was separated from uranium by stripping with dilute HNO_3. The thorium solution was then sent to a second SX cycle. The uranium solution was then sent stripped in the third mixer-settler bank with a 0.01 *M* HNO_3 solution. This recovered uranium was then sent to a second SX cycle, involving cation exchange, precipitation, and oxidation, as described in the first flowsheet.

The extracted thorium solution produced was further processed in a two-step SX process. The thorium solution from the 1B partioning step was evaporated about two fold and then extracted using a 30 wt % TBP solution for additional decontamination of protactinium and other fission products. The thorium solution was then stripped in the second bank (2B) with 0.01 *M* HNO_3. The thorium product solution was then evaporated, the acid concentration reduced by steam stripping in the evaporator and stored as thorium nitrate solution.

Solvent from all extraction cycles in both flowsheets was washed with dilute sodium bicarbonate solution, acidified, and recycled back into the system. Solvent extraction wastes were evaporated, neutralized, and sent to underground waste tanks.

3.2.1.3 Process Performance—Major Results

Over five campaigns, the SRS processed 240 t of thorium and produced about 580 kg of uranium (of which 564 kg was ^{233}U). The product purity of the uranium produced ranged from 91 to 98 wt % ^{233}U. During the three campaigns that uranium and thorium were recovered, total losses of uranium and thorium were less than 1.0 wt %. The uranium product contained less than 1500 parts of thorium per million parts uranium, and the thorium product contained less than two parts uranium per million parts thorium.

One of the limiting factors of the process was the dissolving rate for urania, which exceeded 4 t/d, while the extraction rate for thoria was limited to around 1 t/d. During the campaigns, it was established that the processing rates through the mixer-settlers was stable when run at 0.9 to 1.0 t of thorium per day, but performance deteriorated at or above 1.1 t/d. Due to the extraction properties of protactinium, the uranium stream was processed an average of four times through the second uranium SX cycle to achieve the desired removal of protactinium. Nuclear safety was maintained by limiting uranium concentrations to less than 6 g/L throughout the process.

3.2.1.4 References for Section 3.2.1

A list of references cited for ^{233}U production activities at Savannah River is provided below. This is followed by a list of sources providing additional information.

3.2.1.4.1 References Cited

Orth, D. A. April 1979. "Savannah River Plant Thorium Processing Experience," *Nuclear Technology*, **43**, 63–74, American Nuclear Society, Hinsdale, Ill.

Rathvon, H. C., et al. February 1968. "Recovery of ^{233}U from Irradiated Thoria" pp. 765–824 in *Proceedings of Second International Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee, May 3–6, 1966*, U.S. Atomic Energy Commission, Division of Technical Information, Oak Ridge, Tenn.

3.2.1.4.2 Supplemental Resources

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Goodlett, B., and H. Bull, III. December 1974. *Dissolution of Aluminum-Clad Thoria*, DP-1072, Savannah River Laboratory, Aiken, S.C.

Hyder, M. L., W. E. Prout, and E. R. Russell. July 1966. *Dissolution of Thorium Oxide*, DP-1044, Savannah River Laboratory, Aiken, S.C.

Kishbaugh, A. A. February 1966. *Performance of Mixers—Settlers in the Thorex Process*, DP-1022, Savannah River Laboratory, Aiken, S.C.

Prout, W. E., and A. E. Symonds. January 1967. *Recovery of Thorium and Uranium-233 from Irradiated Thorium Oxide and Metal*, DP-1036, Savannah River Laboratory, Aiken, S.C.

Siddall, T. H., III. October 1956. *Extraction of Thorium Nitrate from Nitric Acid by TBP–"Ultrasene"*, DP-181, Savannah River Laboratory, Aiken, S.C.

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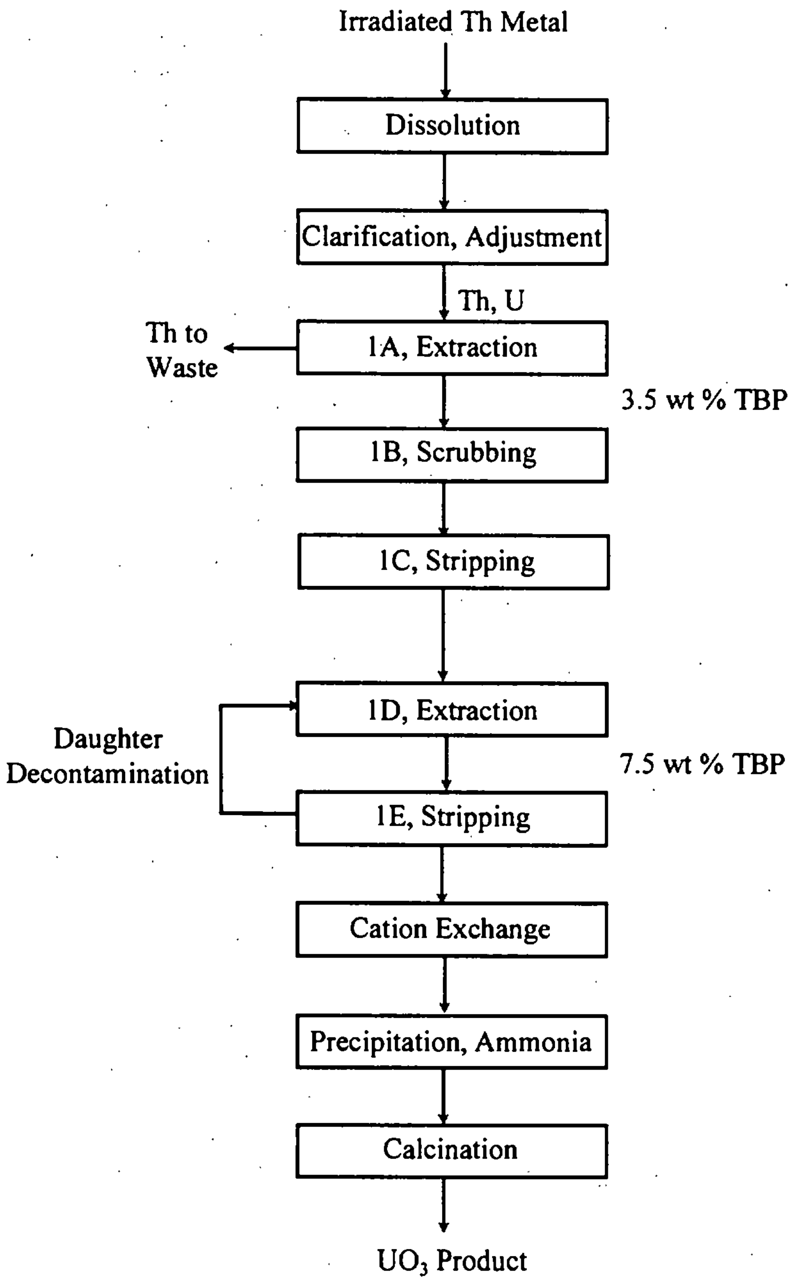

Fig. 3.2.1*a*. Separation of ^{233}U from thorium at the SRS followed by a discard of thorium waste. *From Orth April 1979.*

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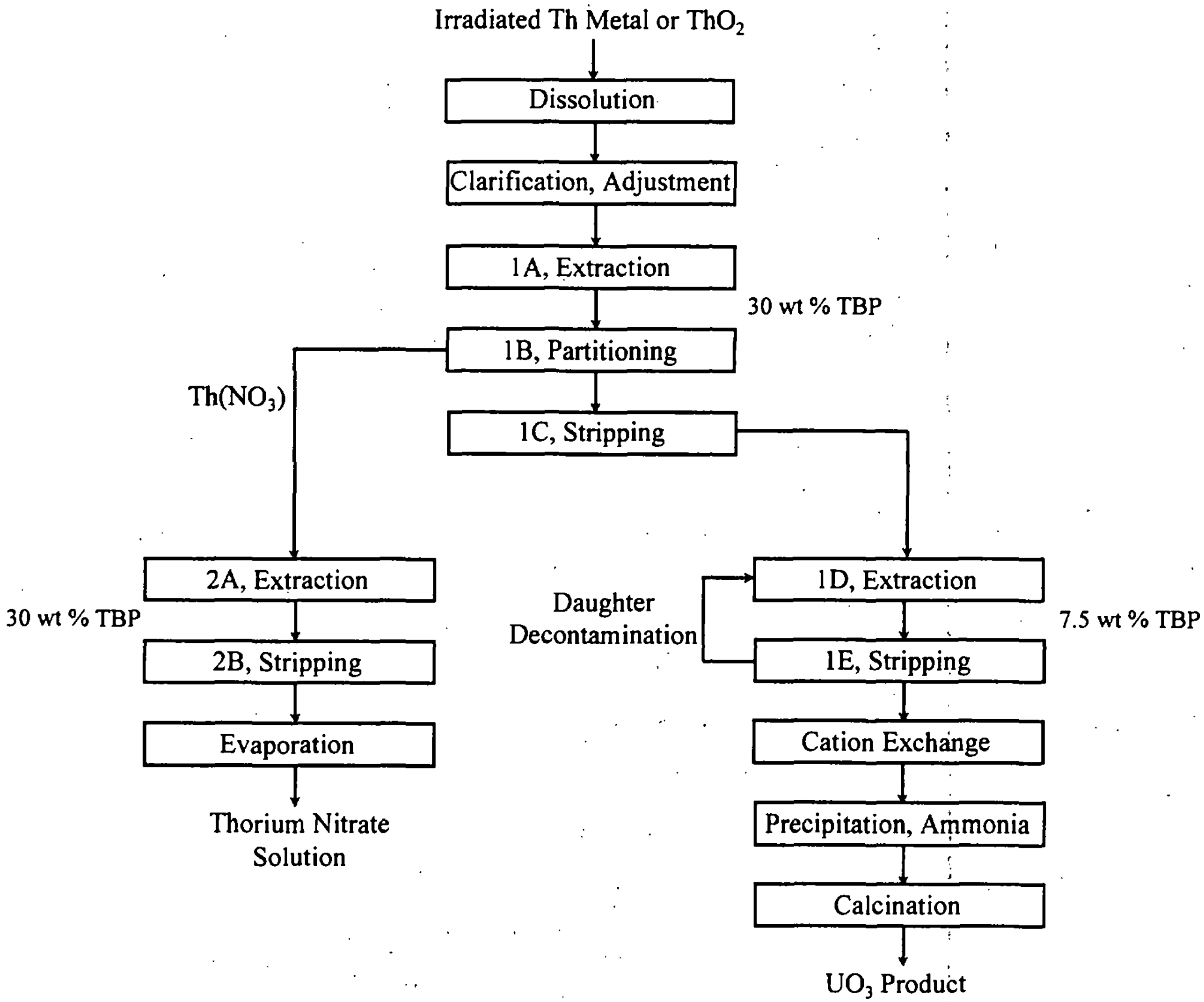

Fig. 3.2.1*b*. Separation of ^{233}U from thorium at the SRS with recovery of both ^{233}U and thorium. *From Orth April 1979.*

3.2.2 Hanford Campaigns

This section provides a summary of the ^{233}U production campaigns at Hanford based on Jackson and Walser (1977), Rathvon et al. (February 1968), and the Atlantic Richfield Hanford Company (Mar. 11, 1968). Additional information is provided in the references listed in Sect. 3.2.2.4.2.

3.2.2.1 Process Objective(s)

To produce ^{233}U for research, the Hanford chemical reprocessing facilities were used to separate and recover ^{233}U from irradiated thorium oxide (ThO_2). To use the reprocessing facilities at Hanford, the existing reprocessing facilities, which were originally used to separate and to purify uranium and plutonium, were adapted to the Thorex process to recover uranium and thorium.

Two separate campaigns were undertaken at the Hanford facilities, one in 1966 and one in 1970. The goal of the 1966 campaign was to produce ^{233}U for research, while the 1970 campaign target was to produce 360 kg of ^{233}U for the LWBR Program.

3.2.2.2 Process Description and Basic Flowsheet

The two campaigns undertaken at Hanford facilities were based on the Thorex II process, which was developed at ORNL. A simplified process flowsheet is shown in Fig. 3.2.2*a*.

3.2.2.2.1 Head-End Operations

The head-end process consisted of three batch operations. The processed thoria targets were aluminum cans filled with 3.6 kg of thoria particles. The thoria targets were first lowered into the dissolver and covered with 1.9 M $NaNO_3$ and then heated to boiling. Then 19 M NaOH was added to remove the aluminum cladding from the thoria. The decladding solution was then cooled and centrifuged to remove any entrained thoria particles. The thoria cake is then digested in a solution of 13 M HNO_3, 0.025 M KF, and 0.1 M $Al(NO_3)_3$ for 6 h to dissolve the thoria. The solution was then transferred to the acid boil-off step, which concentrates the solution to about 1.5 M thorium. The thorium feed solution was then sent to the first SX column cycle, 1A (Fig. 3.2.2*a*).

3.2.2.2.2 Solvent Extraction

The SX process required four cycles. The feed material was decontaminated and partitioned in a four-column first cycle; next the thorium was decontaminated further in a two-column second cycle, while the ^{233}U is decontaminated in two additional two-column cycles. The first-cycle columns and the second-cycle thorium columns are large-diameter columns, while the additional two ^{233}U cycles are small-diameter extractors designed originally for plutonium criticality safety.

In the first column, 1A, uranium and thorium are coextracted using a 30 wt % TBP solvent. A nitric acid salting agent is added to the bottom extraction stage to optimize product decontamination with respect to zirconium (Zr), niobium (Nb), ruthenium (Ru), and protactinium (Pa). Aqueous acidities were maintained at greater than 0.2 *M* to prevent thorium phosphate precipitation. The extracted solution was then sent to the 1BX column, where the ^{233}U and thorium are partitioned by controlling acidity, temperature, and flow ratio. The uranium solution exits the 1BX column with the solvent and is stripped out in the 1C column and then concentrated before proceeding to the second uranium cycle. The thorium leaves the 1BX column in the aqueous stream and is sent to the 1BS column, where it is scrubbed with fresh dilute HNO_3 to remove any uranium remaining. The product is then sent to the second thorium cycle.

The thorium solution produced was further processed in a two-step SX process. The thorium solution from the 1BS column is sent to the 2D extraction column, where the thorium is extracted using a 30 wt % TBP solution for additional decontamination of protactinium and other fission products. The thorium solution was then fed to a stripping column, 2E, where the thorium was stripped from the solvent using dilute acid. The thorium product solution was then evaporated, and the acid concentration was reduced by steam stripping in the evaporator and stored as thorium nitrate.

The uranium solution was then sent from the concentrator to the second and third uranium cycles. Each cycle consists of an extraction-stripping sequence, 2AB and 3AB, using 30 wt % TBP and dilute HNO_3 for the additional decontamination from fission products. The uranyl nitrate solution produced is then sent through adsorption and cation exchange columns to further remove thorium contamination and unconverted protactinium. The final product is then concentrated to final product specifications.

Solvent from all extraction cycles of the flowsheet was washed with dilute sodium bicarbonate solution, acidified, and recycled back from two separate systems. The SX wastes were evaporated, neutralized, and sent to underground storage tanks.

3.2.2.3 Process Performance—Major Results

The 1966 ^{233}U campaign at Hanford produced about 235 kg of ^{233}U from 165 t of thoria. The thorium and ^{233}U met all target specifications—except for the fission product content of the thorium product. The 1970 campaign produced 628 kg of ^{233}U from 470 t of thoria. The total ^{233}U that was recovered (nearly 820 kg) from both of these campaigns met all product specifications. An overall thorium-uranium separation factor of 8.0×10^6 was obtained.

One problem found during the process was that partitioning in the 1BX column degenerated and that a large percentage of ^{233}U would go with the thorium. The ^{233}U was usually re-extracted in the 1BX column and recycled back to the 1A column. However, in some cases, the ^{233}U continued into the second thorium cycle, and the final thorium product had to be reworked. This problem was caused by two conditions: (1) a decrease in the organic-to-aqueous flow ratio in the column and (2) a loss of salting strength because of low thorium concentration in the 1BS feed. Also, the ^{233}U tended to strip out of the organic whenever the thorium nitrate concentration in the 1BS feed dropped.

Nuclear safety was maintained by limiting uranium concentrations to less than 6 g/L throughout the process.

3.2.2.4 References for Sect. 3.2.2

A list of references cited for ^{233}U production activities at Hanford is provided below. This is followed by a list of sources providing additional information.

3.2.2.4.1 References Cited

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Prout, W. E., and A. E. Symonds. January 1967. *Recovery of Thorium and Uranium-233 from Irradiated Thorium Oxide and Metal*, DP-1036, Savannah River Laboratory, Aiken, S.C.

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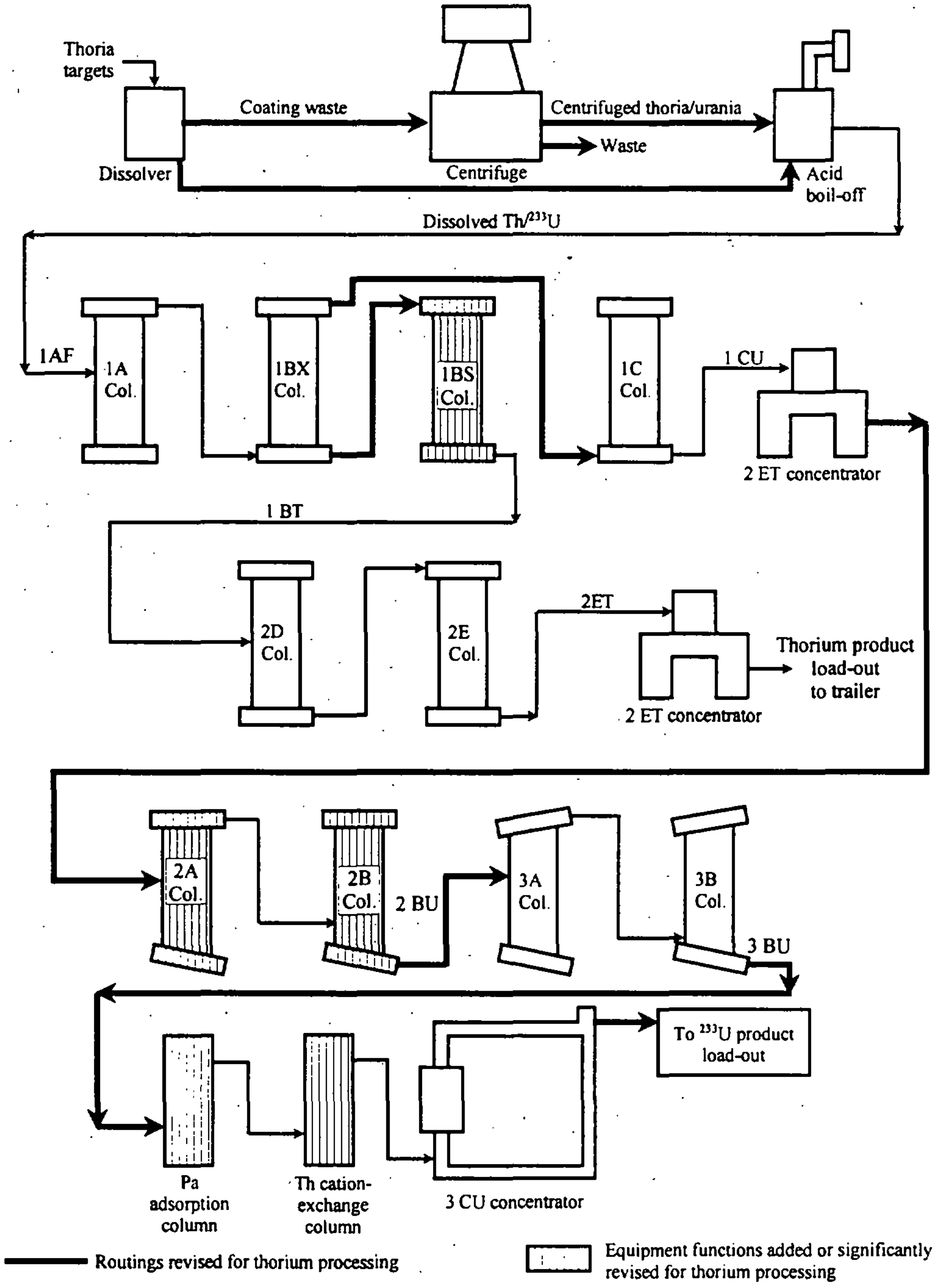

Fig. 3.2.2*a*. Separation of ^{233}U from thorium at the Hanford Site. *From Rathvon et al. February 1968.*

3.2.3 Oak Ridge (ORNL) Campaigns

Major developmental work for the recovery of ^{233}U from irradiated thorium took place at ORNL in the years following World War II. During this time, three major processes were developed and tested:

1. Hexone–23 (or Redox) process (where "23" refers to ^{233}U),
2. TBP Interim–23 process, and
3. Thorex process.

A summary of each of these processes is given in Sects. 3.2.3.1 through 3.2.3.3.

It should be noted that two separate Thorex processes (identified as Nos. 1 and 2) were developed, but only the No. 2 process was used for the demonstration with irradiated materials. The Kilorod pilot plant (discussed in Sect. 3.7.1) was based on the Thorex No. 2 flowsheet (Aßmann et al. 1982).

3.2.3.1 ORNL Hexone–23 (Redox) Campaign

In the years following World War II, significant advances were made in nuclear fuel reprocessing, particularly in those methods that used SX. For nuclear fuels, the basic principle that applies to SX is that the nitrates of uranium and plutonium in the higher oxidation states are readily soluble in certain organic liquids that are immiscible with water. In contrast, the nitrates of fission products are generally insoluble in these liquids.

Argonne National Laboratory (ANL) developed the first successful SX process to recover uranium and plutonium. Called the Redox process, this scheme involved the use of methyl isobutyl ketone, or hexone, as the organic solvent and the addition of aluminum nitrate in the aqueous phase to improve the separation.

From 1945–1951, pilot plant testing of the Redox process was performed at ORNL, Building 3019. This was followed with large-scale plant operations at Hanford in 1952. A description is provided below of the ORNL Redox process tests involving ^{233}U recovery during this period (Aßmann et al. 1982 and Brooksbank, Patton, and Krichinsky August 1994).

3.2.3.1.1 Process Objective(s)

The Hexone–23 (Redox) process resulted from the need to develop a continuous SX process to recover and decontaminate ^{233}U from irradiated thorium [Chemical Technology Division (CTD) Oct. 20, 1949].

3.2.3.1.2 Process Description and Basic Flowsheet

The hexone–23 process has been well documented (Culler 1956 and Stoller and Richards 1961), and a summary flowsheet is provided in Fig. 3.2.3.1*a*. The process began by dissolving irradiated thorium slugs in nitric acid (HNO_3). Then, the resulting thorium nitrate [$Th(NO_3)$], acting as the primary salting agent, was prepared and adjusted as an aqueous feed solution before being introduced into the middle of the uranium extraction column. In this column, ^{233}U was extracted by the solvent methyl isobutyl ketone {hexone [$CH_3(CO)C_4H_9$]} and entered an organic phase. At this point, most of the ^{233}Pa, thorium, and fission products remained in the aqueous phase.

An acid-deficient aqueous scrub solution, containing aluminum nitrate [$Al(NO_3)_3 \bullet 9H_2O$] and ammonium nitrate, was introduced at the top of the uranium extraction column to neutralize some of the acid and further decontaminate the organic product stream from thorium and fission products. The aluminum nitrate was also used as a salting agent to prevent the high concentrations of nitric acid that could be generated in the evaporators from reacting explosively with the hexone (Katz, Seaborg, and Morss 1986).

The organic product stream, containing 99.9 wt % of the original ^{233}U feed, was fed to the bottom of the uranium stripping column, where it was contacted with a 0.04 *N* nitric acid solution to strip the ^{233}U from the organic (hexone) phase. The resulting aqueous solution was subsequently concentrated by evaporation to produce a uranyl nitrate product (CTD February 1950).

The hexone extractant proved useful in the Redox process because it is essentially immiscible (only 2% soluble) with water and was found to extract uranyl nitrate (as well as plutonium nitrate) selectively from fission product nitrates if the aqueous solution had a sufficiently high nitrate ion concentration.

Aqueous wastes from the Redox process included thorium, fission products, and ^{233}Pa. These were stored in stainless steel tanks for further treatment and disposal (General Electric Company July 10, 1951).

3.2.3.1.3 Process Performance—Major Results

Pilot plant tests at ORNL showed a ^{233}U recovery rate of 99.9 wt %, and a ^{233}U product separation factor from thorium, protactinium, and fission products of 10^4. The thorium was sufficiently inextractable in the hexone such as to permit separation factors of greater than 10^4. Decontamination factors for most fission products were 10^5.

Several limitations and disadvantages of the Redox process were identified that resulted in this process being abandoned in favor of the Thorex process (Benedict, Pigford, and Levi 1981; Katz, Seaborg, and Morss 1986). These included:

1. Volatility and flammability of the hexone solvent,
2. Large quantities of aluminum nitrate [$Al(NO_3)_3$] needed as a salting agent in the liquid phase,
3. Inability of the process to recover thorium, and
4. Use limited to long-decayed material (i.e., material decayed until ^{233}U losses as protactinium are very low). This feature was a result of the inability of the Redox process to provide effective separation of ^{233}Pa.

3.2.3.1.4 References for Sect. 3.2.3

Listed below are the references cited in both Sects. 3.2.3 and 3.2.3.1. This is followed by a list of additional resources that provide more detailed information on the Redox process as it was used in ^{233}U recovery.

3.2.3.1.4.1 References Cited

Aßmann, H., et al. 1982. "Reprocessing of Spent ^{232}Th–^{233}U Fuels," pp. 276–351 in *Gmelin Handbook of Inorganic Chemistry*, 8th ed., Supplement Volume A4 (*Uranium*), System 55," (Sect. 2.4), Springer-Verlag, New York.

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General Electric Company. July 10, 1951, *Redox Technical Manual*, HW-18700, Hanford, Richland, Wash.

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Stoller, S. M., and R. B. Richards, eds. 1961. *Reactor Handbook*, Vol. II (*Fuel Reprocessing*), Interscience Publishers, Inc., New York.

3.2.3.1.4.2 Supplemental Resources

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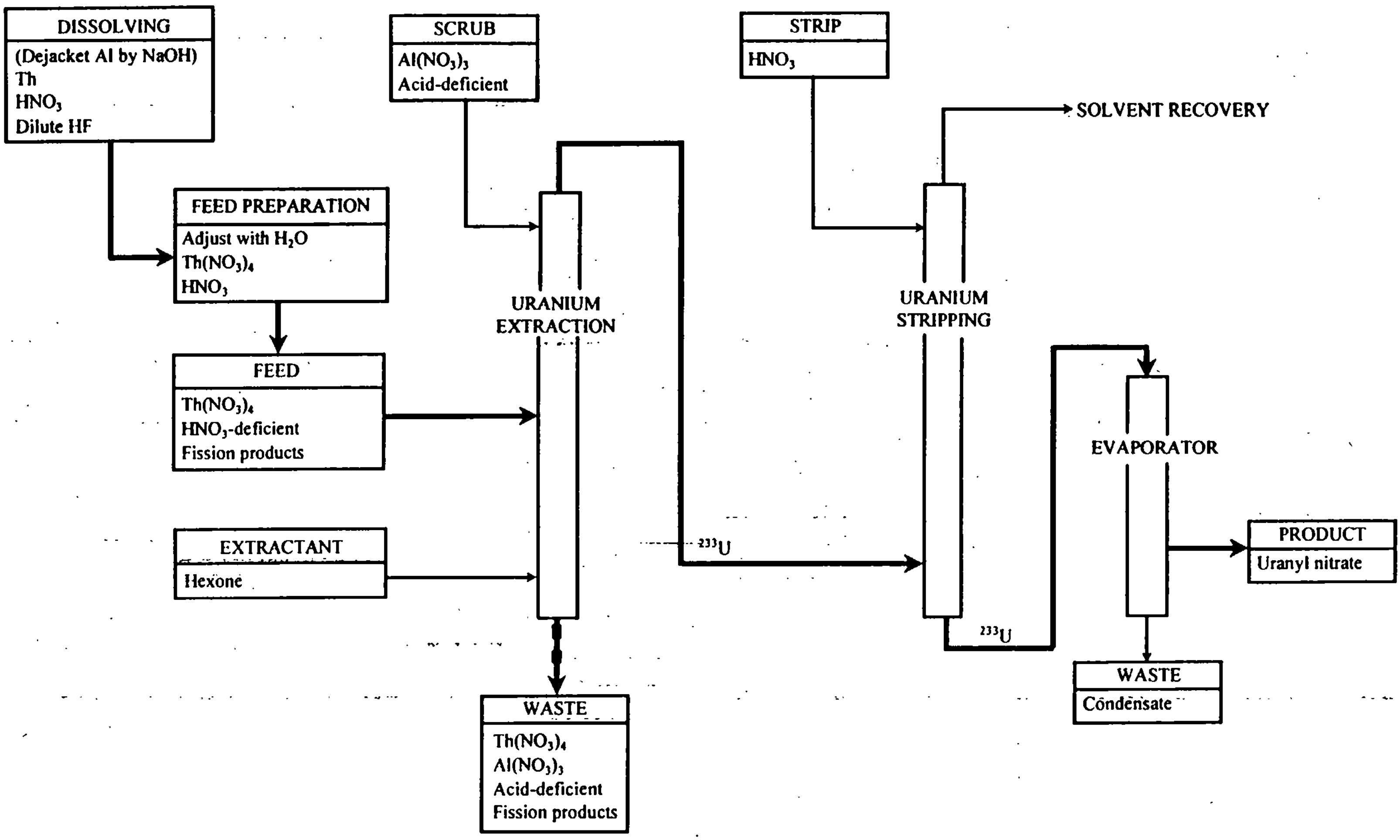

Fig. 3.2.3.1*a*. Summary flowsheet for the hexone-23 process. *Adapted from Culler 1956.*

3.2.3.2 ORNL TBP-Interim 23 Campaign

3.2.3.2.1 Process Objective(s)

This process used TBP [$(C_4H_9O)_3PO$] as the ^{233}U extractant. The TBP-Interim 23 process was developed to use after irradiated thorium had been stored long enough (2 to 3 months) to allow most of the ^{233}Pa to decay to ^{233}U. Isolation of the ^{233}U product was achieved with a mixture of TBP in Amsco™, a commercial hydrocarbon diluent based on a high-grade kerosene.

3.2.3.2.2 Process Description and Basic Flowsheet

Figure 3.2.3.2*a* shows a summary flowsheet of the TBP-Interim 23 process. In this system, the ^{233}U product was extracted from a thorium nitrate solution of the breeder blanket materials with 1.5 wt % TBP in Amsco™ and later back-extracted with 0.05 *N* nitric acid (HNO_3). TBP was used in the process as the preferential ^{233}U extractant. Detailed descriptions of the process are provided in several sources (notably Culler 1956 and Stoller and Richards 1961).

The flowsheet indicates major activities involving feed preparation, uranium extraction, uranium stripping, and final ^{233}U product purification. Initially, thorium slugs were dissolved in nitric acid, and the resulting aqueous thorium nitrate [$Th(NO_3)_4$] solution was adjusted to required process specifications before being introduced into a column for uranium extraction. At the bottom of the uranium extraction column, the organic solvent of TBP in Amsco™ was added to extract ^{233}U from the aqueous nitrate solution. The ^{233}U extraction left fission products, protactinium (^{233}Pa), and thorium in the aqueous waste raffinate from the column. An aluminum nitrate [$Al(NO_3)$] solution was feed at the top of the uranium extraction column to scrub fission products and thorium from the rising organic phase.

An organic extract, rich in ^{233}U, was taken off the top of the uranium extraction column and passed over to the bottom of another column, where it was stripped using a dilute nitric acid solution. At the top of the stripping column, the TBP solvent was recovered, purified, and recycled. At the bottom of the stripping column, the aqueous ^{233}U product was removed for concentration and for further decontamination. The latter involved passing the ^{233}U solution either through a second extraction cycle or through a tail-end purification step that used silica gel adsorption and Dowex-50 ion-exchange resin (Stoller and Richards 1961). If tail-end purification was used, the product was first passed through a silica-gel column for the adsorption of traces of fission products, then through a small resin column for the removal of ionic impurities (e.g., corrosion products and thorium), and finally through a larger resin column for the sorption of ^{233}U. The latter series of steps proved effective for final concentration and decontamination of the ^{233}U product from both radioactive and ionic impurities.

The ^{233}U product left the larger resin column as uranyl acetate [$^{233}UO_2(C_2H_3O_2)_2$], which could be precipitated as a peroxide and redissolved in nitric acid (Culler 1956).

The product was stripped in dilute nitric acid, passed through a silica-gel column for adsorption of traces fission products, through a small resin column for removal of ionic impurities (corrosion products and thorium), and finally through a larger resin column for sorption of the ^{233}U.

3.2.3.2.3 Process Performance—Major Results

During 1952, the ORNL Pilot Plant (Building 3503) separated 2.67 kg of ^{233}U from 3698 kg of Hanford-irradiated thorium using the TBP-Interim 23 process. The recovered ^{233}U had an isotopic assay of 98 at. % (Hylton Dec. 11, 1952).

The TBP-Interim 23 system provided excellent separation of the ^{233}U product from both thorium and highly radioactive materials. It proved to be a suitable SX procedure for producing experimental quantities of ^{233}U.

3.2.3.2.4 References for Sect. 3.2.3.2

A list of cited references documenting the TBP-Interim 23 process is provided below. This is followed by a list of sources providing additional information.

3.2.3.2.4.1 References Cited

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Stoller, S. M., and R. B. Richards, eds. 1961. *Reactor Handbook*, Vol. II (*Fuel Reprocessing*), Interscience Publishers, Inc., New York.

3.2.3.2.4.2 Supplemental Resources

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Chemical Technology Division. Sept. 30, 1952*b*. "Interim-23 Process," pp. 5–7 in *Chemical Technology Division Progress Report for Period Ending May 20, 1952*, ORNL-1328, Oak Ridge National Laboratory, Oak Ridge, Tenn.

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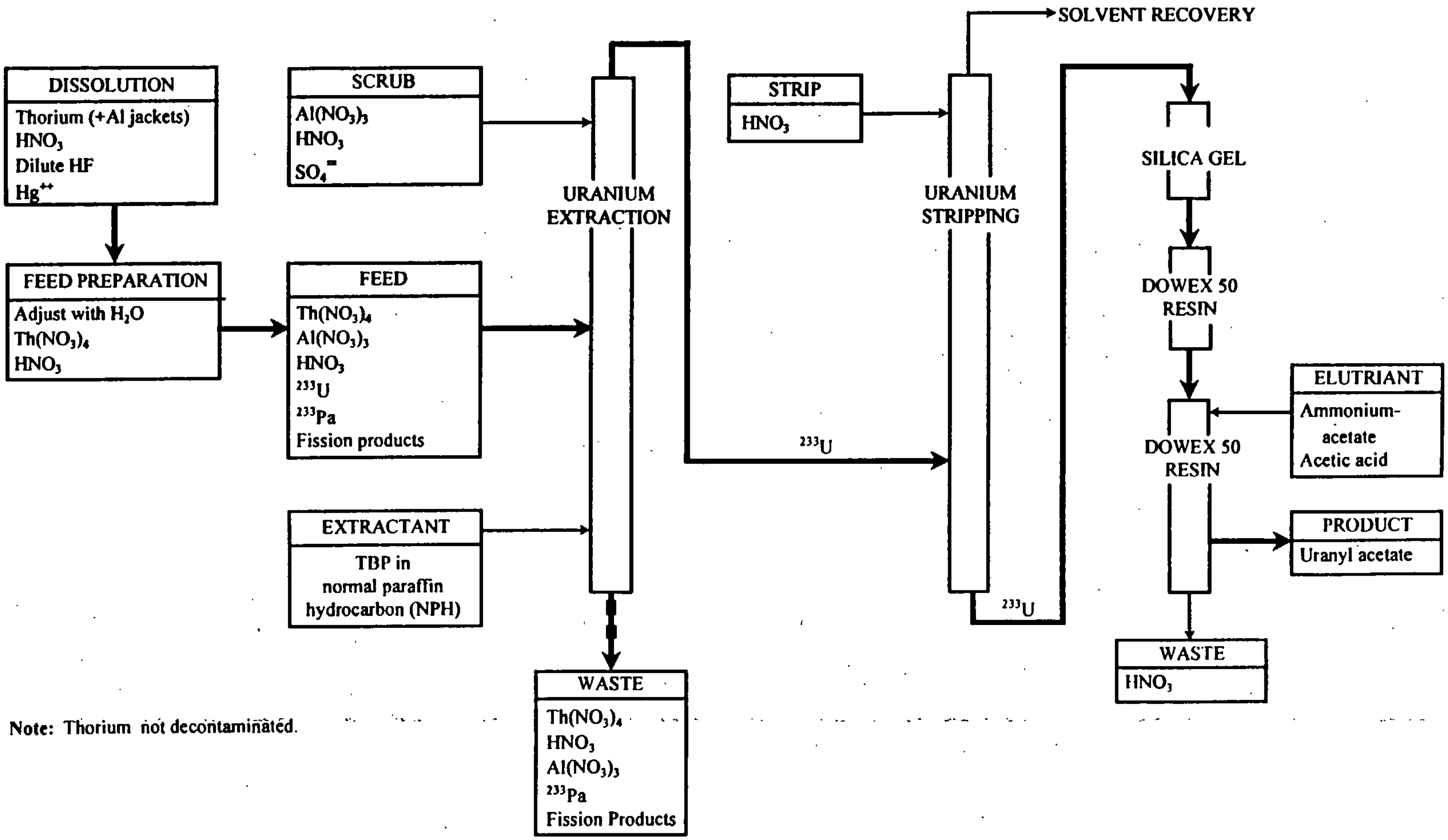

Note: Thorium not decontaminated.

Fig. 3.2.3.2*a*. **Summary flowsheet for the TBP-Interim 23 process.** *Adapted from Culler 1956.*

3.2.3.3 ORNL Thorex Campaigns

To reprocess irradiated thorium-based nuclear fuels, the solvent-exchange-based Thorex process was developed at ORNL during the 1950s. The ORNL work was performed in the Pilot Plant of Building 3019 and was the forerunner to the process used in the subsequent recovery of ^{233}U from the spent Consolidated Edison IP-1 fuel at the West Valley NFS site (discussed in Sect. 3.4).

3.2.3.3.1 Process Objective(s)

The Thorex process was developed for separating and decontaminating thorium, ^{233}U, and ^{233}Pa from neutron-irradiated thorium. It is a SX process which uses TBP as the extractant, nitric acid catalyzed with fluoride as the thorium-dissolution agent, and either aluminum nitrate [$Al(NO_3)_3$] or nitric acid as the salting agent (Culler 1956).

Two versions of the Thorex process have been developed and described, Thorex No.1 and Thorex No.2 (Gresky, A. T., et al. Dec. 17, 1952). Each of these versions are described below. Thorex No.1 is an acid-based process that was developed and demonstrated only on a laboratory scale (Stoller and Richards 1961). By contrast, Thorex No.2 is an acid-deficient process and has shown greater engineering feasibility in the reprocessing of thorium-based fuels (see Sect. 3.4). For this reason, Thorex No. 2 is commonly referred to as the Thorex process.

3.2.3.3.2 Process Description and Basic Flowsheet

Separate flowcharts for the Thorex No. 1 and No. 2 processes are provided in Figs. 3.2.3.3*a* and 3.2.3.3*b*, respectively. Each flowchart depicts a schematic for a one-cycle process. These flowcharts represent typical Thorex processes developed at ORNL and are separately discussed below. For certain applications at some sites [e.g., Knolls Atomic Power Laboratory (KAPL)], other Thorex process flowcharts were developed (see Sect. 3.4).

3.2.3.3.2.1 Thorex No. 1 Process

The Thorex No. 1 process was a tentative approach to thorium–^{233}U–^{233}Pa separation and decontamination. As the flowchart of Fig. 3.2.3.3*a* indicates, the process featured the following major steps, in order:

1. Extraction of ^{233}Pa in diisobutyl carbinol [(DISC) $(i — C_4H_9)_2 — CHOH$],
2. Extraction of ^{233}U in 5 wt % TBP, and

3. Extraction of ^{232}Th in a solvent mixed with 45 wt % TBP, 15 wt % benzene (C_6H_6), and 40 wt % Amsco™.

Process No. 1 began with irradiated thorium dissolution, after which the feed solution was adjusted and fed into the middle of the column for extraction of ^{233}Pa by DISC. While the aqueous acidity favors the ^{233}Pa extraction, some ^{233}U, thorium, and fission products were also extracted; however, these were effectively scrubbed from the extractant by an $Al(NO_3)_3$ solution entering at the top of the ^{233}Pa extraction column. The extract from this column was sent to a stripping column, where the organic solution was stripped with a slightly acidic strip solution. The spent DISC solvent was purified and recycled, while the aqueous stream containing the ^{233}Pa product was stored for decay prior to ^{233}U recovery. The aqueous raffinate from the ^{233}Pa extraction column, containing the ^{233}U, thorium, and fission products, was fed into the ^{233}U extraction column, where the aqueous phase was mixed with a solvent stream of 5 wt % TBP in Amsco™.

Under flowsheet conditions, the ^{233}U is extracted by the TBP solvent and scrubbed with a HNO_3 solution to remove thorium and fission products. The organic stream leaving the ^{233}U extraction column cascades to a stripping column, where the ^{233}U is stripped using a weak acid solution. The TBP solvent stream is purified and then recycled back to the ^{233}U column. The raffinate from this column is fed into a third column for thorium extraction, where the aqueous phase is mixed with 45 wt % TBP–15 wt % benzene in Amsco™. Under flowsheet conditions, thorium is extracted by the solvent and scrubbed by an $Al(NO_3)_3$ solution to remove fission products. The aqueous waste containing the fission products leaves at the bottom of the thorium-extraction column and is stored. The organic stream containing the thorium product passes over the top of the thorium-extraction column to the bottom of the third stripping column, where a HNO_3 solution is used to strip the thorium from the organic phase. The TBP solvent leaves the top of the stripping column and is purified prior to recycle to the thorium-extraction column. Further purification and concentration of the ^{233}Pa, ^{233}U, and thorium streams may be achieved by additional extraction cycles if required (Gresky et al. Dec. 17, 1952).

3.2.3.3.2.2 Thorex No. 2 Process

The Thorex No. 2 process was designed to accomplish the separations previously described for the No. 1 process using only TBP as the extraction solvent. In addition, the No. 2 process uses acid-deficient $Al(NO_3)_3$ in place of HNO_3 as a salting agent in the initial separation cycle.

As the flowchart of Fig. 3.2.3.3*b* indicates, the process featured the following major steps, in order:

1. Extraction of ^{233}Pa in TBP,
2. Partitioning of ^{233}U from thorium in TBP, and
3. Stripping and isolation of the ^{233}U product by ion exchange.

The Thorex No. 2 process begins with the dissolution of irradiated thorium fuel in concentrated nitric acid. Typically, the fuel is in the form of ThO_2 pellets in aluminum cladding. Feed dissolution is followed by a digestion and feed adjustment step to remove excess nitric acid.

The aqueous feed is introduced near the middle of the extraction column. An aqueous scrub solution of acid-deficient aluminum nitrate, ferrous sulfate, and dilute phosphoric acid enters at the top of the column. TBP diluted with Amsco™ 125–82 (an inert paraffinic diluent) enters at the bottom of the column and is used to extract thorium and ^{233}U. The primary TBP-nitrate complexes of these elements are $Th(NO_3)_4 \cdot 4TBP$ and $UO_2(NO_3)_2 \cdot 2TBP$. The corresponding complex of the nitric acid is $HNO_3 \cdot TBP$.

Because of the acid-deficient conditions of the aqueous phase, the ^{233}Pa and most of the troublesome fission products are not extractable. However, the aqueous scrub solution added at the top of the extraction column provides for additional ^{233}Pa and fission product removal from the product extract. The scrub solution includes the phosphate ion, which assists in the decontamination from ^{233}Pa, and the ferrous ion, which prevents extraction of an oxidized chromium compound that is produced during the head-end treatment of the feed.

The aqueous raffinate from the extraction column contains aluminum nitrate, is acid deficient, and contains any ^{233}Pa that has not decayed to ^{233}U, fission products, and other impurities. To minimize its storage requirements, the raffinate is evaporated to reduce its volume.

The organic extract from the extraction column, containing ^{232}Th, ^{234}Th, ^{233}U, traces of fission products, and any ^{233}Pa that may be present, is introduced into the middle of the partitioning column. The thorium is stripped into an aqueous phase of nitric acid, which flows down the partitioning column; this aqueous solution is scrubbed by the organic stream of TBP introduced at the bottom of the column. The aqueous strip stream represents the combined flow of an acid solution introduced at some distance below the top of the column and a water stream introduced at the top of the column. This achieves the maintenance of slightly acidic aqueous conditions, which, in turn, will permit thorium stripping into the aqueous stream and retention of the ^{233}U in the organic stream. Although the water stream entering the top of the column results in some ^{233}U reflux, this step is necessary to remove nitric acid from the organic phase so that the subsequent uranium-stripping cycle will operate at maximum efficiency.

The organic effluent from the partitioning column, contains all the ^{233}U and some traces of nitric acid. This effluent is passed to the bottom of the uranium-stripping column. An aqueous phase of dilute nitric acid is introduced at the top of the column to strip the ^{233}U from the rising organic stream. The aqueous effluent is then passed through the following: a silica-gel column for removal of trace quantities of fission products, a small column containing a cation-exchange resin for the retention of traces of thorium and corrosion products, and a larger cation-exchange resin for concentrating and further decontaminating the ^{233}U product. The effluent from the uranium-stripping column is discarded as a chemical waste, and the ^{233}U product is eluted by a solution of ammonium acetate ($NH_4C_2H_3O_2$) and acetic acid ($HC_2H_3O_2$) (Culler 1956).

The laboratory development of the Thorex process is described in several reports (Gresky et al. Dec. 17, 1952, and Rainey, Meservey, and Mansfield Feb. 11, 1959), and the reader is referred to these documents for further details.

3.2.3.3.3 Process Performance—Major Results

3.2.3.3.3.1 Thorex No. 1 Process

While the Thorex No. 1 process appeared potentially adequate from the standpoint of separation and decontamination, several engineering and chemical problems were noted and documented (Gresky et al. Dec. 17, 1952) during its development phase. The objectionable engineering features included the necessity for:

1. Equipment and operational control of three different solvents (DISC, TBP, and TBP-benzene);
2. Extra solvent vessels for storage, pumping, holdup, and chemical treatment; and
3. The excessive number of first-cycle columns (six) required for separation, at least four of which would be contaminated with radioactivity.

The chemical problems associated with Thorex No. 1 involved:

1. Incomplete stripping of ^{233}Pa from the diisobutyl carbinol,
2. The need for aromatics such as benzene in the TBP extractant to prevent two-phase organic layers when the TBP is saturated with thorium,
3. Incomplete ^{233}Pa decontamination in the thorium removal step because of its TBP extractability in acidic systems, and

4. The uncertain attainment of equilibrium or steady-state in the complicated TBP-thorium-nitric acid system.

3.2.3.3.3.2 Thorex No. 2 Process

The Thorex No. 2 process is still potentially useful for reprocessing irradiated thorium-based fuels. Use of the Thorex process to isolate ^{233}U from irradiated thorium has been demonstrated on an industrial scale. Detailed flowcharts for such processes may be found in several documents (ORNL February 1968 and CTD July 1971).

3.2.3.3.4 References for Section 3.2.3.3

A list of cited references documenting the Thorex process is provided below. This is followed by a list of sources providing additional information.

3.2.3.3.4.1 References Cited

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Culler, F. L. 1956. "Reprocessing of Reactor Fuel and Blanket Materials by Solvent Extraction," pp. 464–83 in *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, Vol. 9, R5.1-1030, United Nations, New York.

Gresky, A. T. et al. Dec. 17, 1952. *Progress Report: Laboratory Development of the Thorex Process*, ORNL-1367, Oak Ridge National Laboratory, Oak Ridge, Tenn.

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3.2.3.3.4.2 Supplemental Resources

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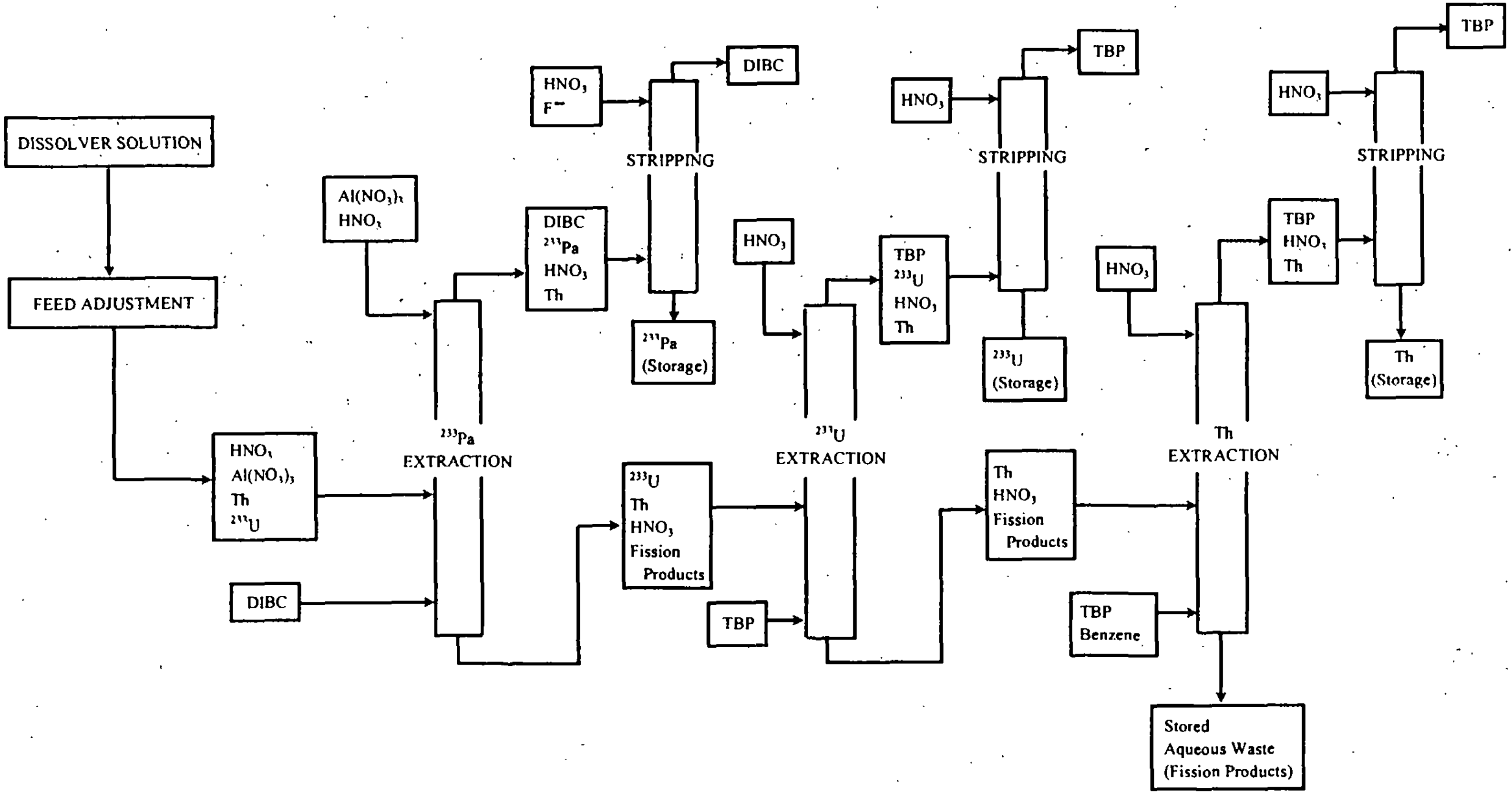

Fig. 3.2.3.3*a*. Summary flowsheet for a typical ORNL Thorex No. 1 (acid-based) process. *Adapted from Gresky et al. December 17, 1952.*

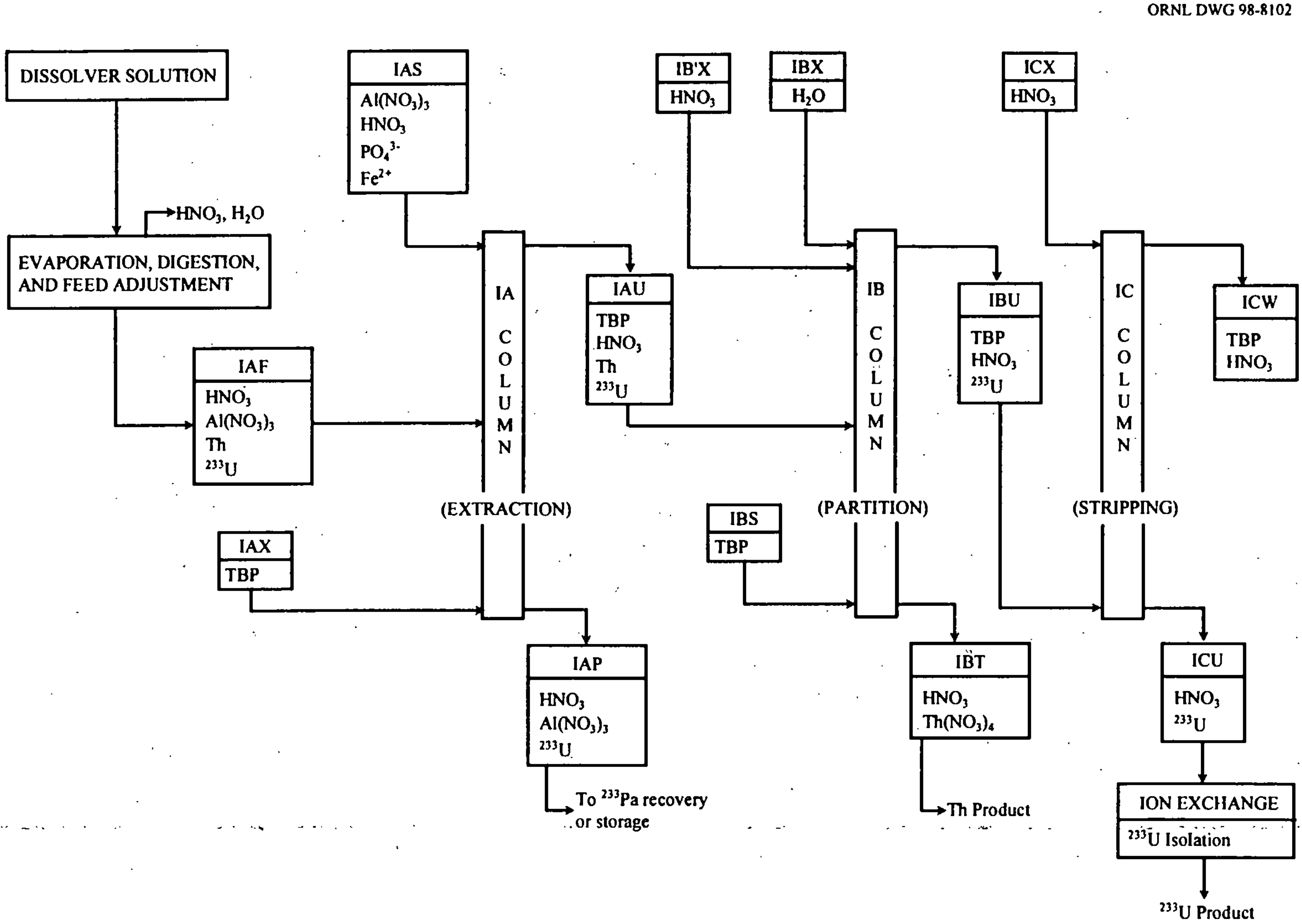

Fig. 3.2.3.3*b*. Summary flowsheet for a typical ORNL Thorex No. 2 (acid-deficient) process. *Adapted from Culler 1956.*

3.3 PROGENY INGROWTH REMOVAL

Processing ^{233}U-bearing materials in glove boxes may be facilitated temporarily by using SX or ion exchange (IX) to remove selected radioactive daughters. The role of each of these processes is discussed in several sources (notably, Parrott et al. September 1979) and is summarized below.

The overall objective of daughter removal is to break the ^{232}U decay chain by extracting and removing the longer-lived daughters (particularly ^{228}Th, $t_{½}$ = 1.9 years; and ^{224}Ra, $t_{½}$ = 3.7 d). This greatly reduces the intense radiation field from subsequent decay products and briefly allows processing some ^{233}U-bearing materials in unshielded glove boxes. Unfortunately, the ^{232}U decay chain lacks a long-lived "stopper" isotope (like ^{229}Th with $t_{½}$ = 7340 years in the ^{233}U decay chain) that can be used to "break" the decay chain for an extended period (i.e., for months or longer) through a chemical separation. Therefore, very brief periods (i.e., up to weeks) of relief from penetrating gamma emitters can be realized by removing the longer-lived daughters of ^{232}U.

It must be recognized, however, that gamma radiation relief in unshielded glove boxes is dependent upon the absence of (or vigilant housekeeping to remove) aging ^{233}U–^{232}U residues left in equipment from earlier processing. Such residues can provide a field that would preclude continued, unshielded processing.

Unshielded glove box processing is practical only for short periods with material involving very small quantities of ^{232}U (i.e., much less than 20 ppm of ^{232}U). Therefore, any strategy of daughter ingrowth removal to allow subsequent unshielded glove box processing must consider the quantity and isotopic purity of the material to be processed in addition to the time frame that includes both the duration of processing and the time after purification.

3.3.1 SX

A modified Interim-23 SX flowsheet has been used effectively to separate and remove bulk nitrate salts (e.g., thorium nitrate, aluminum nitrate or sodium nitrate), excess nitric acid, transuranium element impurities, and ^{232}U decay daughters from ^{233}U-bearing materials. SX removes essentially all ^{232}U daughters from uranium-bearing solutions, which results in a dramatic and immediate reduction in the radiation that is produced by ^{232}U progeny (notably ^{208}Tl). However, where thorium is present in substantial feed concentrations (i.e., comprising a large portion of the nitrate salt concentration), the SX process will allow some small concentration of thorium (≤0.01 wt %) in the feed to remain with the uranium. The presence of the thorium from ^{232}U decay (i.e., ^{228}Th–$t_{½}$ = 1.9 years) will hasten the return of a substantial radiation field that is associated with the uranium product of SX. Feed solutions for this process are prepared from either ^{233}U–Th nitrate dissolver solutions or ammonium acetate—nitric acid recycle solutions from the IX system, which is discussed below.

The SX flowsheet for ^{233}U separation is shown in Fig. 3.3*a*. Because of criticality safety considerations where large feed tankage is used, the feed solution typically contains ^{233}U in concentrations that are no more than 8 g/L. The feed solution also typically contains a high concentration of inextractable nitrate salts (aluminum, ammonium, sodium, thorium, etc.) and may include up to 5 *M* nitric acid. The organic extraction solvent used in this flowsheet is 5 vol % of di-sec-butyl-phenyl phosphonate (DSBPP) in diethylbenzene (DEB), although TBP in DEB has also been used. The saturated solution of total uranium in this solvent is typically 20 to 25 g/L. The inventory of organic solvent used in the SX system is typically about 600 L. Only a small portion of the solvent actually resides in the columns; the bulk of it resides in a special storage tank. During operation of the SX system, the organic solvent exiting the strip column is transferred via this storage tank back to the extraction column. When the SX system is not operating, the entire batch of organic solvent is periodically washed with sodium carbonate to remove solvent degradation products.

During SX operation, the feed is contacted with the organic solvent in the extraction column and the aqueous raffinate solution is usually a waste stream. The organic solvent, which contains the ^{233}U-bearing product, is scrubbed with an inextractable aluminum nitrate solution in the scrubbing column and is then stripped with dilute acid in the stripping column. The stripped uranium product solution is concentrated by means of an evaporator or further processing and then stored in product solution tanks to await additional processing (e.g., product conversion to oxide or polishing in the IX system).

3.3.2 IX

IX is used to remove trace impurities from a solution. For ^{233}U, IX is used to remove ^{232}U decay daughters from the uranium by preferentially absorbing the ^{228}Th daughter. (In this process, most ^{224}Ra is also adsorbed.) The removal of ^{228}Th and ^{224}Ra interrupts the ^{232}U decay chain and substantially reduces the radiation that is produced by the subsequent decay products (notably ^{208}Tl) of that chain. Feed for the IX system is either the product from the SX system or the dissolver solution from the uranium dissolver.

A typical IX flowsheet is given in Fig. 3.3*b*. The IX column contains about 10 L of a cross-linked, organic-based cation exchange resin (200 to 400 mesh size). Prior to processing a uranium solution, dilute nitric acid is passed through the column to convert the resin to the H+ form. The feed solution is then passed through the column to absorb the thorium (^{228}Th) and radium (^{224}Ra) impurities; during this process, most of the resin is converted into the uranium form. In this manner, 2 to 3 kg of uranium is retained in the column along with the impurities. The remaining uranium passes through the column to the product tanks. When the impurities are eluted (washed out), 2 to 3 kg of retained uranium are also removed from the column. The eluate solution is then stored for subsequent recovery of the uranium by means of the SX system.

The IX product solution can be processed to produce a stable solid form. Another IX process is described in Sect. 3.3.3.2.

3.3.3 Applications

The thorium ingrowth removal process has provided a promising medical application. Certain decay products of the ^{233}U decay chain may play a critical role in the treatment of certain cancers (see Sect. 5.2). In recent years, the recovery of ^{229}Th from the ^{233}U decay chain has proven useful for the subsequent production of alpha generators like ^{213}Bi, which can be used for such medical applications. This section describes the recovery of ^{229}Th from ^{233}U-bearing materials for the subsequent use of ^{213}Bi (Hall July 22, 1998). As part of the ^{233}U decay chain (see Fig. 2.1*a* in Sect. 2.1), ^{213}Bi is an alpha emitter with a short half-life (46 min). Decay occurs through two chains. About 98% of the number of decays of ^{213}Bi involve the emission of an 8.4-MeV alpha particle from the ^{213}Po daughter (half-life, 4.2 μs). The other 2% of the ^{213}Bi atoms decay by direct emission of an alpha particle (5.8 MeV). In the treatment of some types of cancers (e.g., leukemia, lymphoma, ovarian, and lung), ^{213}Bi is attached to monoclonal antibodies* that are used to target certain types of cancer cells. The alpha emissions from ^{213}Bi have a very localized impact on cell tissue because of their short range in tissue. The high linear energy transfer emitted by ^{213}Bi has a path length of 50–80 μm (Jurcic et al. Nov. 15, 1997). This feature enables the ^{213}Bi alpha radiation to kill cancer cells with a high degree of efficiency and precision (Nadis Oct. 14, 1997). Further discussion of this application is provided in Sect. 5.2.

3.3.3.1 Process Objective(s)

Thorium-229 (half-life, 7,340 years), the first daughter of ^{233}U, can be purified from inventories of ^{233}U-bearing materials as a first step in providing ^{213}Bi for medical applications. Significant quantities of ^{229}Th exist in the ^{233}U stockpiles. The extraction and recovery process

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*A monoclonal antibody is a protein molecule that attaches to the outside of a cell membrane.

described in the following also removes the ^{232}U decay products that are associated with the ^{233}U inventory. The ^{232}U decay daughters will grow back to equilibrium in ~10 years.

A major hindrance to extracting ^{213}Bi precursors from ^{233}U is the extremely slow production of ^{213}Bi that results from the relatively long half-life (159,200 years) of ^{233}U. In addition, as previously discussed in Sect. 2.1.2, ^{232}U is an isotope associated with inventories of ^{233}U. Uranium-232 has undesirable gamma-emitting daughters which can significantly complicate handling. Uranium-233 is also fissile.

3.3.3.2 Process Description and Basic Flowsheet

A summary flowsheet that shows the extraction of ^{229}Th and the recovery of ^{213}Bi is provided in Fig. 3.3*c*. Three major phases are involved in the process, and each phase involves a series of related steps.

In the first phase, ^{233}U oxides are dissolved in nitric acid (HNO_3). Thorium-229 is then separated from the ^{233}U by ion exchange. The resulting thorium-bearing solution contains essentially no fissile nuclides and thus poses no complications regarding nuclear weapons use, safeguards, and criticality. The remaining uranium in solution can be resolidified and stored in standard packages for future use or disposal. After allowing several years for the ingrowth of additional ^{229}Th from the decay of the ^{233}U in these packages, the entire ^{229}Th extraction process can be repeated.

In the next major phase of ^{213}Bi recovery, ^{225}Ac is separated from ^{229}Th and other decay products of the ^{233}U and ^{232}U decay chains. Because there are no actinium daughters in the ^{232}U decay chain, this separation results in a product of pure ^{213}Bi precursor.

The final phase in the ^{213}Bi recovery flowsheet involves loading a biomedical generator system with ^{225}Ac, from which ^{213}Bi can be extracted or "milked" as ^{225}Ac decays. (As Fig. 3.3*c* shows, different nuclides are milked at different sites: ^{229}Th at ORNL and ^{213}Bi at the hospital.)

Thorium-229 has been extracted at ORNL from two different sources. The first source was a very limited amount of ^{229}Th residues that had been saved from previous ^{233}U processing. This material was contaminated with small amounts of metals and uranium. The second source is the inventory of stored ^{233}U. The ^{229}Th is present at milligram (10^{-3} g) quantities as a result of the natural decay of kilogram quantities of ^{233}U oxides. Reillex HPQ™[*] anion-exchange resin has been used to extract thorium from the first of these source materials (Webb et al. 1997). The Reillex

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[*] The Reillex HPQ™ (resin product name) is produced by Reilly Industries, Indianapolis, Indiana.

HPQ did not perform well when challenged with the removal of trace thorium from bulk ^{233}U. Modifications to the separation and different resins were required for this separation. A second resin, BioRad MP-1™,[**] and a finely controlled process were shown to be much more effective at separating trace quantities of ^{229}Th from the ^{233}U parent (Webb Sept. 10, 1998).

The ORNL process for purifying residual materials (thorium materials contaminated with small quantities of metals) from prior ^{233}U processing began with dissolution in a high concentration of nitric acid (HNO_3) followed by filtration. The thorium was selectively retained on a Reillex HPQ resin in HNO_3, while uranium, actinium, iron, aluminum, radium, and lead were eluted. To speed thorium extraction and minimize worker radiation exposure, an open-top ion exchange column was maintained at an elevated temperature (70°C) and gravity-fed with extraction solution at a high flow rate (10 cm^3/min). The thorium was then stripped by a dilute solution of HNO_3 and collected for further purification.

In the second ORNL extraction process, ^{229}Th was recovered from stored ^{233}U oxides. The ^{229}Th in these stored oxides resulted from the natural decay of the ^{233}U. The ^{229}Th extraction began by dissolving the ^{233}U oxides in strong HNO_3, followed by filtration and ion exchange. The thorium was stripped from the resin using dilute HNO_3 for further purification. Afterwards, the ^{233}U was solidified and calcined for storage.

3.3.3.3 Process Performance—Major Results

At ORNL, the extracted ^{229}Th product has been separated from a waste stream of ^{233}U processing that had been stored in several waste tanks. The ^{233}U-bearing material used in this extraction was originally produced at ORNL during the mid-1970s as part of the Light-Water Breeder Reactor Program. A Reillex HPQ™ anion exchange resin was used to separate the ^{229}Th product (Webb et al. 1997).

The ^{229}Th extraction process, currently being developed and used at ORNL, has involved the use of a strong-acid, ion-exchange solution to separate milligram (10^{-3} g) quantities of ^{229}Th from kilogram quantities of ^{233}U. Most of the thorium product has been recovered in a single pass through the anion exchanger (Webb et al. 1998).

The recovery of ^{213}Bi for medical applications has shown much promise. Preliminary results using ^{213}Bi in the treatment of several cancers (e.g., leukemia, prostate, melanoma, breast, and lymphoma) have been promising. Details are discussed in Sect. 5.2. The amount of ^{213}Bi needed to

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[**] The BioRad Mp-1™ (resin product name) is produced by Bio-Rad Laboratories, Hercules, California.

treat a heavy tumor load is on the order of a few nanograms (10^{-9} g). The potential amount of ^{213}Bi that could be harvested annually from the current domestic ^{233}U inventory could support research and treatment for hundreds of thousands of patients (Webb et al. 1998*b*). The potential pool of ^{229}Th will continue to increase for centuries as the ^{233}U continues to decay. However, this pool faces a major threat of depletion as a result of processing losses.

Separation of ^{229}Th can be costly because of the low concentration of ^{229}Th (in the parts-per-million range amongst the bulk ^{233}U) and precautions that need to be taken for ^{233}U criticality, safety, safeguards, and radiological protection from progeny of the contaminant ^{232}U isotope. In addition, the short half-lives of ^{225}Ac ($t_{½}$ = 10 d) and ^{213}Bi ($t_{½}$ = 46 min) require that the ^{213}Bi nuclide be harvested shortly before medical use (Jurcic et al. Nov. 15, 1997.)

3.3.4 References for Section 3.3

A list of cited references on thorium ingrowth removal is provided below. This is followed by a list of supplemental references that provide additional information on this subject.

3.3.4.1 References Cited

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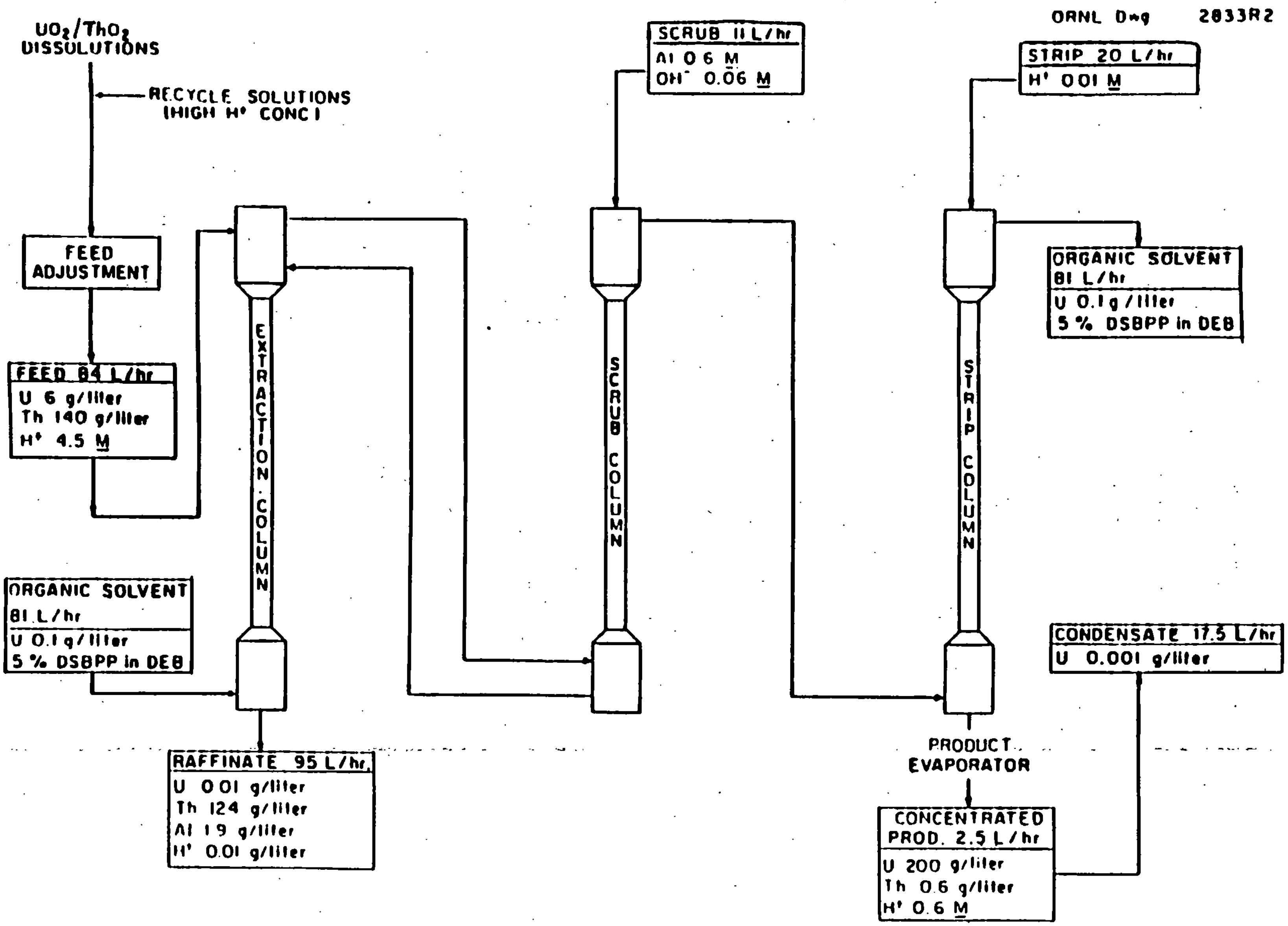
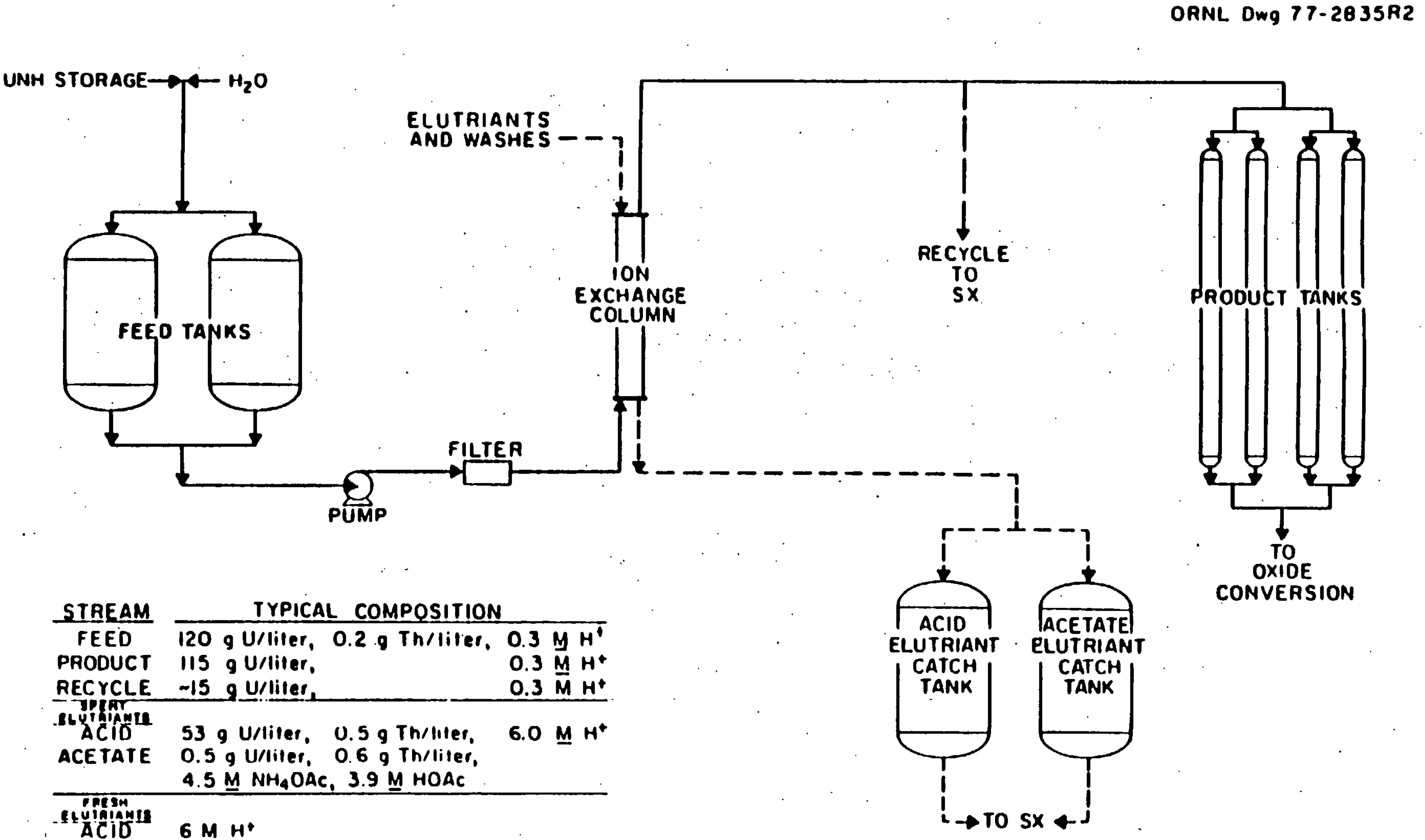


Fig. 3.3*a*. Modified Interim-23 SX flowsheet.



STREAM	TYPICAL COMPOSITION		
FEED	120 g U/liter,	0.2 g Th/liter,	0.3 M H^+
PRODUCT	115 g U/liter,		0.3 M H^+
RECYCLE	~15 g U/liter,		0.3 M H^+
SPENT ELUTRIANTS			
ACID	53 g U/liter,	0.5 g Th/liter,	6.0 M H^+
ACETATE	0.5 g U/liter, 4.5 M NH_4OAc, 3.9 M HOAc	0.6 g Th/liter,	
FRESH ELUTRIANTS			
ACID	6 M H^+		
ACETATE	4.5 M NH_4OAc, 3.9 M HOAc		

Fig. 3.3*b*. Typical IX flowsheet for purifying uranyl nitrate from trace contaminants.

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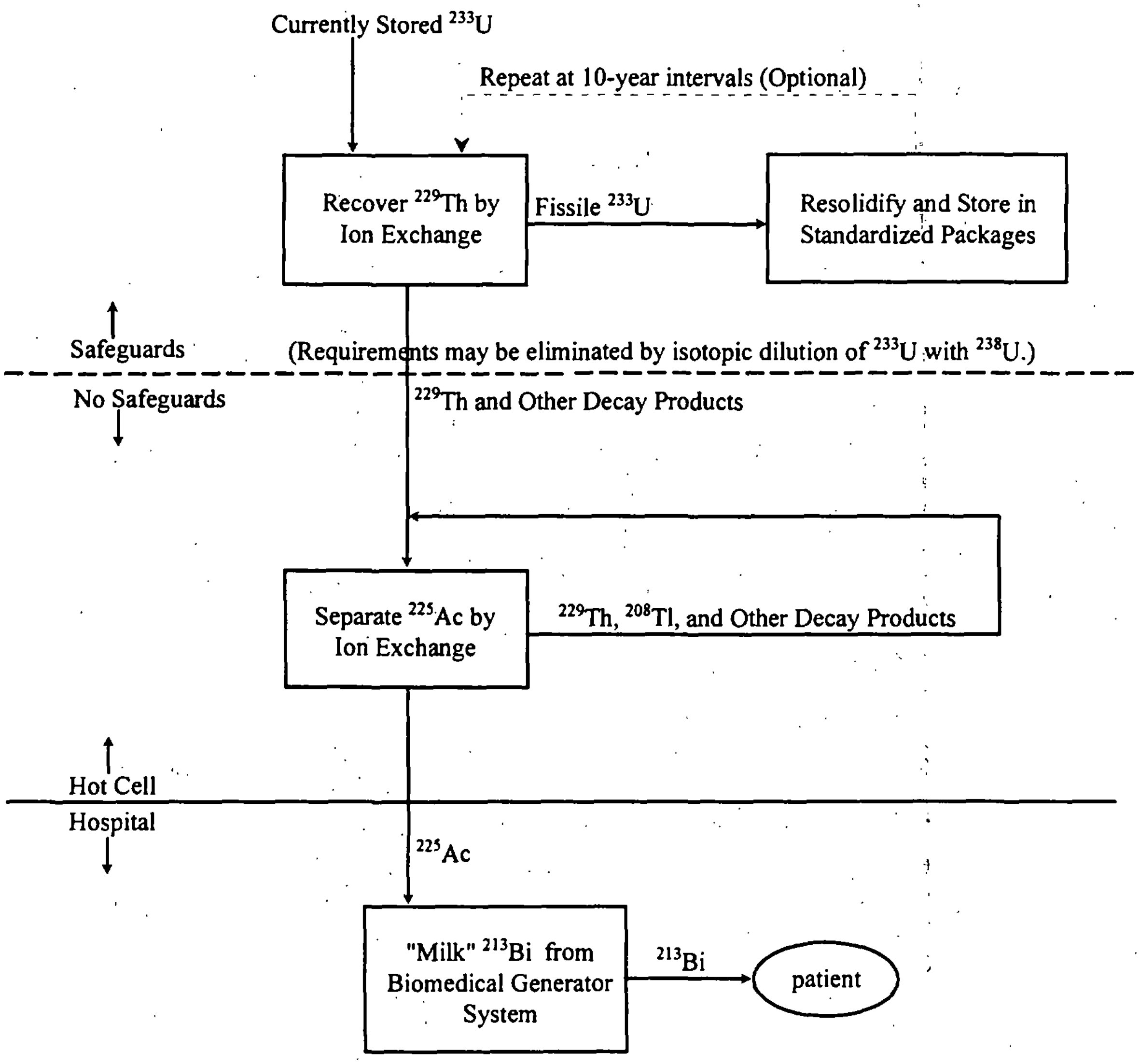

Fig. 3.3*c*. Flowsheet for ^{213}Bi production.

3.4 URANIUM-233 SEPARATION FROM FISSION PRODUCTS (REPROCESSING)

This section discusses the application of the Thorex process to the separation and removal of thorium from ^{233}U in SNF. The type of process discussed is more commonly referred to as nuclear fuel reprocessing. When irradiating ^{232}Th to produce ^{233}U, ^{233}Pa, with a half-life of 27 d, is the intermediate product that decays to ^{233}U. As a consequence, if ^{233}U is to be recovered from freshly irradiated thorium, it is necessary to recover both ^{233}U and ^{233}Pa. The recovered ^{233}Pa will then decay into ^{233}U.

3.4.1 History and Process Objective(s)

A history of reprocessing thorium-based reactor fuels is provided in Benedict, Pigford, and Levi 1981. As their discussion indicates, ORNL (Rainey and Moore May 11, 1962) performed small-scale experiments on the application of the Thorex (No. 1 or acid-based) process to SNF containing uranium, thorium, and tracer quantities of principal fission products. The overall objective of the ORNL analysis was to simulate recovery of uranium and thorium from irradiated 6 wt % uranium and 94 wt % thorium fuel that was used in the initial loading of the Consolidated Edison IP-1 PWR. Spent uranium-thorium fuel from the IP-1 PWR was subsequently reprocessed in 1971 at the West Valley NFS Plant, near Buffalo, for recovery of uranium, but without separation of thorium from fission products. No account of this separation has been published (Benedict, Pigford, and Levi 1981).

The other full-scale applications of the Thorex process have involved the separation of ^{233}U from thorium irradiated in government production reactors at the SRS and Hanford. These campaigns were previously discussed in Sects. 3.2.1 (SRS) and 3.2.2 (Hanford). A summary description is provided below of the ORNL Thorex reprocessing experiments as documented in several sources (Blanco, Ferris, and Ferguson Feb. 28, 1998; Rainey and Moore May 11, 1962).

3.4.2 Process Description and Basic Flowsheet

The basic process used to separate ^{233}U and thorium from fission products by SX was described in a conference paper by A. T. Gresky (1956). This process used nitric acid as the thorium dissolution agent, TBP as the extractant, and aluminum nitrate and nitric acid as the aqueous salting agents. In the final step, ^{233}U is isolated by ion exchange. The basic process described is the original Thorex flowsheet, which was discussed in Sect. 3.2.3.3.

Figure *3.3a* illustrates the acid Thorex flowchart (Blanco, Ferris, and Ferguson Feb. 28, 1998) that was used to reprocess SNF containing ^{233}U from the Consolidated Edison IP-1 reactor. In this process, nitric acid is used as the "salting agent" in the SX of thorium and uranium from an acid-deficient feed with 30 wt % TBP in Amsco. The process was demonstrated in laboratory equipment for the recovery of synthetic Consolidated Edison thorium reactor fuel containing tracer fission products (Rainey and Moore May 11, 1962).

In the first cycle of Fig. 3.3*a*, the adjusted (acid-deficient) feed contains 265 g/L of thorium and 15 g/L of uranium along with concentrations of 0.115 M Al^{3+}, 0.046 M F^{-1}, and 0.1 M $NaHSO_3$. As the flowchart indicates, the feed is contacted with 30 wt % TBP and scrubbed with nitric acid (HNO_3) to coextract thorium and uranium in the first column. The extract is scrubbed in the first column with HNO_3, H_3PO_4, and $Fe(NH_2SO_3)_2$ to decrease the extraction of fission products, protactinium, and CrO_4^{-2} (from stainless-steel corrosion), respectively. In the second column, the thorium is partitioned from uranium with 0.008 M $Al(NO_3)_3$, and the uranium is stripped from the solvent with 0.008 M $Al(NO_3)_3$ in the third column. The thorium and uranium are each processed through an extraction cycle for additional decontamination to sufficiently ensure that the fission product activities are not greater than those of the daughters of the ^{232}U decay chain.

3.4.3 Process Performance—Major Results

In the laboratory experiments at ORNL, the flowchart of Fig. *3.3a* was demonstrated using three 2-in.-diam pulsed columns with 12-ft sections for extraction, scrubbing, partitioning, (thorium stripping and uranium scrubbing), and uranium stripping. A single extraction step in the flowchart of Fig. 3.3*a* resulted in typical decontamination factors of 1,000, 5,000, 10,000, and 100,000, respectively, from ruthenium, zirconium-niobium, protactinium, and rare-earth elements. Uranium losses were ≤0.01 wt %, and thorium losses were ≤0.3 wt %. Most losses are a result of incomplete separation of thorium and uranium in the partitioning column, where good flow control is required (Ryon Jan. 17, 1961). The extracted thorium and uranium may be selectively stripped or costripped as desired, and additional SX cycles may be used to increase decontamination.

For thorium fuel reprocessing, the acid Thorex flowsheet was found to be very flexible and may be varied to give maximum decontamination of feeds with various fission product ratios or adapted to available process equipment (Rainey and Moore May 11, 1962). Another major advantage found with the acid Thorex process was the ten-fold improvement in waste concentration compared to the process that uses aluminum nitrate for salting.

3.4.4 References for Section 3.4

A list of cited references documenting the reprocessing of spent ^{233}U-bearing fuel is provided below. This is followed by a list of sources providing additional information.

3.4.4.1 References Cited

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Chemical Technology Division. Sept. 14, 1961. *Annual Progress Report for Period Ending May 31, 1961*, ORNL-3153, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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3.4.4.2 Supplemental Resources

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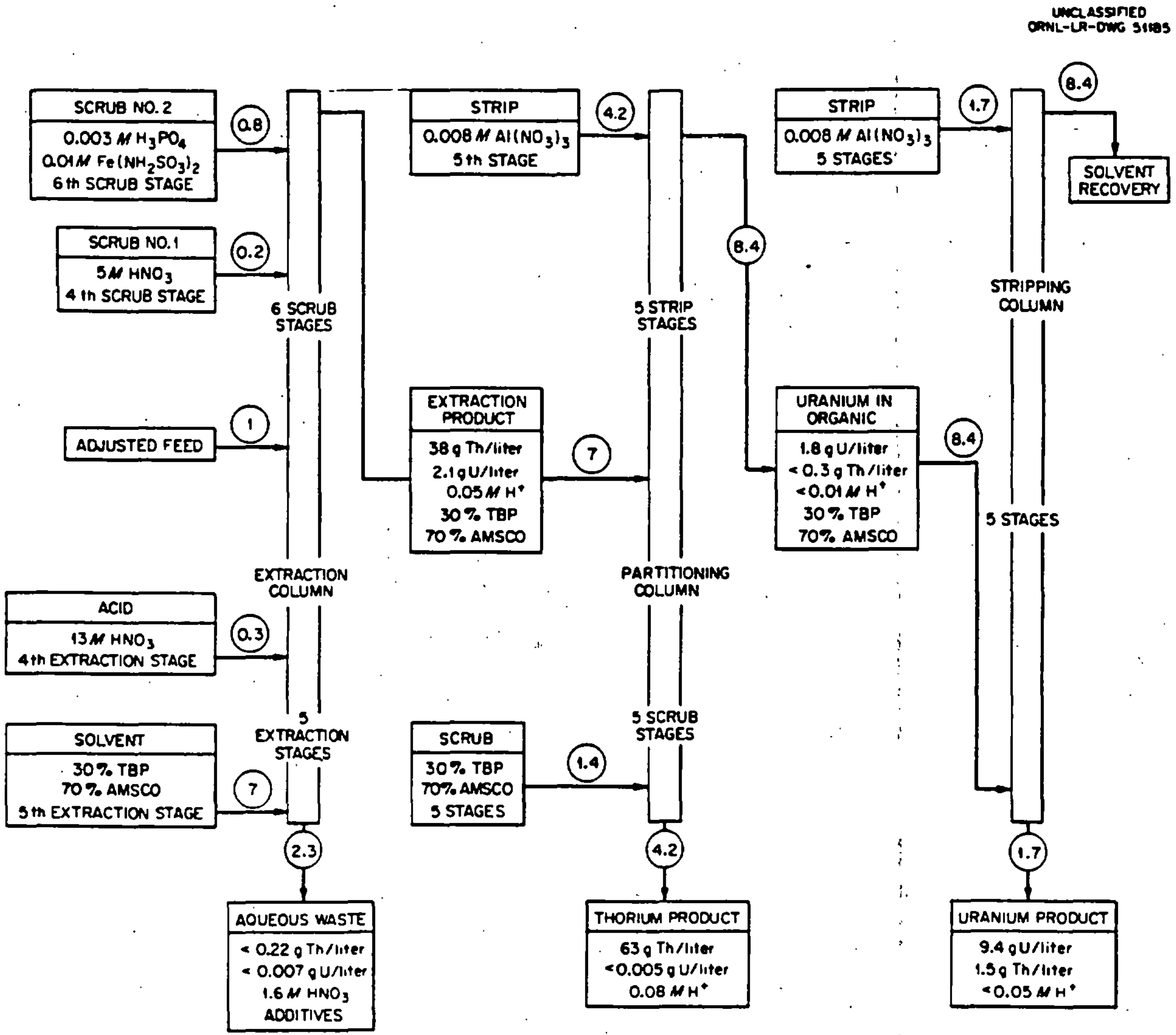

Fig. 3.4*a*. Acid thorex flowsheet for Consolidated Edison fuel. *From Blanco, Ferris, and Ferguson Feb. 28, 1962.*

3.5 ^{233}U OXIDE PREPARATION

This section describes the major programs involving the preparation of ^{233}U oxides. Three ORNL programs are described: the LWBR Support Program, the CEUSP, and the recent MSRE Fuel Stabilization Program.

3.5.1 Production of Fuel-Grade $^{233}UO_2$—LWBR Demonstration Support Program

During the period 1973–1976, ORNL, under contract with BAPL, prepared metric-ton quantities of ^{233}U as dioxide powder ($^{233}UO_2$) in the 3019 Building Pilot Plant for use in the Shippingport LWBR Demonstration Program (Parrott 1980). The ^{233}U for this activity was separated originally at the SRS and Hanford Site (as discussed in Sects. 3.2.1 and 3.2.2, respectively).

3.5.1.1 Program Objectives and Scope

The objective of this program was to convert kilogram quantities of ^{233}U to UO_2 powder directly suitable to use in preparing ThO_2-UO_2 fuel pellets for the Shippingport LWBR. As specified in ORNL's contract with BAPL, the prepared UO_2 powder was to meet rigid chemical and physical specifications and be freshly separated from the decay daughters of ^{232}U just before shipment to BAPL. The UO_2 powder production campaign was conducted in Cells 5, 6, and 7 and the oxide conversion facility of the Building 3019 Pilot Plant.

3.5.1.2 Process Description and Flowsheet

The oxide preparation process began with purification of a uranyl nitrate [$UO_2(NO_3)_2$] solution by ion exchange (see Fig. 3.3*b*) to remove the ^{232}U decay daughters. The resulting solution was converted to oxide (UO_2) and generally shipped not more than 16 d after purification so that the BAPL fuel fabrication operations for the LWBR could be performed unshielded in a relatively low radiation field at a rate of 15–20 kg U per week (Horton et al. March 1972). Reject $^{233}UO_2$-ThO_2 pellets were returned to ORNL, granulated, and dissolved in nitric acid catalyzed with hydrofluoric acid. The ^{233}U was recovered from the thorium by a modified Interim-23 SX process (see Fig. 3.3*a*) before it was purified again by ion exchange.

A summary flowsheet of the $^{233}UO_2$ preparation campaign is given in Fig. 3.5.1*a* (Parrott 1980). The isotopic purity of the ^{233}U used was greater than 97.5 wt %, and the associated ^{232}U content was <10 ppm. The uranium was produced by the irradiation of thorium in the Hanford and SRS production reactors and separated from the residual thorium and fission products at those sites. ORNL received about 65 wt % of the total ^{233}U (as a uranyl nitrate solution) from Hanford and the remainder (as UO_3) from SRS. These materials were stored at ORNL until needed for the production of UO_2. This storage lasted several years and necessitated processing of the material immediately before its conversion. A high-pressure, cation-exchange technique was used to effectively remove the ^{228}Th and ^{224}Ra, both of which had formed from the decay of ^{232}U (Rainey December 1972). During the ensuing 3-d period, the resulting solution was allowed to decay to 0.2% of the mass equilibrium concentration for ^{208}Tl, the principal gamma emitter in the ^{232}U decay chain.

The flowsheet of Fig. 3.5.1*a* shows the major steps used in the conversion process: precipitation, drying, reduction, and blending. The uranium was converted in 1-kg batches, with one batch being fed to the system every 4 h. Nominally, a 10-L solution of uranium (having a concentration of 100 gU/L) was transferred to a metering vessel (calibrated to measure system input) and then transferred to a precipitation vessel. While the solution was being recirculated in the vessel, a stream of ammonia gas was bled into the recirculating pump's suction line until the pH of the solution reached 8.25. The pump discharge was then rerouted to a rotating centrifuge, which contained a Teflon™ liner. The supernate overflowed, leaving the wet ammonium diuranate (ADU) [$(NH_4)_2U_2O_7$] cake in the liner. After the cake had been washed with water to remove the residual nitrate, the centrifuge was shut down.

Following removal from the centrifuge, the Teflon liner was placed into a microwave oven equipped with a turntable. The cake was dried while being subjected to a microwave power level of 2 kW for 1 h followed by 1 kW for 1 h. Since Teflon does not absorb microwave energy, the liner was able to be reused several hundred times.

The dried cake was then passed through a 100-mesh granulator and loaded into the furnace boats. Each 1-kg batch was distributed evenly into four boats. Calcination and reduction were conducted in a continuous-belt, multizone, controlled-atmosphere furnace featuring a distinct hydrogen region in the midsection bounded by argon regions at the ends. The powder was heated to 625 °C in argon, then passed into the hydrogen atmosphere, where it was heated to 650 °C and held for 6 h to achieve reduction. Following this treatment, the powder was reintroduced into an argon atmosphere and cooled to ambient temperature.

The UO_2 leaving the furnace was pyrophoric and, thus, would have rapidly oxidized to U_3O_8 on exposure to air. To prevent such oxidation, a thin outer layer of the powder was stabilized by contact with moist air. The final oxygen:metal (O:M) ratio varied between 2.03 and 2.07, which was well below the specified maximum of 2.18. The resulting moisture content varied between 0.10 and 0.36 wt %, which was well below its specified maximum of 0.5 wt %.

Following stabilization, the powder was granulated through a 100-mesh screen, and the UO_2 product from a week's operation (25–35 kg) was mixed in a V-blender to achieve uniformity. The blender was then inverted, and the UO_2 was vibrated into stainless-steel cans (each containing 400 g of UO_2) for packaging and shipment to BAPL.

3.5.1.3 Process Performance and Results

Major highlights (Parrott 1980) from the ORNL preparation of ^{233}U for the LWBR Demonstration Program are as follows:

1. The ^{233}U was handled in glove boxes within 10 d following the removal of the high-energy ^{232}U daughters, and 1 d/week was spent in cleaning the glove boxes. However, in spite of these precautions, the radiation exposure to operating personnel still resulted in being 20–30 mrem/person-week.
2. Specification-grade UO_2 was produced during the initial batch processing.
3. Of the total quantity of UO_2 produced (2030 kg), only 99 kg failed to meet all specifications. No material was rejected by BAPL.
4. Microwave drying of the ADU [$(NH_4)_2U_2O_7$] before calcining eliminates the effects of precipitation on the final UO_2 powder characteristics.
5. ORNL's contract with BAPL called for delivery of the UO_2 product within 16 d of purification. Only 1 shipment of 188 to BAPL was not delivered on time.

3.5.1.4 References for Section 3.5.1

A list of cited references documenting the LWBR Support Demonstration Program at ORNL is provided below. This is followed by a list of sources providing additional information.

3.5.1.4.1 References Cited

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Parrott, J. R. 1980. "Preparation of $^{233}UO_2$ for the Light-Water Breeder Reactor Demonstration Program," *Transactions of the American Nuclear Society*, 34, 434–35, ISSN: 0003-018X, American Nuclear Society, La Grange Park, Ill.

3.5.1.4.2 Supplemental Resources

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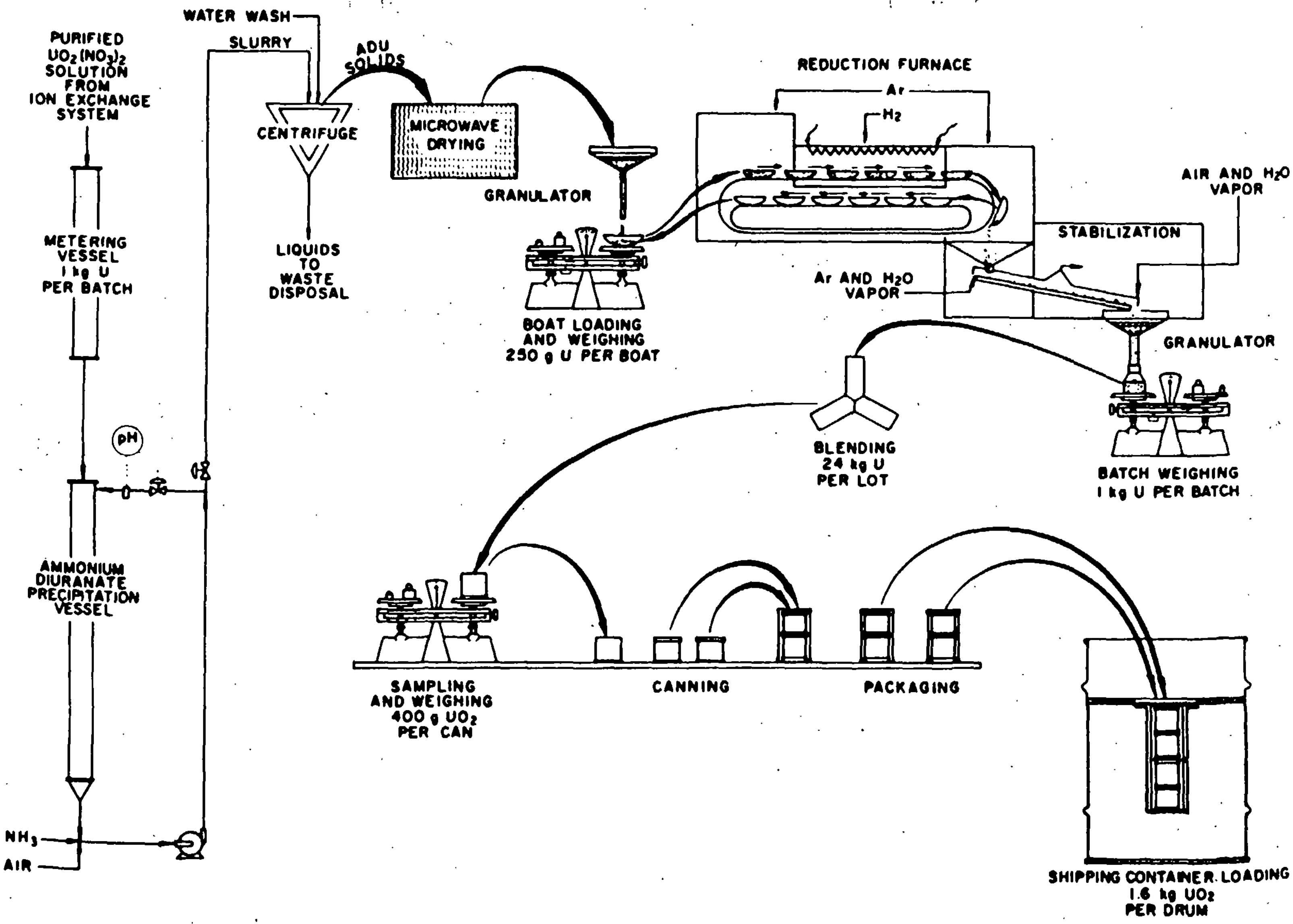

Fig. 3.5.1*a*. Flowsheet of the ORNL $^{233}UO_2$ pr ation campaign. *Courtesy of Parrott 1980.*

3.5.2 Conversion of Uranium Nitrate to Oxide for Storage—Consolidated Edison Uranium Solidification Program (CEUSP)

3.5.2.1 Program Objectives and Background

The CEUSP developed a unique conversion and solidification process that was carried out at ORNL (Building 3019) to prepare a stable uranium form for long-term, safe storage. During 1985–1986, an evaporation–thermal denitration process was developed, operated, and maintained at ORNL to achieve the solidification and safe storage of about 1000 kg of highly radioactive and fissile uranium, which had been stored in a nitrate solution.

The uranium processed by CEUSP originated from the irradiation of a ThO_2-UO_2 fuel core in the Consolidated Edison IP-1 reactor during the early 1960s. The irradiated fuel was reprocessed in 1968 at the NFS plant in West Valley, New York, and the uranium nitrate product solution was sent to ORNL for storage in 1969. The nitrate liquid was placed into an underground storage tank located in a vault outside Building 3019 and stored there until 1986. During this time, soluble poisons (cadmium nitrate and gadolinium nitrate) were added to ensure subcriticality. Because no apparent use was found for the uranium while the nitrate solution was in storage, the CEUSP was developed to solidify the material during 1985–1986 for long-term, safe storage (Parrott August 1978 and McGinnis et al. 1986).

3.5.2.2 Process Description and Flowsheet

A schematic diagram of the CEUSP process flowsheet is given in Fig. 3.5.2*a* (McGinnis, Collins, and Patton 1986). The processed uranium nitrate solution had a concentration of 130 gU/L and contained about 1000 kg of highly radioactive and fissile uranium. The material was divided and processed into about 400 batches, each containing about 2.6 kg U. The CEUSP used methods in remotely operated evaporation–acid destruction, thermal denitration–solidification, and solid-material handling. The major steps included:

1. Batch evaporation to concentrate the uranium-cadmium-gadolinium nitrate solution to slightly less than the saturation concentration,
2. Use of formaldehyde in an evaporator to destroy nitric acid so that crystallization of the nitrate salts due to supersaturation would not occur,
3. Thermal denitration to form the oxide in situ in the storage can,

4. Remote welding of the can lid and installation of a crimp-sealed, secondary containment canister, and
5. Transfer of the finished package to a shielded storage well.

While a simple solidification process was utilized, several constraints (McGinnis, Collins, and Patton 1986) complicated the use of equipment and facilities. These included:

1. The presence of ^{232}U (140 ppm) and its associated decay daughters (see Sect. 2), thus requiring massive shielding and alpha containment;
2. The large mass of fissile uranium (^{233}U and ^{235}U), which necessitated equipment designs geometrically favorable to subcriticality;
3. Limited available in-cell processing space,
4. Intricate mechanical equipment needed for the remote operation and transport of the product storage cans, and
5. The available facilities required direct, hands-on maintenance of the processing equipment.

As shown in Fig. 3.5.2*a*, an evaporator was included in the process design to utilize evaporation in reducing the overall time required for solidification. The feed solution to the evaporator was concentrated by a factor of about 2.5. Evaporation of a feed batch took 2 to 3 h and was much faster than the downstream thermal denitration process, which took about 1 d. Thus, the CEUSP facility equipment had three thermal denitration systems, which were operated in a parallel mode, but only one evaporation system.

The evaporation step incorporated the need for a destruction process using formaldehyde to remove part of the nitric acid. This addition was necessary because, with the desired feed concentration in the absence of any acid destruction, a supersaturated concentrated solution would have been produced that would have salted out solids, plugging the process equipment.

Major features of the evaporation–acid destruction step and thermal denitration step of the CEUSP process are described below. Further details of the CEUSP operational experience are provided in McGinnis et al. 1986.

3.5.2.2.1 Evaporation—Acid Destruction

As shown in Fig. 3.5.2*b*, the CEUSP evaporation–acid destruction step, which concentrated the fissile uranium–cadmium solutions, was performed in a thermosiphon-type evaporator vessel. The vessel was operated semicontinuously to concentrate about 21-L batches of feed solution to an 8-L volume (Hall, Patton, and Hass 1986). The CEUSP feed solution and formaldehyde entered the evaporator through a common nozzle and were swept downward through the evaporator by the recirculating liquid from the thermosiphon leg. The reaction of formaldehyde with nitric acid was conducted at temperatures above 95°C to obtain an instantaneous, controllable reaction (Healy and Davis Feb. 22, 1956).

3.5.2.2.2 Thermal Denitration—Solidification

The CEUSP system configuration for thermal denitration–solidification occurred in a combination reactor/storage can, as shown in Fig. 3.5.2*c*. The thermal denitration step was a semicontinuous process in which batches of the concentrated CEU solution (each containing ~2.6 kg U) was fed into a can located inside a three-zoned cylindrical heating furnace (Vedder, Collins, and Hass 1986). As the solution was fed in, it was evaporated to dryness, and the nitrate was decomposed, leaving a solid cake in the can, which also served as a storage container, thereby minimizing any problems associated with handling solids. An entire batch was fed at a rate of ~9 mL/min during a 16-h period in which the temperatures in the bottom, middle, and top zones of the furnace were independently increased by a programmable controller. Following the feed addition, a bakeout period of 3 h at ~800°C was used to complete the solidification. Off-gases from the denitration, primarily water vapor and nitrogen oxides, exited the can through a jacketed line to a liquid collection tank. During the feed addition period, the off-gas line was washed with nitric acid to dissolve any entrained solids. The collection tank was vented through a chilled-water-cooled condenser, and condensables were drained back into the tank. Figure 3.5.2*c* also shows that the feed and purged air entered the can through a process connection nozzle. Gases evolved during the denitration exited the can through the same nozzle.

The CEUSP material was loaded into its packaging by placing each container in a high-temperature furnace, in which the uranium (mostly ^{233}U and ^{235}U) was added as a nitrate solution. In the package, the nitrate decomposed to an oxide (U_3O_8), forming a cast-in-place solid monolith.

3.5.2.2.3 Solid Material Handling

The solidified CEUSP material was placed in over 400 stainless steel cans, which were welded shut and placed in Cell 4 of ORNL Building 3019. The design of a CEUSP storage inner can assembly is given in Fig. 3.5.2*d*. The inner cans have 3.5-in. outer diam (OD) and 24.25 in. length. Each inner can was placed inside a double-seamed, tin-plate outer canister (not shown). The outer canisters have a 3.625-in. interior diam (ID) and a 24.75-in. length (Martin Marietta Energy Systems, Inc. June 1984).

A summary of the major characteristics of the solidified CEUSP material stored at ORNL is provided in Table 3.5.2*a* (Peer Consultants and Engineering, Design, Geosciences Group Dec. 23, 1987). Collectively, over 400 welded CEUSP canisters contain 1043 kg of uranium, most (898 kg) of which is fissile.

3.5.2.3 Process Performance and Results

The CEUSP project achieved its major goals of converting hazardous liquid uranium nitrate to a stable form and placing that stable form into safe storage. Over 1000 kg of highly radioactive and fissile uranium, containing about 75 wt % ^{235}U, about 10 wt % ^{233}U, and about 140 ppm ^{232}U, was processed and solidified in over 400 canisters as an oxide.

3.5.2.4 References for Section 3.5.2

A list of cited CEUSP references is provided below. This is followed by a list of sources providing additional information.

3.5.2.4.1 References Cited

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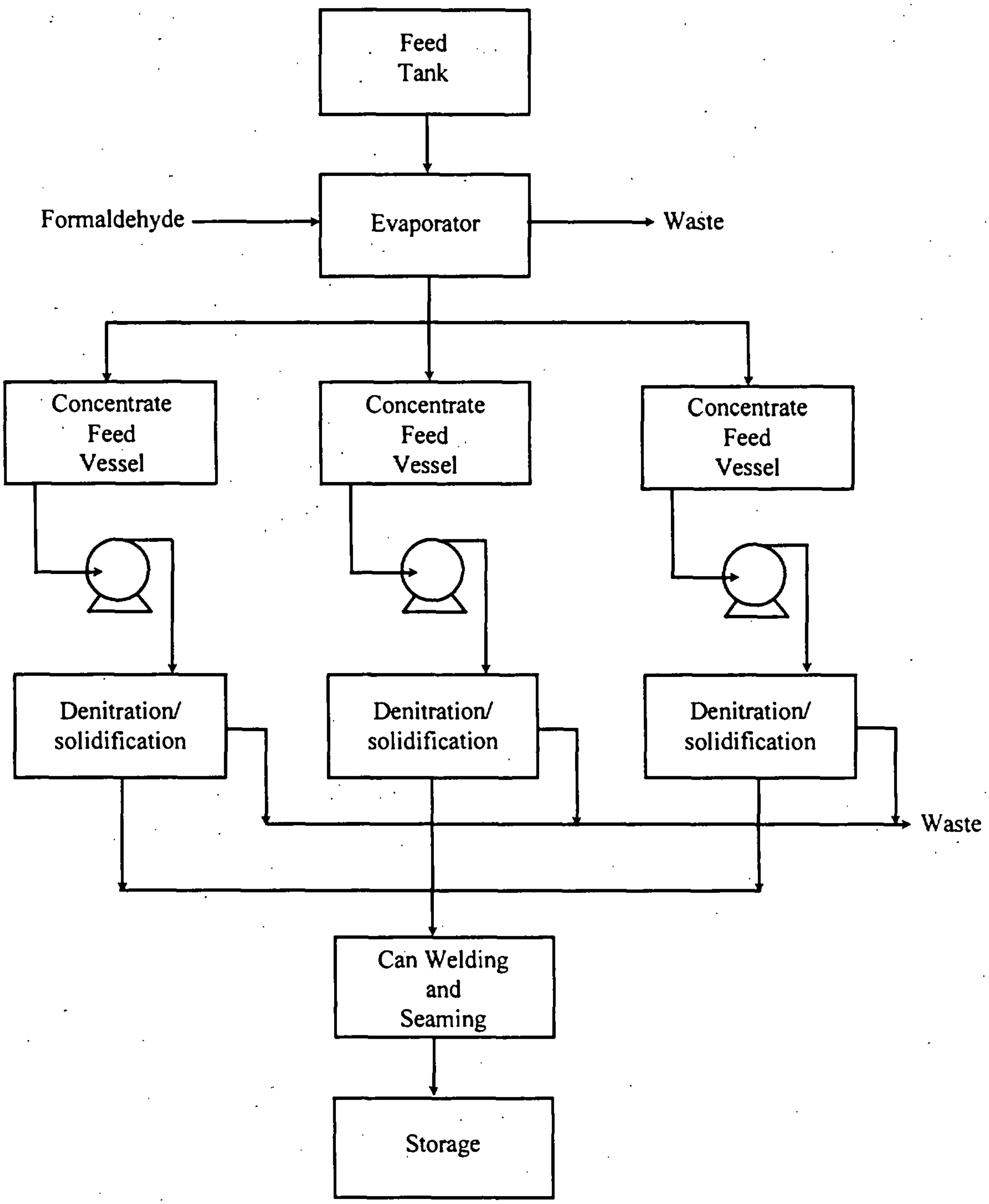

Fig. 3.5.2*a*. Simplified CEUSP process flowsheet.

ORNL DWG 98-8110

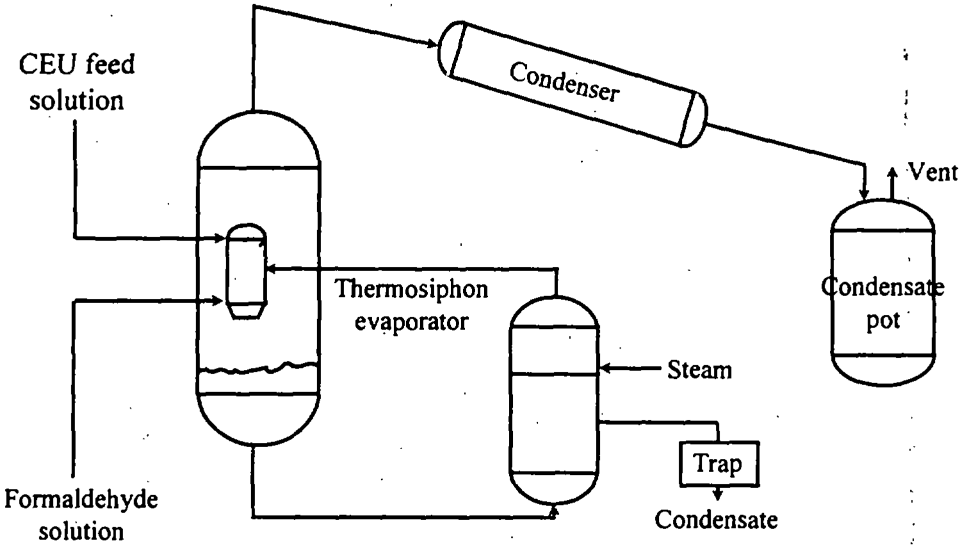

Fig. 3.5.2*b*. CEUSP process equipment for concentrating fissile uranium/cadmium solutions into a thermosiphon evaporator. *From McGinnis et al. March 1987.*

ORNL DWG 98-8111

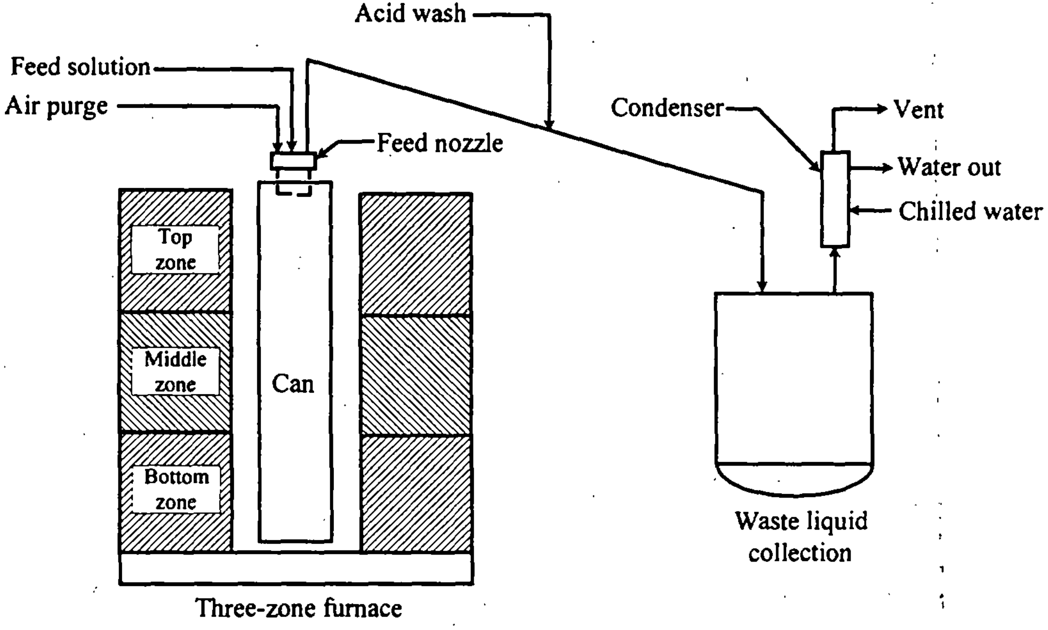

Fig. 3.5.2*c*. CEUSP system configuration for denitration and solidification. *From McGinnis et al. March 1987.*

ORNL 97-123509

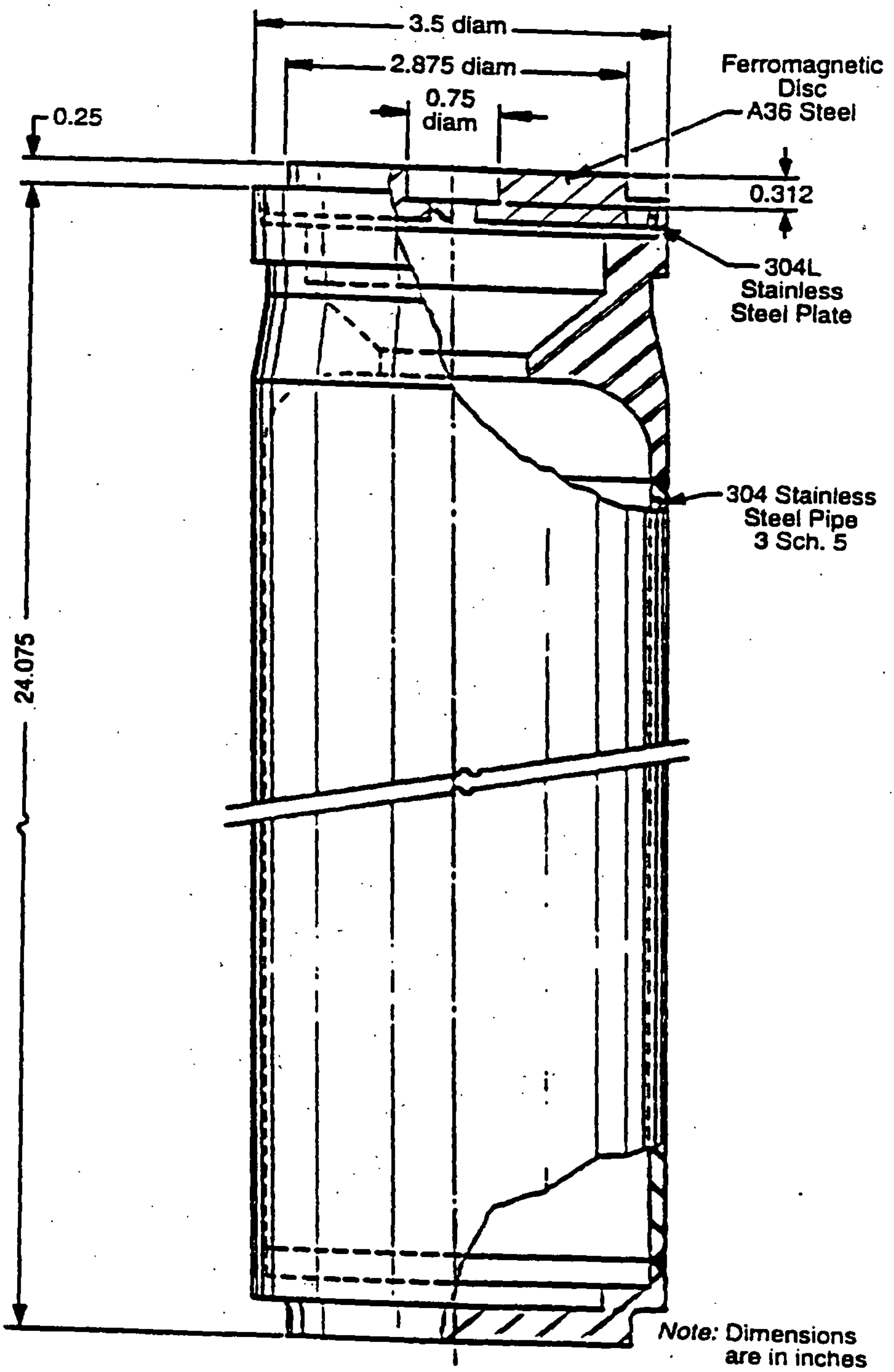

Fig. 3.5.2*d.* Storage-can assembly for CEUSP solidified waste.

Table 3.5.2*a*. Characteristics of Consolidated Edison Uranium Solidification Program material at ORNL[a]

Description

Monolithic uranium oxide material (radioactive and hazardous)

Storage location

Radiochemical Processing Plant (Building 3019, ORNL), Cell 4

Material inventory, kg

Total material	1673.3
Total U	1042.6
^{235}U	796.4
^{233}U	101.1

Uranium isotopic composition, wt %

^{233}U	9.69
^{234}U	1.39
^{235}U	76.52
^{236}U	5.60
^{238}U	6.80
^{232}U	~0.01 (about 140 ppm)

Chemical composition, wt %

U_3O_8	75.6
CdO[b]	21.7
Gd_2O_8[b]	2.7
Metal contaminants	(Trace amounts of Si, Fe, Al, P, and Cr)

Storage containers

403 welded canisters; each inner can is placed inside a tin-plate outer can (Fig. 3.5.2*d*).

Inner can: 3.5 in. OD by 24.25 in. length
Outer can: 3.625 in. OD by 24.75 in. length

Average radiation levels from storage containers

At surface: 300–350 rem/h
At 1 ft from surface: 60–80 rem/h

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[a] Based on Peer Consultants, P.C., and Engineering, Design, and Geosciences Group, Inc. Dec. 23, 1987.

[b] Neutron poisons cadmium and gadolinium were added to the CEUSP material to reduce the risk of a criticality accident during its 17-year period of storage as a liquid.

3.5.3 Conversion of Uranium Fluorides to Oxides for Storage—Molten Salt Reactor Experiment (MSRE) Fuel Stabilization

3.5.3.1 Process Background and Objective(s)

As noted in Sect. 3.1.2.5, the MSRE operated at ORNL from 1965 through 1969, at which time it was shut down and the fuel, flush, and coolant salts were allowed to freeze in their respective drain tanks. At the time of shutdown, it was expected that a waste repository would be available in a few years and that the storage period at MSRE would be brief. Irradiation of solid salt was known to result in the liberation of fluorine from the salt matrix, and a procedure to heat (not melt) the solid salt to recombine fluorine was instituted. After the salts were not moved for several years, an evaluation of continued storage was performed (Notz September 1985). In 1994, a gas sample taken from the off-gas system serving the fuel and flush tanks showed that fluorine had escaped the fuel salt in significant quantities and that uranium was present as UF_6 at a partial pressure near the saturation pressure. Recent experiments have shown that the annual heatup procedure likely resulted in the oxidation of UF_4 in the salt to volatile UF_6 (Williams, Loghry, and Toth January 1998). Further investigations identified a deposit of uranium in a charcoal bed connected to the off-gas system (Fig. 3.5.3*a*). The MSRE Remediation Project was established to stabilize conditions at MSRE, recover uranium from the off-gas system and the charcoal bed, and remove, process, and package the fuel and flush salts (Peretz et al. September 1998).

The MSRE Remediation Project consists of the following activities:

- Stabilization of the facility, including improvements in nuclear criticality safety and material confinement;
- Removal of the uranium present as a gas and as solid deposits in the off-gas system;
- Removal of the uranium deposit present in the auxiliary charcoal bed;
- Removal of the fuel and flush salts, separation of the uranium remaining in the salts stabilization and packaging of the salts for long-term storage; and
- Conversion of uranium to U_3O_8 for long-term storage.

In the conduct of the MSRE Remediation Project, several technologies applicable to the general handling of ^{233}U are being applied. These include:

- Radiological surveys based on ^{232}U daughter products,
- Trapping of UF_6 on sodium fluoride,
- Restoration of the oxidation state of uranium during melting of radiolytically reduced salt,

- Separation of $^{233}UF_4$ from salt by oxidation to UF_6 using a fluorine gas sparge,
- Desorption of UF_6 from sodium fluoride and conversion to U_3O_8,
- Conversion of uranium-carbon compounds to U_3O_8, and
- Maintaining nuclear criticality safety handling significant quantities of ^{233}U in various process configurations.

The MSRE Remediation Project has been the subject of various reviews, including a review by the National Research Council (Margrave 1997). It is being conducted as a CERCLA project under the Oak Ridge Federal Facilities Agreement (FFA).

3.5.3.2 Process Descriptions and Basic Flowsheets

3.5.3.2.1 Recovery of UF_6 from Off-Gas System

Based on the analysis of the initial sample taken from the MSRE off-gas system, it was determined that there was at least 5 kg of uranium present as volatile $^{233}UF_6$ in a gas stream consisting of equal parts fluorine and helium. An unknown quantity (now estimated at about 18 kg) was expected to be present as solid deposits of UF_6, which had condensed in cool portions of the off-gas system. A reactive gas removal process was installed to recover the uranium on a sodium fluoride trap and to react fluorine on an alumina trap (Fig. 3.5.3*b*). This selection was based on a review of trapping technology (Trowbridge et al. August 1995), and process parameters were confirmed in the laboratory (Rudolph et al. July 1997). On-line evaluation of UF_6 concentrations was installed using Fourier-transform infrared (FTIR) spectrometers. Gas was withdrawn from the off-gas system into previously evacuated decay tanks. The residual gas was held for the decay of ^{220}Rn and its daughter products. Thermal profiles in the traps were used to monitor trap filling, and gamma radiation transmission was used to positively identify progress of the uranium front past specific locations. Final inventory control was achieved by weighing the traps. This equipment has proven effective for the removal of volatile UF_6 as long as the piping transporting the gas is clear.

Several plugs in the off-gas piping existed; these were initially postulated as solid UF_6 deposits. However, reducing the partial pressure of UF_6 in the off-gas system did not cause the material to sublime. It was then postulated that the plugs consisted of either UO_2F_2 produced by contact with moisture, or of UF_4 or UF_5 produced radiolytically by the high alpha activity of the ^{233}U and its ^{232}U contaminant. Treatment of these plugs with ClF_3 to oxidize the uranium back to volatile UF_6 was selected (Trowbridge June 1997) and demonstrated in the laboratory

(Williams et al. April 1997). These gas treatments have been successful in removing the plugs, and reaction products indicate that the material was most likely radiolytically reduced uranium fluoride.

3.5.3.2.2 Recovery of Uranium-Bearing Charcoal Deposit

When the uranium deposit was discovered in the auxiliary charcoal bed, concerns developed over both the form of uranium present in the charcoal and the potential chemical reactivity of carbon-fluorine compounds formed in the water-cooled bed. A series of laboratory tests were conducted to identify the carbon-fluorine-uranium chemistry under the conditions at which fluorine and UF_6 were loaded on the bed (Del Cul et al. September 1998). This work identified the formation of a C_xF compound at 23 °C with an approximate C:F ratio of 2.6. This compound can react exothermally to form higher fluorides, such as CF_4. A process to safely react the C_xF with ammonia, producing nonreactive carbon, NH_4F, and nitrogen, was then demonstrated (Del Cul et al. October 1997) and implemented to prevent undesirable chemical reactions during removal of the uranium.

The same series of tests demonstrated that uranium deposited in activated charcoal from a UF_6/F_2 gas stream is in the form of nonvolatile uranium fluorides and uranium oxyfluorides that are intercalated in the micrographitic structure of charcoal. The uranium-laden charcoal was visually indistinguishable from virgin-activated charcoal. A process was developed to physically tap into the auxiliary charcoal bed below the deposit and vacuum the uranium-laden charcoal into a critically safe centrifugal separator and collector vessel (Fig. 3.5.3*c*). After HEPA filtration, the exhaust was then passed through a charcoal bed for retention of ^{220}Rn for decay. A flow test of a prototype charcoal bed was performed to demonstrate the effectiveness of this radon decay bed (Coleman March 1999).

A recent initial entry into the auxiliary charcoal bed has identified a hard, nongranular structure in the top several inches of the bed. As a result, modifications to the removal process described above is now being developed. It is likely that physical removal of the top of the bed vessel will be required, allowing either direct removal of a portion of the deposit or access to break up the charcoal matrix prior to pneumatic transfer.

3.5.3.2.3 Recovery of UF_4 from Fuel and Flush Salts as UF_6

The MSRE fuel salt is divided between two drain tanks; a similar flush salt used to rinse the reactor loop before and after maintenance is stored in a third tank. The salt content was well-documented throughout the reactor's operation, and fission-product inventories can be estimated by accounting for decay (Williams, Del Cul, and Toth January 1996). Because of the fluorine lost directly from the salt and the fluorine lost by the evolution of UF_6, the solid-fuel salt matrix is in a net- reducing condition. Although no impact is observed with solid salt, when the salt is melted, a series of reactions takes place (Williams, Toth, and Del Cul November 1996). These reactions lead to the reduction of UF_4 to UF_3, after which both zirconium and uranium metal is formed. These metallic species may be seen in the salt, and they tend to interact with the walls of the container. Furthermore, a clear melt is not achieved with radiolytically reduced salt. Instead, clumps of nonflowing material appear in the salt.

An evaluation of alternatives for the removal, processing, and disposition of the salt has been performed (Peretz August 1996). This evaluation identifies the advantages of removing the salt as a liquid and then separating the uranium from the salt using the same fluorination process as was used to remove the initial ^{235}U charge in 1968. The ^{233}U can then be managed along with the rest of the uranium being removed from MSRE, and UF_6 can no longer be liberated from the salt. A chemical getter can be used to prevent pressurization of the salt containers. These alternatives have been documented using the CERCLA process, and a Record of Decision (ROD) to melt, process, and store the salt has been approved (Jacobs EM Team July 1998). The overall block diagram of the process being used is shown in Fig. 3.5.3*d*.

In order to safely melt the salt and obtain a clear liquid with all the uranium in solution, a pool of salt will be melted near the solid-salt surface, and the liquid in that pool will be treated with a HF/H_2 gas sparge (Toth, Williams, and Del Cul July 1996). This pool-melt process has been tested on simple salts (Williams, Loghry, and Toth January 1998), and tests using the nonradioactive MSRE coolant salt are about to commence.

3.5.3.2.4 Conversion of UF_6 to U_3O_8 for Long-Term Storage

A $2NaF{\cdot}UF_6$ complex is produced by trapping UF_6 from the off-gas system and from fluorinating the fuel and flush salts. In addition, the uranium-laden carbon removed from the auxiliary charcoal bed is not suitable for long-term storage. Consequently, a facility is being constructed to convert the uranium to the stable oxide U_3O_8 (Del Cul, Icenhour, and Toth November 1997). Because of the 2.6-MeV gamma radiation produced by the ^{208}Tl daughter of ^{232}U, this process must be installed in a hot cell and operated remotely. The main criteria used to select the conversion process were:

- Minimal loss;
- Minimal secondary wastes and contamination;
- Adaptability to small-scale, hot-cell operation;
- No moving parts, stirring, mixing, or transfers between vessels;
- Minimal product purity requirements; and
- Adaptability to a variety of uranium feed materials, including the 2NaF•UF_6 complex, uranium-laden charcoal, and miscellaneous materials such as uranium deposits in piping.

The process operates in batch mode, using either a NaF trap from the off-gas recovery process or the salt fluorination process, or a container of charcoal as the processing batch.

The process consists of two uranium-recovery schemes interconnected with a common oxide conversion unit. The first recovery unit is shown in Fig. 3.5.3*e*. UF_6 is desorbed from the NaF trap by heating the trap to 400–450°C in a closed-loop recirculating system. UF_6 is then condensed and cooled in a process vessel. A small amount of fluorine gas is continually circulated through this loop—first, as a carrier gas for UF_6 and, secondly, to convert any oxyfluorides or lower fluorides of uranium into UF_6. Two in-line infrared gas cells are used to monitor the completeness of the recovery–condensation operation. The pressure in this loop is kept below atmospheric pressure. A soda-lime trap is located before the vacuum pump to ensure that no fluorine or uranium leaves the system.

The charcoal recovery scheme is shown in Fig. 3.5.3*f*. A charcoal container is connected to the FTIR gas cells and the condenser/conversion vessel. An intermediate room-temperature trap (an empty vessel) is included for the initial heating of the passivated charcoal to allow the condensation of ammonium fluoride that emanates first from the charcoal container. Once the charcoal reaches 600°C, it will be reacted with F_2 to produce, primarily, CF_4 and smaller quantities of other carbon fluorides. Accompanying this combustion of charcoal in fluorine will be the formation of UF_6 from the lower fluorides and oxyfluorides present in the charcoal. The volatile UF_6 will be carried over to the condenser-conversion vessel, where it will condense and be cooled.

The conversion of the frozen UF_6 to U_3O_8 will be conducted using the process shown in Fig. 3.5.3*g*, in the same vessel used to freeze the UF_6. Initially, a slight excess of water vapor (the amount needed to stoichiometrically react with the UF_6) will be condensed as ice on top of the UF_6. The vessel will be allowed to warm to room temperature, thus resulting in the formation of the contents into solid UO_2F_2•xH_2O and HF. The resulting solid will be heated and contacted with pressurized steam, which will penetrate into the cake and react with the oxyfluoride-oxide mixture to produce HF. A NaOH solution will be used to neutralize this HF. Air will then be passed over the solid when the temperature reaches 750°C to convert the uranium oxides formed at lower temperatures into the air-stable oxide U_3O_8.

Laboratory testing of this process has been completed with both $2NaF \cdot UF_6$ and uranium-laden charcoal feeds. This testing is being integrated with the development of a storage standard for ^{233}U oxide material. Construction of the final process equipment is beginning in the high bay above the hot cell, prior to relocating the pretested hardware into the cell.

3.5.3.3 Anticipated Process Performance and Results

The removal of UF_6 from the off-gas system is now nearly complete, with residual volatile uranium concentrations in most of the system near or below the detection limit. No significant uranium plugs remain in the off-gas system. Passivation of the charcoal bed with ammonia is complete, and initial entry into the auxiliary charcoal bed is underway. Modifications to the process for removal of the uranium-laden charcoal are needed to account for the solid mass identified by the early entry activities. Access has been gained to the drain tank cell, equipment in the cell has been examined and found suitable for use, and removal of the coolant salt is underway. Testing of the salt melting and uranium recovery processes, using both the coolant salt and smaller batches of salt irradiated to reproduce the radiolytically reduced conditions of the fuel salt, is now underway. The conversion process has been tested with both $2NaF \cdot UF_6$ and uranium-laden charcoal feeds, and construction of the final process equipment is beginning.

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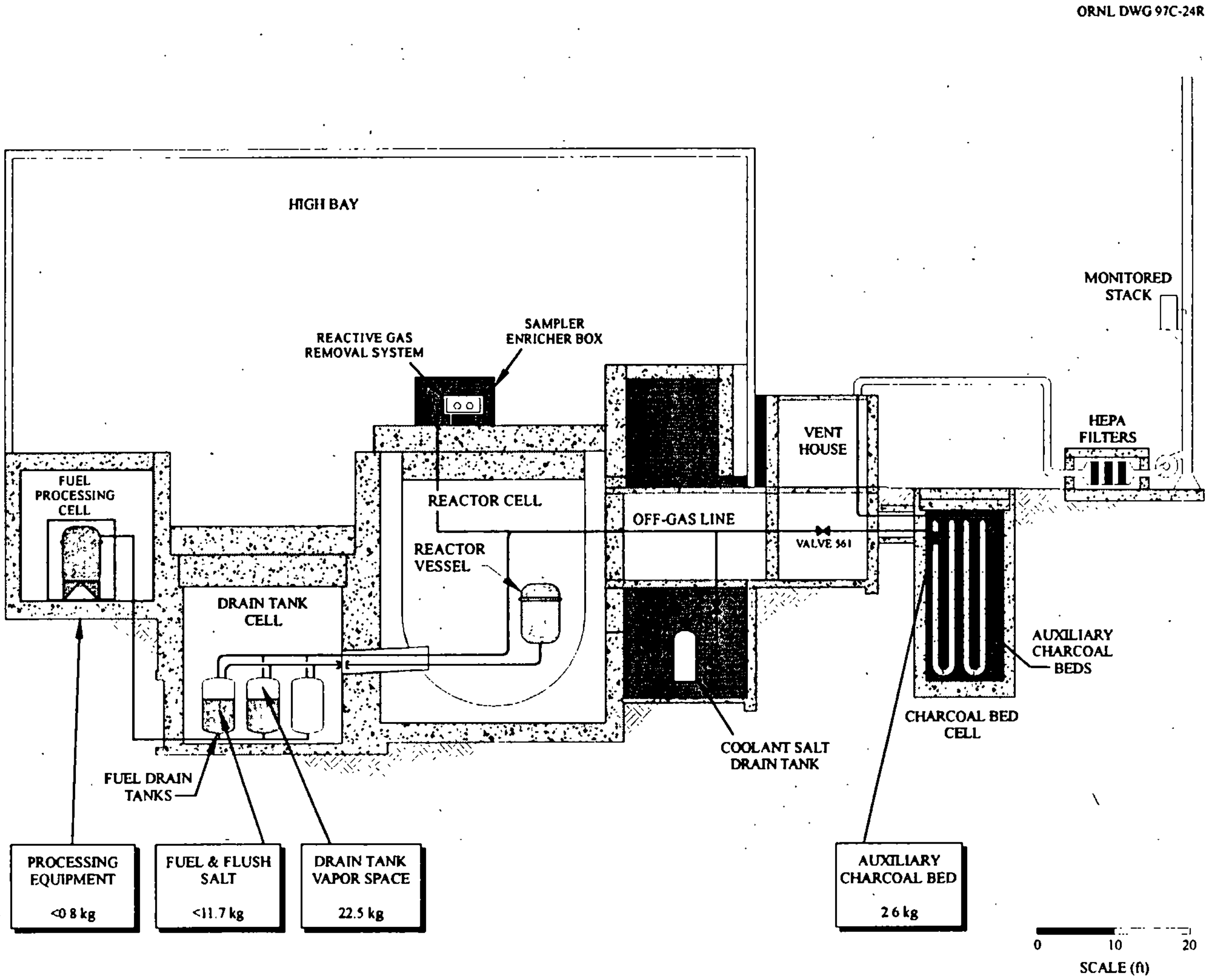

Fig. 3.5.3*a*. As-found uranium inventories in the MSRE facility.

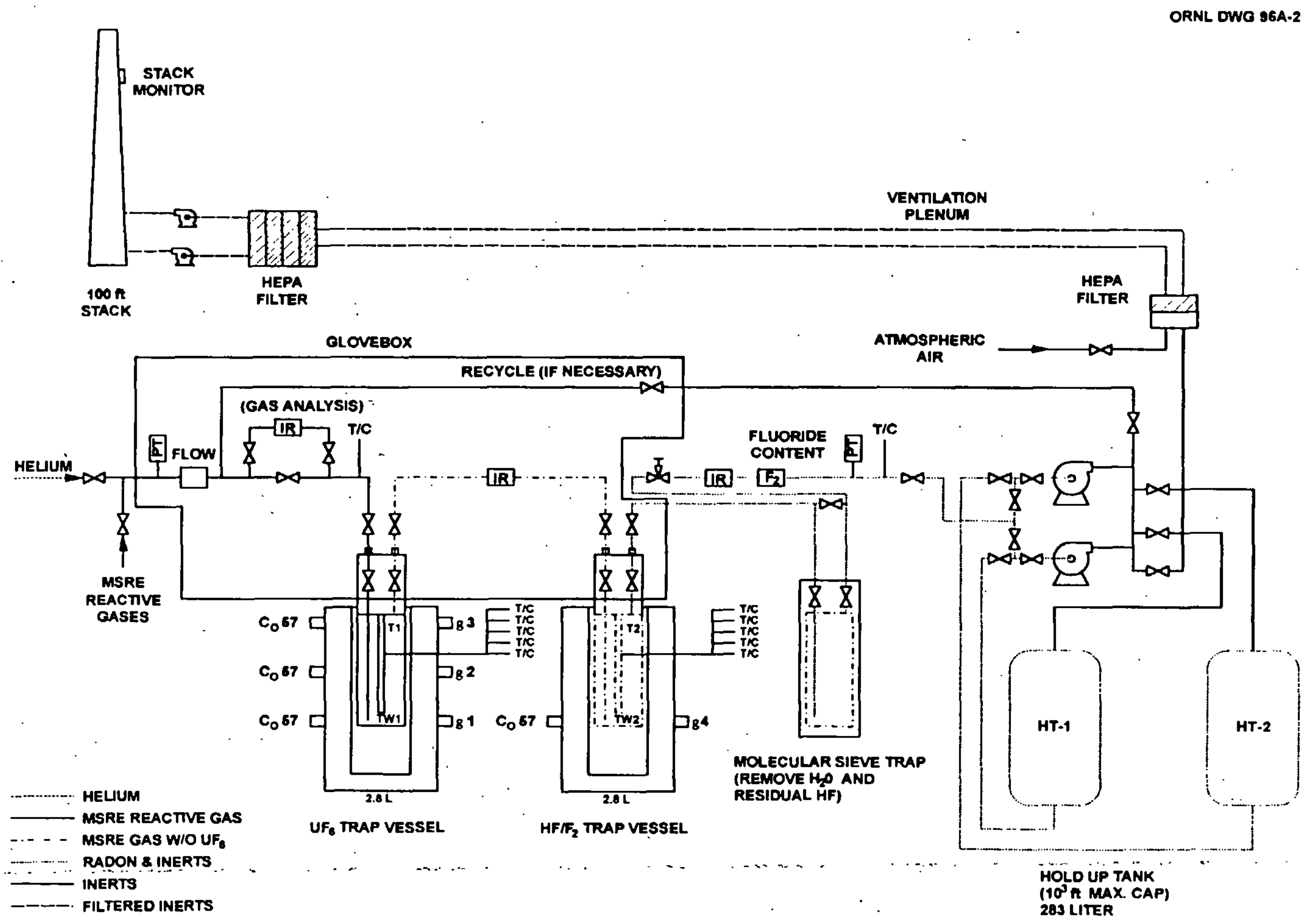

Fig. 3.5.3*b*. Flowsheet of the MSRE reactive gas removal process.

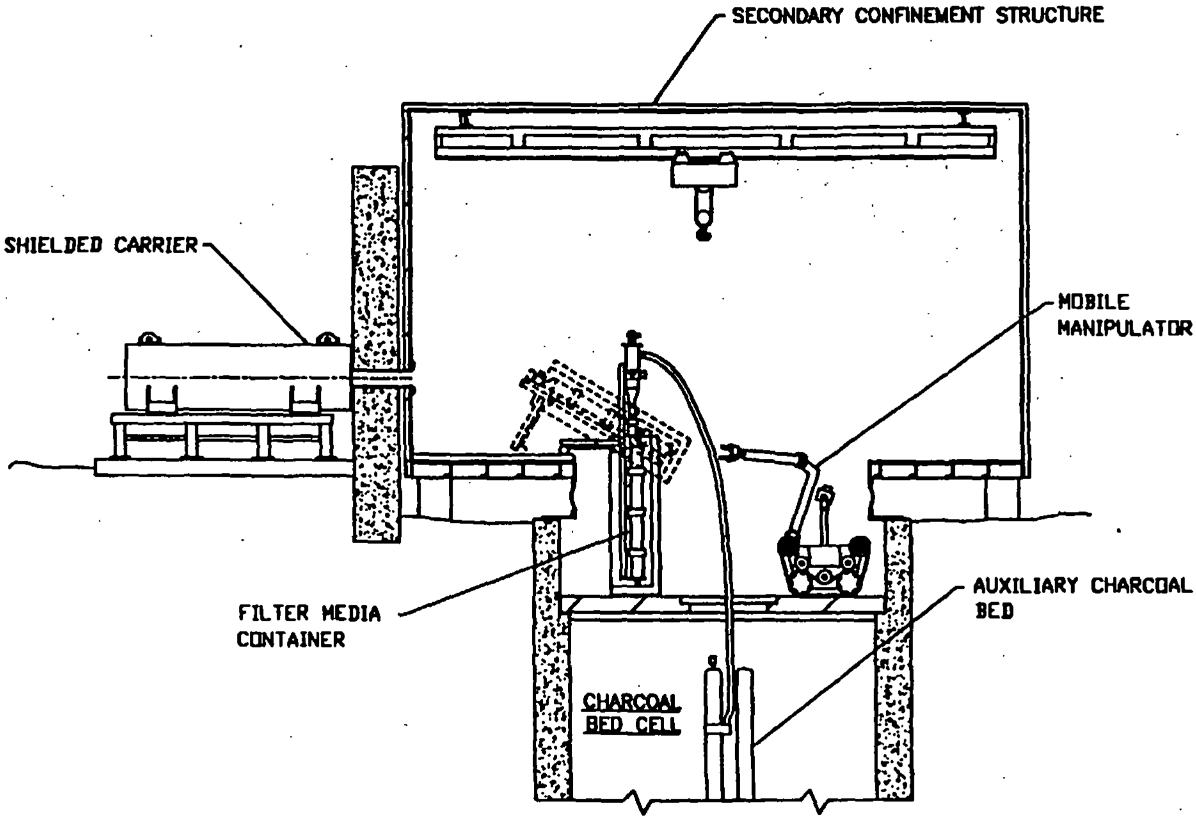

Fig. 3.5.3*c*. Depiction of the auxiliary charcoal bed uranium deposit removal concept.

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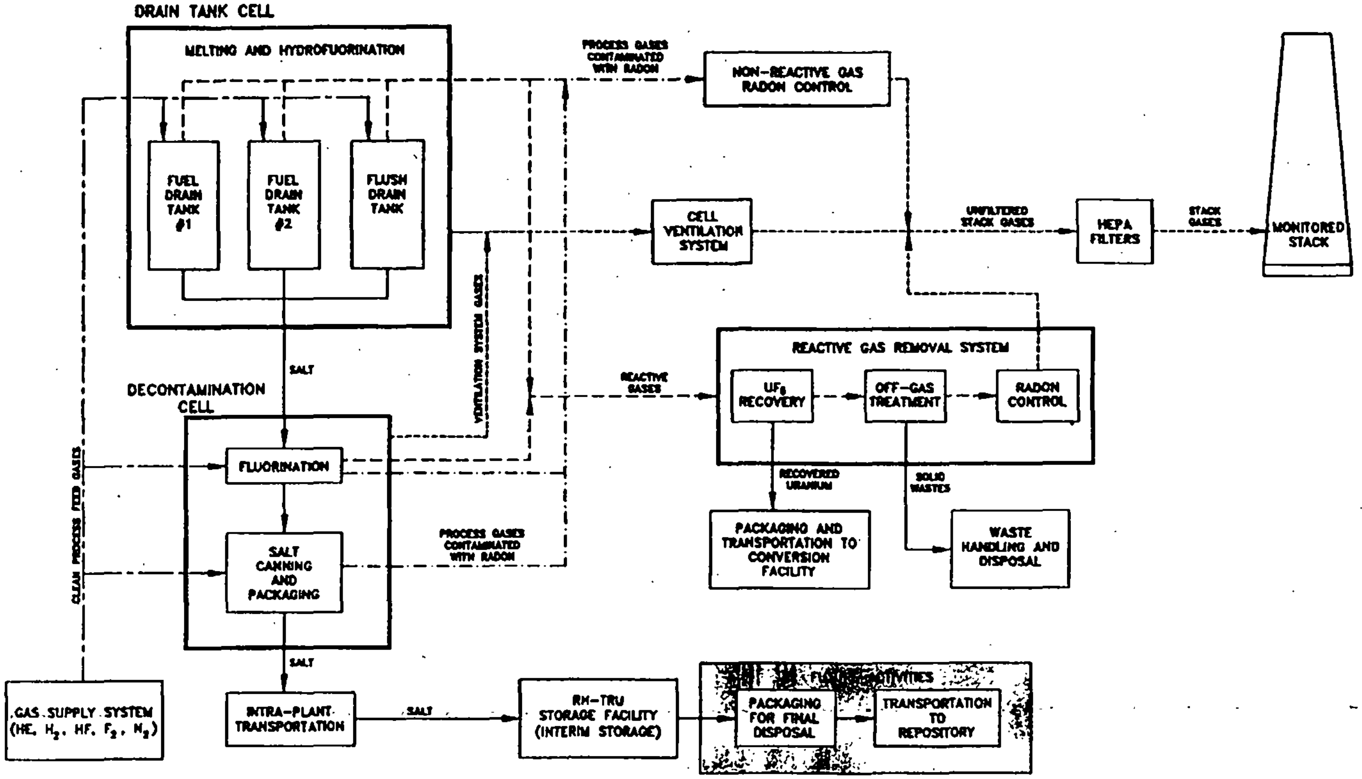

Fig. 3.5.3*d*. Block diagram of fuel salt disposition activities.

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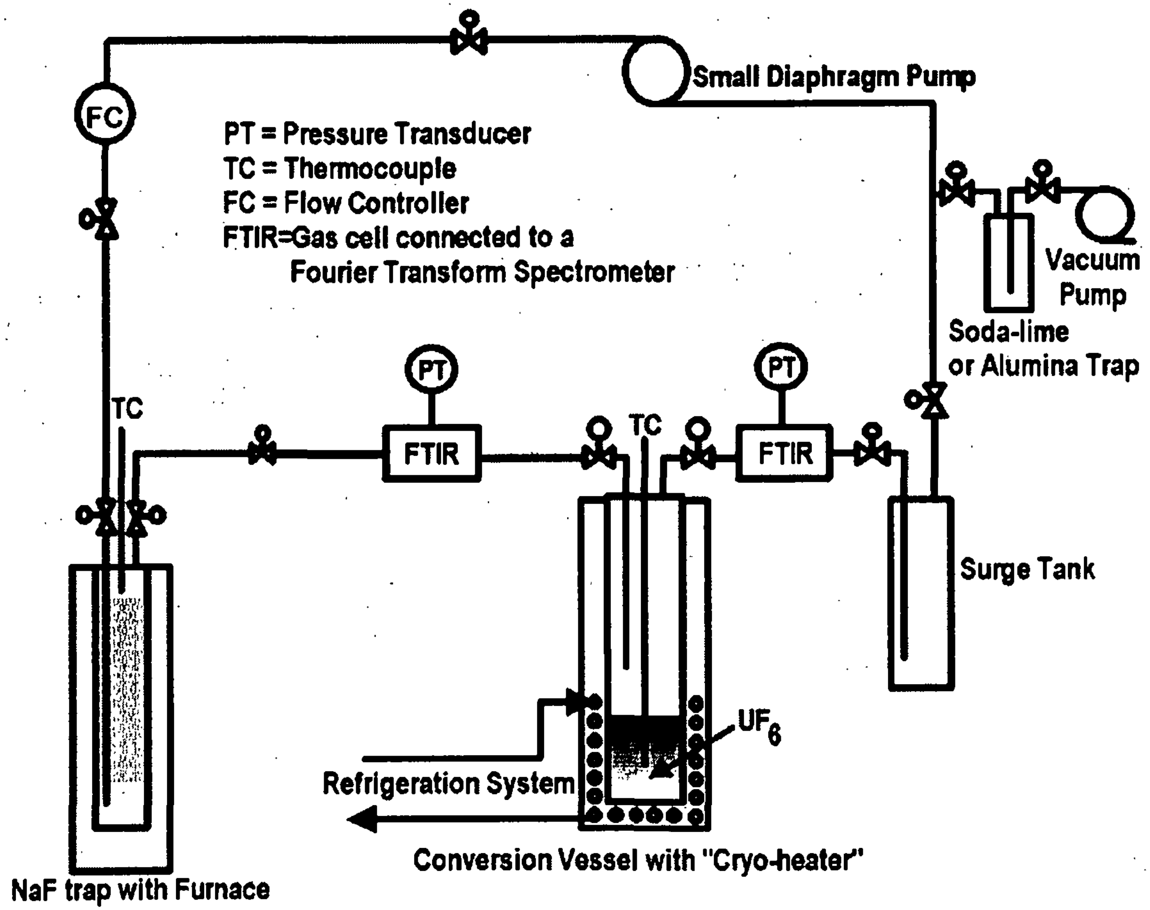

Fig. 3.5.3*e*. Recovery of uranium from MSRE NaF traps.

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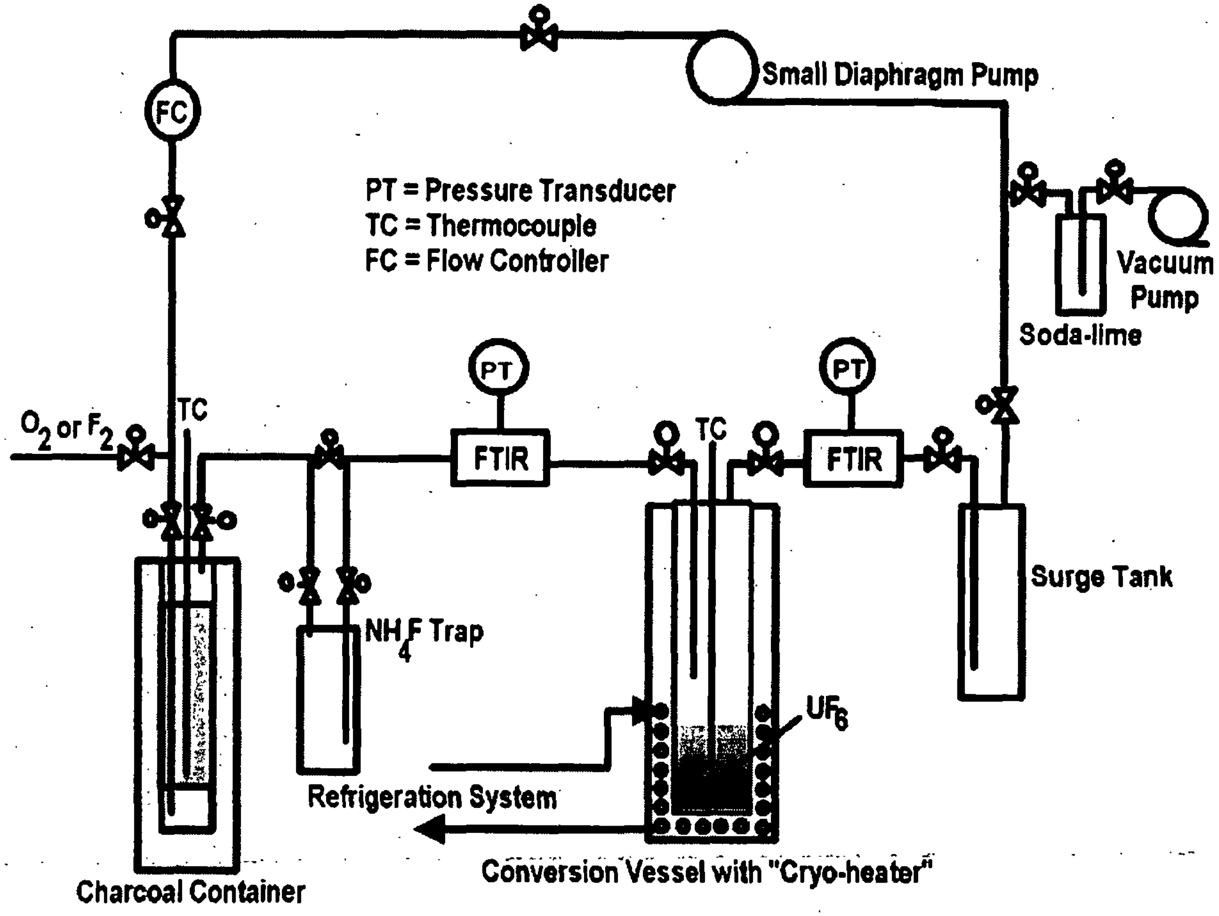

Fig. 3.5.3*f*. Recovery of uranium from MSRE charcoal containers.

ORNL DWG 98-8123

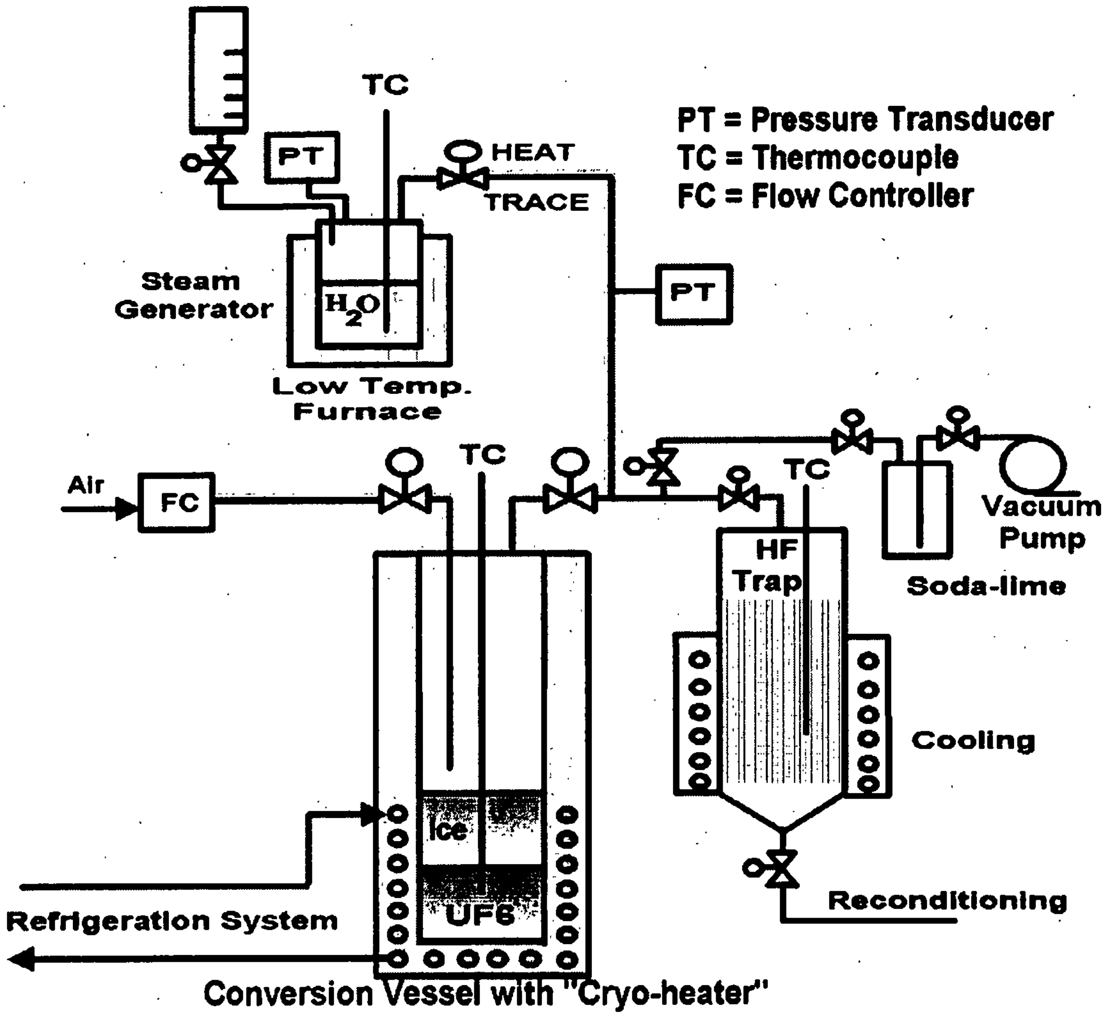

Fig. 3.5.3*g*. Diagram of conversion of UF_6 to oxide.

3.6 URANIUM-233 METAL PREPARATION AND APPLICATION

3.6.1 Process Objective(s)

The preparation of uranium metal is needed for weapons component manufacture and other uses.

3.6.2 Process Description and Basic Flowsheet

Uranium metal is produced using the industrial batch, metallothermic reduction process, where magnesium metal (Mg) is used to reduce uranium tetrafluoride (UF_4) to uranium metal and magnesium fluoride (MgF_2) by-product (Harrington and Ruehle 1959). The reaction is represented by the following equation:

$$UF_4 + 2Mg \rightarrow U + 2MgF_2 \,.$$

A flowsheet of the conversion process, shown as part of the process of conventional uranium refining, is given in Fig. 3.6*a* (Rich et al. June 1988). This is followed by Fig. 3.6*b* (Rich et al. June 1988), which shows a detailed flowsheet of uranium metal production by the reduction of UF_4 with magnesium. A summary description of the metal preparation process is provided in the following sections. The information presented is based on several references (Harrington and Ruehle 1959, Klima July 30, 1962, Rich June 1988, and Wilhelm 1956).

3.6.2.1 UF_4 Reduction to Metal

The conversion of UF_4 to uranium metal is undertaken using a batch operation. The UF_4 is first added to a double-cone mixer, and then Mg particles are added. The amount of magnesium added is approximately 4 wt % more than is theoretically required for the reduction of UF_4. The UF_4 and magnesium is then mixed until they are well blended. The mixed solids are then emptied into a graphite-lined, steel retort vessel. After the retort vessel has been filled, it is transferred to a capping station. At the capping station, a graphite lid is first inserted into the vessel, and then a steel lid is bolted onto the retort. No gaskets are used in order to allow gases to escape the vessel and to not allow pressurization of the vessel.

After the vessel has been capped, it is moved to a furnace, where it is heated from 40 to 540°C for several hours. This heating induces the reduction reaction, which produces an exothermic reaction that heats the retort contents to about 1650°C. As the reaction progresses, molten uranium metal forms and settles to the bottom of the retort to form a uranium metal ingot. The MgF_2 forms as a solid slag at the top of the vessel above the ingot. The total time for the reaction to go to completeness is about 13 h. At this point, the vessel is then cooled.

The retort is first moved from the furnace to an air-cooling chamber. The vessel is allowed to air cool until the surface temperature reaches 540°C. At this point, the vessel is moved into a water bath, where it continues to cool until it reaches room temperature. After the vessel is cooled, it is moved on to the breakout station.

At the breakout station, the two lids are removed, and the retort vessel is inverted and jolted. This action removes both the uranium ingot and the MgF_2 slag from the retort. The retort is then sent to the refurbishment station, where it is cleaned and inspected for use in the next batch. The ingot and slag are sent to the separation step, where they are separated. The ingot is sent to cleanup, and the slag is sent to slag processing (Dubrin et al. May 1997).

3.6.2.2 Slag Processing

The MgF_2 slag material that is recovered from the retort is then processed, and uranium particles are recovered. The MgF_2 slag is first fed into a crusher, which reduces the slag to about 1/4-in.-size pieces of MgF_2 and deforms any uranium metal remaining in the slag into larger sizes. The crushed material is then fed to a vibrating screen, which allows the MgF_2 to pass through but retains any uranium metal pieces. These uranium metal pieces are then collected and held until enough material has been collected. When enough uranium metal has been collected, it is sent to an induction furnace in which the metal is melted into an ingot and then sent to the ingot cleanup area. The MgF_2 that is collected is sent to a roasting furnace in which it is heated to 540°C to oxidize any remaining uranium and excess magnesium. After the material is cooled, it is sent to a hammer and ball mill to produce fine MgF_2 particles, which are then sent to a leaching system. The MgF_2 is leached with nitric acid to reduce the uranium content (predominantly ^{238}U) to less than 90 ppm (<35 pCi/g) so that it may be disposed of in an ordinary landfill (Dubrin et al. May 1997).

3.6.2.3 Ingot Cleanup

The ingots that are received from the separation station and from the slag-processing system are cleaned to remove any slag or other surface impurities. The ingots are first sent to a roasting furnace in which they are heated to about 650°C. This causes the surface of the ingot to oxidize. The ingot is then put in a water quench tank which causes the oxidized surface layer to fall off.

The ingots are then dried in an oven and cleaned up for packaging and shipment. The quench water is filtered to remove the uranium oxide and then recycled back into the quench tank. The oxide is dried and stored for recovery.

3.6.3 Process Performance—Major Results

During the reduction of UF_4 with magnesium, several things must be watched to produce high-purity metal. A high moisture content in the bomb charge can cause side reactions which will lower the yield and quality of the uranium metal produced. High oxygen content in the UF_4 charge in the form of uranyl fluoride (UO_2F_2) will lower the uranium-metal yield and lead to poorer slag separation. For acceptable metal yields, the UF_4 should be around 98% pure or better. Another factor is the packing density of the UF_4. The higher the packing density, the greater the amount of heat generated per unit area of the container. A charge with a higher packing density usually has a better heat conductivity, which, in turn, will lead to better yields. A packing density of at least 3 g/cm^3 for the UF_4 is recommended (Wilhelm 1956).

3.6.4 Application of ^{233}U-Bearing Metal—The Jezabel Critical Assembly

One example of a use of ^{233}U metal was the Jezabel Critical Assembly (JCA), which is described in Klima July 30, 1962. The ^{233}U associated with the JCA, its components, and scrap were used as source of uranium feed material for fuel rods fabricated in ORNL Building 3019 for use at Brookhaven National Laboratory (BNL). Six small discs, machine chips, and JCA fabrication residues were repackaged at Los Alamos National Laboratory (LANL) into aluminum cans furnished by ORNL. This repackaging was done in order to eliminate scraps of cloth, paper, wax, and metal other than uranium or aluminum. ORNL furnished aluminum wool, which was stuffed into the cans at LANL to prevent the rattling of the ^{233}U metal pieces during shipment. After arrival at ORNL, the recanned metallic pieces were stored until transfer to Building 3019 for charging into a dissolver and subsequent fabrication into fuel rods for use at BNL.

3.6.5 References for Sect. 3.6

A list of references documenting information on uranium metal preparation is provided below. Additional information on this topic is provided in the supplemental resources indicated.

3.6.5.1 References Cited

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ORNL DWG 98-8115

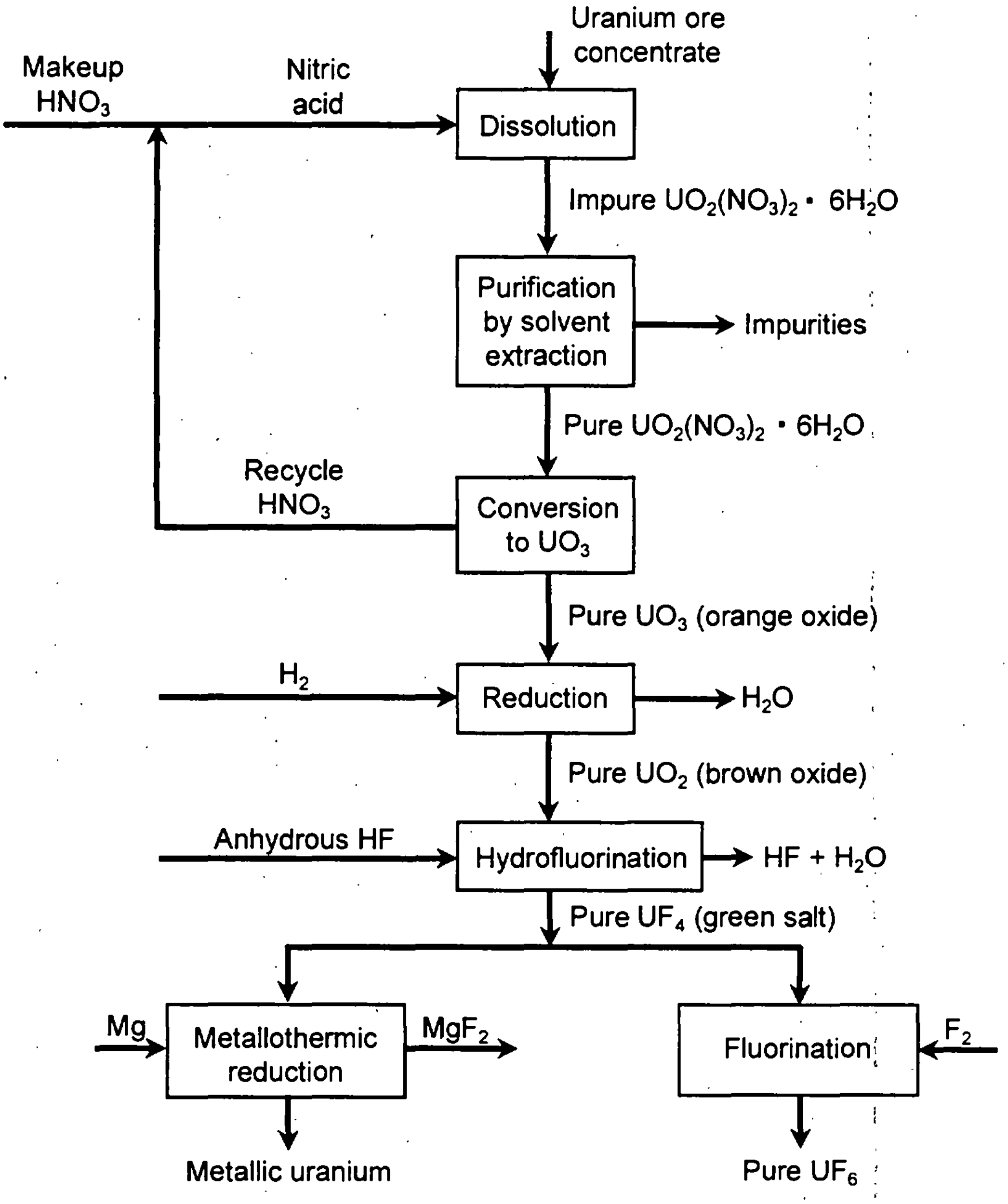

Fig. 3.6*a*. Steps in conventional uranium refining processes. *Adapted from Rich et al. June 1988.*

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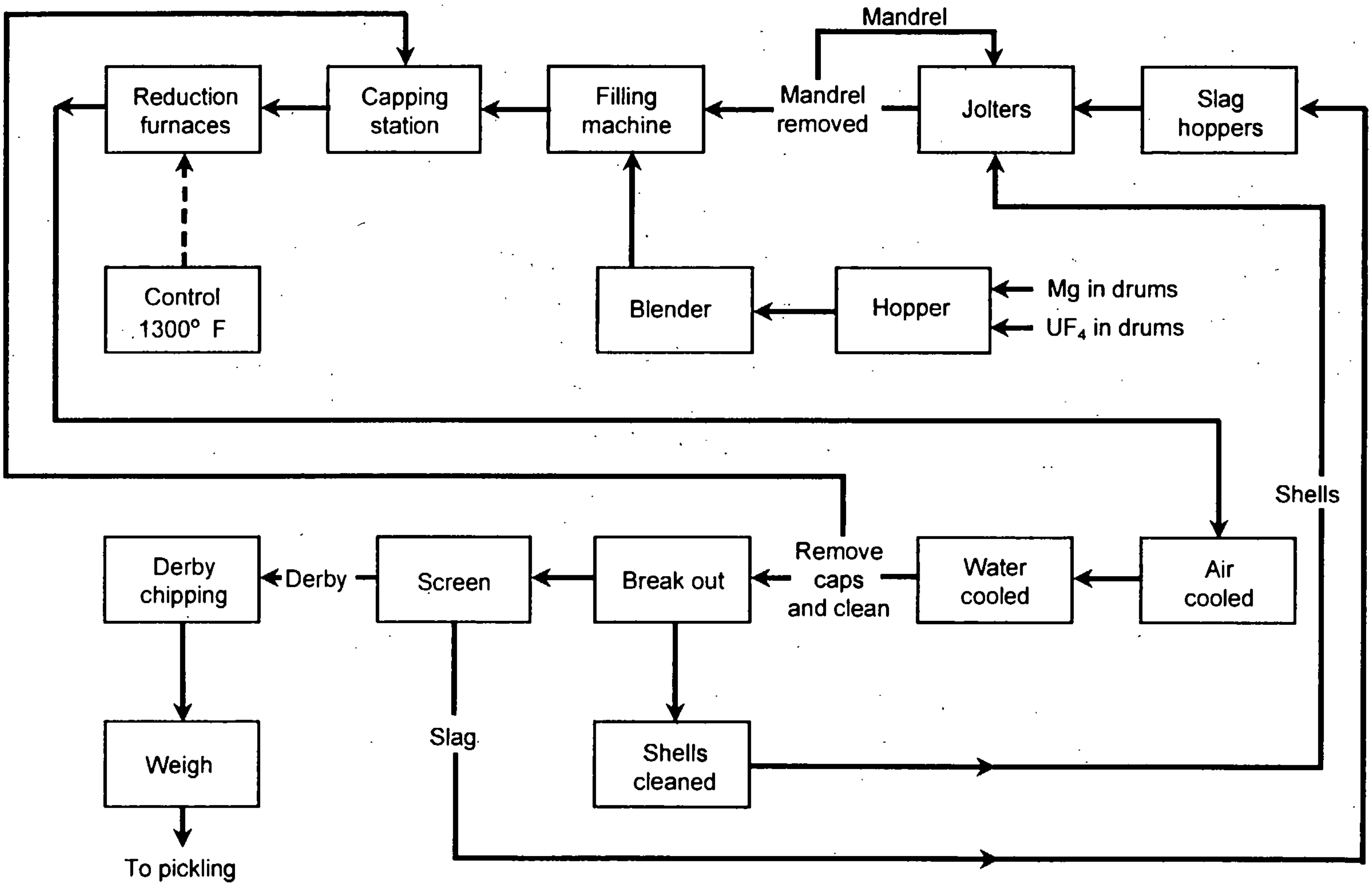

Fig. 3.6*b*. Flowsheet for the production of uranium metal by the reduction of UF_4 with magnesium. *Adapted from Rich et al. June 1988.*

3.7 FABRICATION OF ^{233}U-Th FUEL

Historically, two major programs were involved with the fabrication of ^{233}U-bearing fuels for nuclear reactors: the ORNL Kilorod Facility and the fabrication of thoria-urania (ThO_2-UO_2) fuel for the Shippingport LWBR Program. The fuel fabrication activities associated with each of these major programs are described below followed by discussions of the Babcock and Wilcox (B&W) experience with direct fabrication of ^{233}U fuel elements, the fabrication of fuel elements for the Idaho ANL–West (ANL–W) Zero-Power Physics Reactor (ZPPR), and the fabrication of other ^{233}U fuels.

3.7.1 ORNL Kilorod Facility

The Kilorod Facility was designed, constructed, and operated during 1960–1964 as a pilot facility for demonstrating ^{233}U-Th fuel fabrication. The facility was located in ORNL Building 3019, where a single cell (No. 4) was renovated to receive the equipment for this pilot-plant program. Because of the energetic gamma radioactivity resulting from the decay of the daughter products of ^{232}U normally present in ^{233}U, an economical ^{233}U-Th fuel cycle requires chemical and mechanical processes easily adaptable to remote, fuel-handling procedures. The Kilorod pilot-plant demonstration showed the feasibility for the remote fabrication of ^{233}U-bearing fuel. The Kilorod Facility provided a complete system for making ^{233}U fuel elements by coupling the sol-gel process with the vibratory-compaction loading of fuel tubes (Lotts et al. December 1962 and CTD November 1964).

3.7.1.1 Process Objectives

The specific objectives of the Kilorod Facility demonstration program (Brooksbank, Nichols, and Lotts February 1968) were to:

1. Prepare about 1000 Zircaloy-clad rods containing 3 wt % $^{233}UO_2$–97 wt % ThO_2 in order to fulfill a request for ^{233}U fuel rods needed in criticality experiments at Brookhaven National Laboratory (BNL).
2. Determine the radiation levels and personnel exposures encountered in the fabrication of ^{233}U-bearing fuels.
3. Provide base-line engineering information for future ^{233}U fuel fabrication plants.

3.7.1.2 Process Description and Basic Flowsheet

A summary flowsheet for the Kilorod Facility, which is provided in Fig. 3.7.1*a*, indicates the involvement of three major operations:

1. preparation of feed materials—involving hydrothermal denitration and SX,
2. sol-gel process—involving preparation of the sintered solids, and
3. fuel-rod fabrication—involving powder preparation as well as rod fabrication.

Preparation of the feed materials included both the purification of ^{233}U and the preparation of ThO_2. Uranium-233 was purified by using a one-cycle SX process to remove the daughter products of ^{232}U from ^{233}U in a $^{233}UO_2(NO_3)_2$ solution. Thoria was prepared by denitration of thorium nitrate crystals under a superheated steam atmosphere at 450 to 500°C. The SX process used to purify the ^{233}U demonstrated the use of a new extractant, 2.5 wt % di-sec-butylphenylphosphonate in diethylbenzene.

In the sol-gel process, $^{233}UO_2(NO_3)_2$ and ThO_2 feed stocks were blended at 80°C to form a stable sol (3 wt % $^{233}UO_2$–97 wt % ThO_2). A flowsheet (Haws et al. August 1965) is provided in Fig. 3.7.1*b*. In the Kilorod Facility, the sol was dried to a gel at 80°C and afterward calcined and reduced in an Ar-4% H_2 atmosphere at 1150°C to produce a sintered, fragmented mixed $^{233}UO_2$-ThO_2 product.

Fuel rods were fabricated by grinding and sizing the $^{233}UO_2$-ThO_2 fragments and loading the oxide powder into Zircaloy-2 fuel tubes by vibratory compaction. In the sizing operation, the solids were screened through a 6-mesh screen onto a 16-mesh screen. The remainder of the solids were ball-milled to a powder of "smeared" size distribution. The powders were then blended in proper proportions and loaded into Zircaloy tubes by vibratory compaction. Following compaction, the end of each rod was closed by welding and inspected for leak-tightness and uniformity of packing. Finally each completed fuel rod was decontaminated. A flowsheet of the major steps taken in the fuel rod fabrication process is shown in Fig. 3.7.1*c* (Sease, Lotts, and Davis April 1964).

Figure 3.7.1*d* gives a cross-section overview of both of the Kilorod sol-gel (solids-preparation) and rod fabrication areas (Brooksbank, Nichols, and Lotts February 1968).

3.7.1.3 Process Performance—Major Results

The Kilorod process produced a total of 1100 fuel rods. Of this total, 900 rods each contained 890 g of mixed oxide (3 wt % $^{233}UO_2$–97 wt % ThO_2), and 200 shorter rods each contained 310 g of the same mixed oxide. Most of the rods were needed for criticality experiments at BNL. The basic design features of each BNL fuel rod required in these experiments are shown in Fig. 3.7.1*e*. These rods had a Zircaloy-2 clad and measured 0.5 in. diam by 46 in. in length.

In addition to the production of over 1000 ^{233}U-bearing fuel rods, the Kilorod pilot-plant demonstration also provided encouraging results regarding worker exposure in the fabrication of ^{233}U fuels. Data were also collected on parameters affecting radiation dose rates. This enabled estimations to be made of the allowable ^{232}U content in similar ^{233}U fuel fabrication lines. From this information, a model was developed to provide a basis for extrapolating personnel dose rates to fuel fabrication lines having a nominal capacity of 10 kg of product oxide ($^{233}UO_2$–ThO_2) per day. The Kilorod demonstration showed that this pilot ^{233}U fabrication process could be readily scaled to larger operations. This result provided a basis for estimating the design parameters of conceptual ^{233}U-Th fuel fabricating plants having capacities ranging from 60 to 3700 kg of heavy metal (U and Th) per day (CTD November 1964).

3.7.1.4 References for Section 3.7.1

A list of cited references documenting the ORNL Kilorod Facility pilot-plant demonstration is provided below. This is followed by a list of sources providing additional information.

3.7.1.4.1 References Cited

Brooksbank, Sr., R. E., J. P. Nichols, and A. L. Lotts. February 1968. "The Impact of Kilorod Facility Operational Experience on the Design of Fabrication Plants for ^{233}U–Th Fuels," pp. 321–40 in *Proceedings of Second International Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee, May 3–6, 1966*, U.S. Atomic Energy Commission, Division of Technical Information, Oak Ridge, Tenn.

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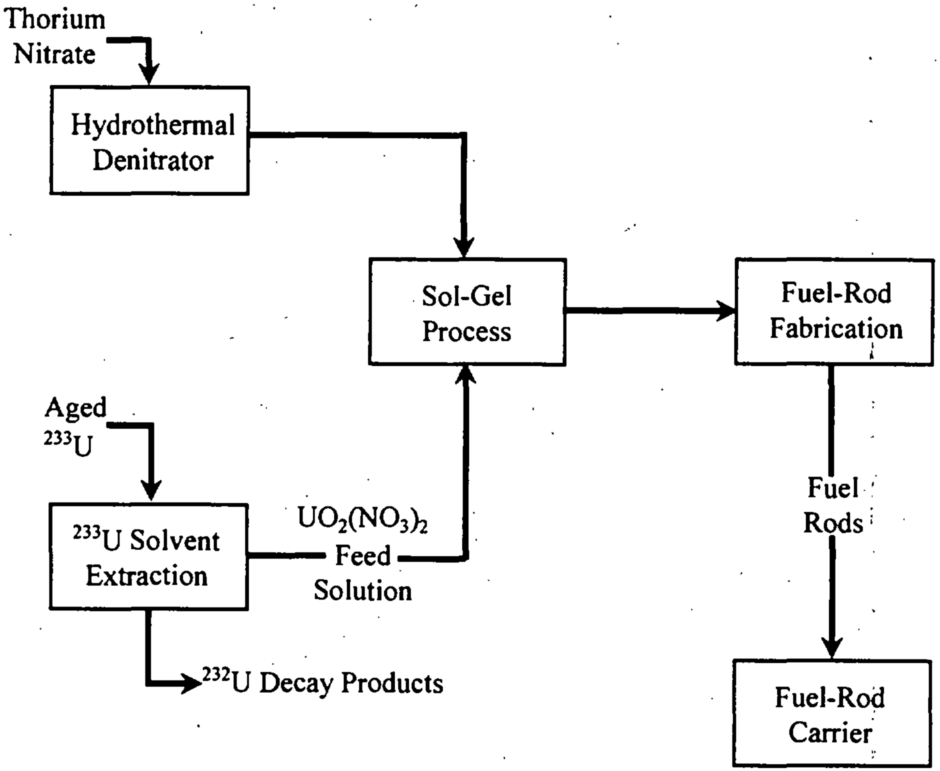

Fig. 3.7.1*a*. Summary flowsheet for ORNL Kilorod facility.

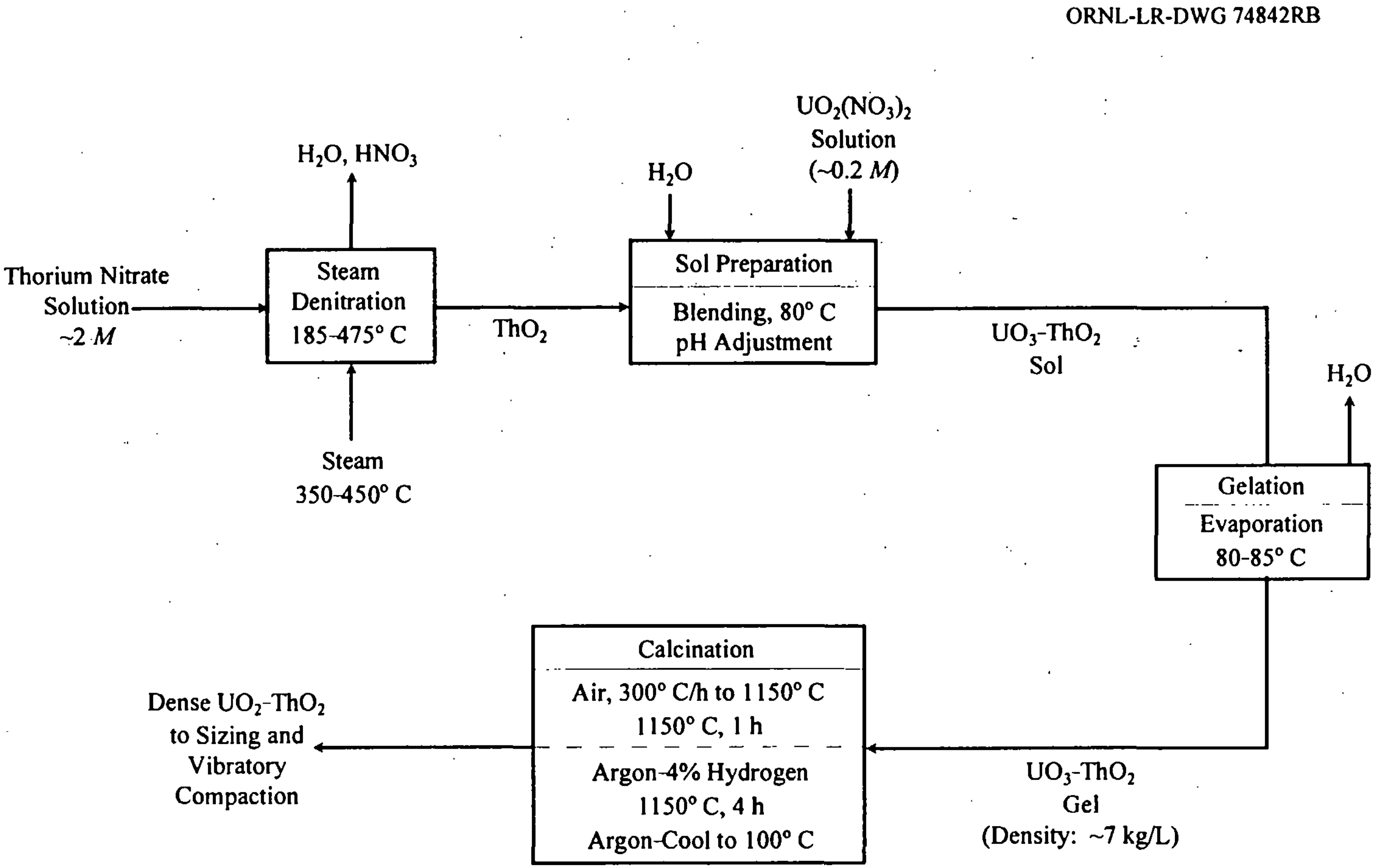

Fig. 3.7.1*b*. Flowsheet for the sol-gel process.

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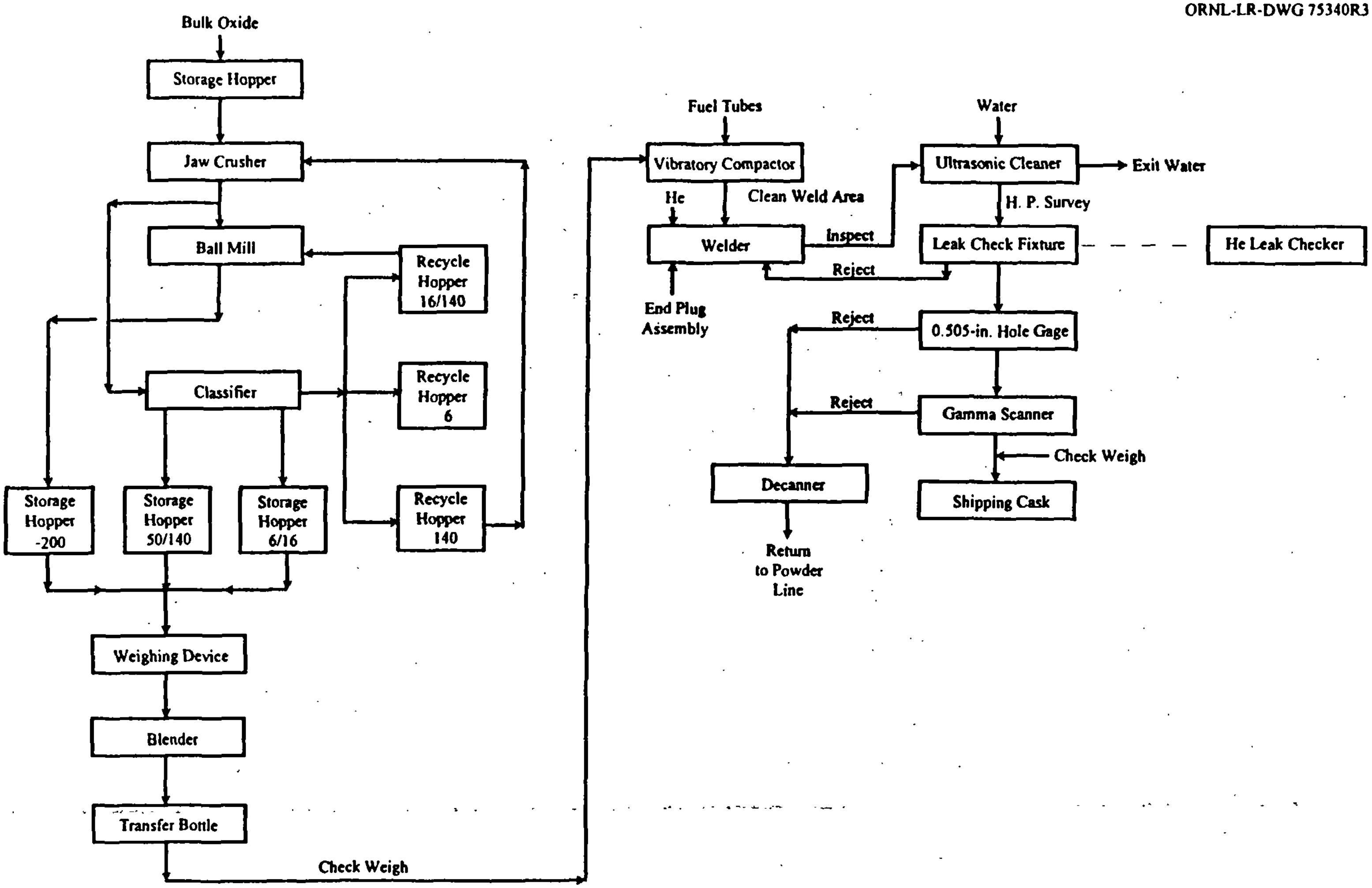

Fig. 3.7.1*c*. Flowsheet for fuel-rod fabrication process.

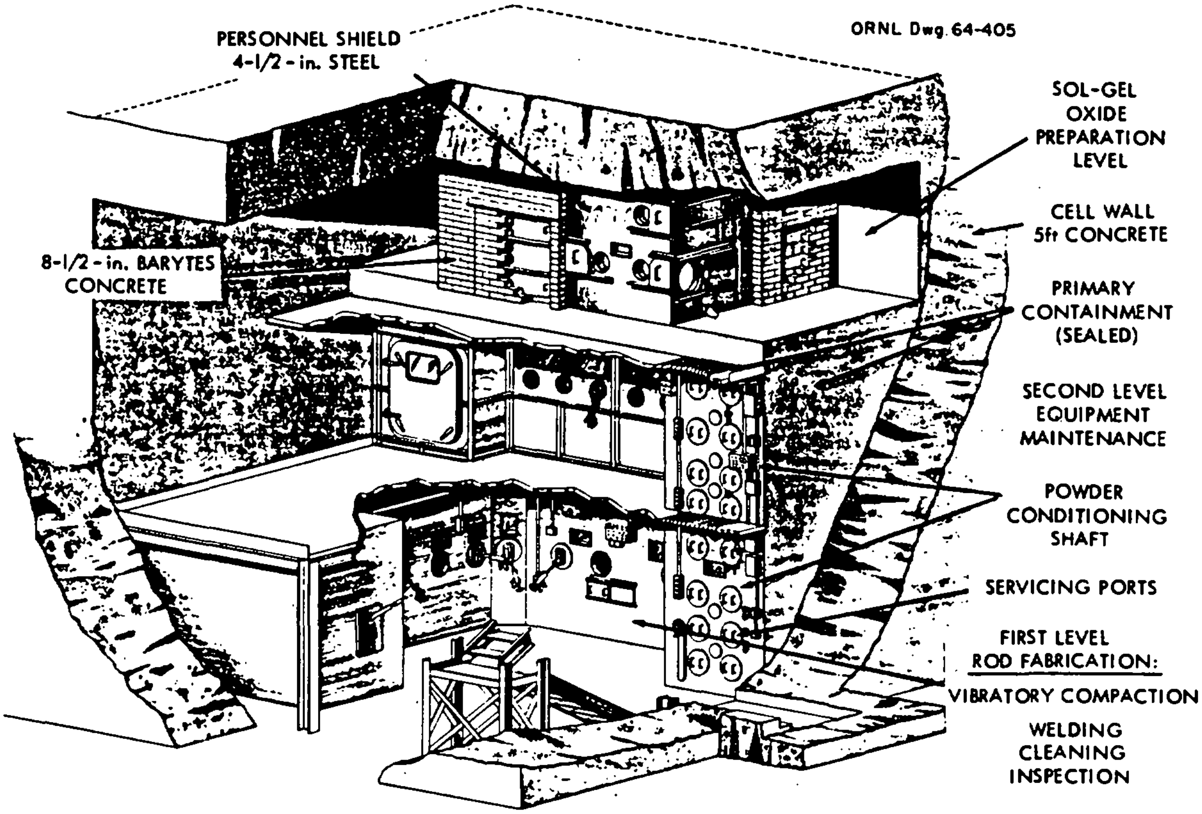

Fig. 3.7.1*d*. Kilorod solids-preparation and rod-fabrication facility. *(The process flow began at the top left with sol blending, flowed to the right where the solids were fired, passed down the vertical shaft as the powder was prepared, and finally flowed across the bottom as the rods were loaded and tested.)*

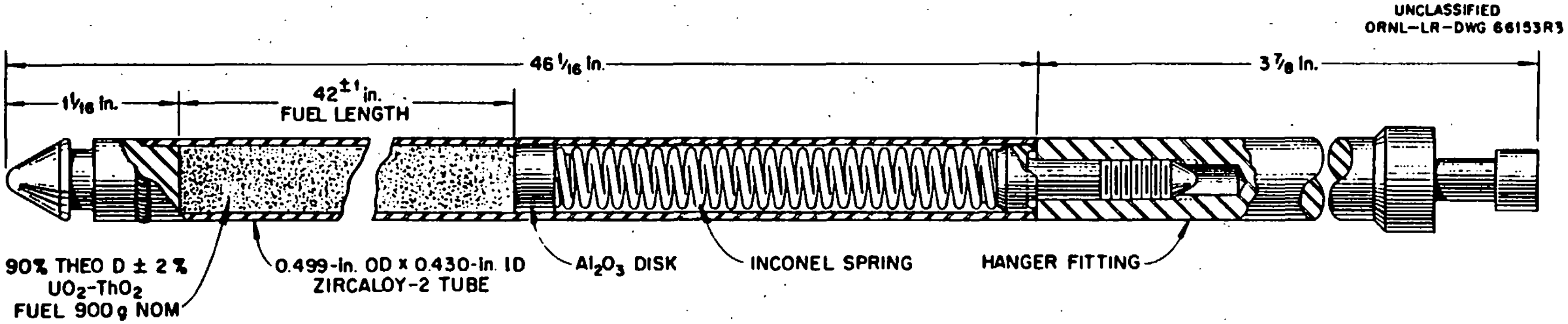

Fig. 3.7.1*e*. Design features of the BNL fuel rod.

3.7.2 Light-Water Breeder Reactor Fuel Fabrication

3.7.2.1 Process Objectives and LWBR History

During 1975–1981, ^{233}U-bearing fuel was fabricated at BAPL for the core of the Shippingport reactor, which was modified from PWR design to that of an LWBR in order to demonstrate and verify nuclear fuel breeding capability.

The fuel pellets of the LWBR core had a right-circular-cylinder shape and were comprised of thoria (ThO_2), or thoria with a low content (1–6 wt %) of uranium dioxide ($^{233}UO_2$), or urania. The ceramic thoria–urania (ThO_2–$^{233}UO_2$), or binary fuels were similar to UO_2, but they had higher melting temperatures, more creep resistance at higher temperature, better corrosion stability, and released less fission product gases (Atherton et al. October 1987).

Fabrication of the LWBR fuel pellets was based on sintering, which is a single-fire process that offered the advantages of less radiation exposure to personnel and the need for less processing equipment.

Figures 3.7.2*a* through 3.7.2*e* give an overview of the basic design of the LWBR core, fuel rods and assemblies, and fuel pellets. The LWBR core in the Shippingport reactor was a uniquely designed seed-blanket type, as shown in Fig. 3.7.2*a* (Connors et al. January 1979). This core operated in the Shippingport Power Station in Pennsylvania from 1977 to 1982. As shown in Fig. 3.2.7*b* (DiGuiseppe and Johnson July 1982), the LWBR core consisted of 12 "seed" fuel assemblies—hexagonal modules arranged in a symmetrical array, surrounded by a reflector-blanket region. Each module contained an axially movable "seed" region [which had a multiplication factor (k) greater than unity], and a stationary, annular hexagonal blanket (which had $k < 1$). Each of these regions, in turn, consisted of arrays of tightly packed, but not touching, fuel rods, which contained pellets of ThO_2 (thoria) and $^{233}UO_2$ (urania), the latter in varying amounts from 0 to 6 wt % in the seed and from 0 to 3% in the blanket region (Lamarsh 1975). Figure 3.7.2*c* (Bolton, Christensen, and Hallinan March 1989) gives a cutaway view of an LWBR seed module, and a similar view for an LWBR blanket module is provided in Fig. 3.7.2*d*. The seed-blanket module combination provided a unique binary (thoria and urania) fuel control and distribution scheme, which is described in detail in several sources (Connors et al. January 1979 and Heckler June 1979). The design of typical seed, blanket, and reflector pellets are shown in Fig. 3.7.2*e* (Belle et al. January 1976). More detailed information on the features of the LWBR fuel components just described is provided in the references listed in Sect. 3.7.2.4.

3.7.2.2 Process Description and Basic Flowsheet

Specific activities required for fabricating the Shippingport LWBR fuel pellets, rods, and assemblies are discussed below. In Sect. 3.7.2.2.1 fuel pellet manufacture is discussed, and in Sect. 3.7.2.2.2, the production of the fuel rods and supporting assemblies are discussed.

Major features of the LWBR fuel fabrication facility are described in LWBR Program Summary report (Atherton October 1987). For thoria fuels, the processing of powder into pellets involved dealing with only low level amounts of alpha radiation, which enabled this work to be performed in either hoods or other exhaust-controlled containment areas relatively free from shielding. More stringent requirements needed to be observed for binary fuels, however. Areas of the fabrication facility for producing binary fuels had to be designed and constructed to incorporate the following features:

- precluding inadvertent criticality,
- controlling the escape of contamination,
- providing for material security and control, and
- minimizing radiation exposure of personnel.

A major consideration in the facility design was that the binary fuel contains low levels (<10 ppm) of the beta-gamma-emitting ^{232}U, which requires a shielded facility and procedures to minimize radiation exposure. For this reason, the binary fuel area used a continuous system of shielded glove boxes connected by short tunnels and similar enclosures.

3.7.2.2.1 Fabrication of Fuel Pellets

As described by BAPL (Belle et al. January 1976), the fabrication of high-structural-integrity, high-density thoria and binary fuel pellets was based on a single-fire process (sintering) and included the following 14 major activities shown in the order of their occurrence in the flowcharts of Figs. 3.2.7*f* (thoria fuel pellets) and 3.2.7*g* (binary fuel pellets):

1. Blending,
2. Micronizing,
3. Secondary blending,
4. Agglomeration,
5. Granule drying,
6. Final blending,
7. Lubricant addition,

8. Compaction,
9. Pretreatment,
10. Sintering,
11. Pellet grinding,
12. Cleaning and drying,
13. Inspection and evaluation, and
14. Degassing.

Detailed process parameters of each of these activities are provided in the LWBR pellet manufacture document (Belle et al. January 1976), which was prepared by BAPL. It should be noted that the dashed lines shown in Figs. 3.7.2*f* and 3.7.2*g* refer to process control operations that were added to deal with product variability and material losses in achieving a satisfactory fuel-pellet product. A summary description of the role and function of each of the major fabrication process activities follows. The order followed in this description is the same as the sequence used in the fabrication process.

1. ***Blending***. The fabrication of binary fuel pellets first requires blending the as-received thoria and urania powders to a mixed feed material suitable for further intermixing and processing. The initial (or primary) blending operation serves as an important safety precaution with respect to criticality control because it provides well-dispersed, small-sized UO_2 aggregates before release for further processing. Rigid housekeeping practices and cleanliness for avoiding the presence of foreign materials are essential in the initial blending process.
2. ***Micronizing***. Micronizing, powder comminution, and mixing are performed on the as-received calcined fuel powder to activate the powder to a level suitable for meeting final density specifications and uranium homogeneity. Activation in this context refers to the process of increasing the surface area of the powder by decreasing the particle size by grinding the particles together. The as-received powder is not inherently active because of the relatively high temperatures (980 to 1040°C) used during manufacture of the powder by calcination. Such high temperatures result in increased crystalline size and reduction in surface area. Micronizing of binary powder mixtures is also required to ensure that stringent uranium homogeneity requirements are met. For binary fuels, micronizing provides a highly efficient mixing or homogenizing operation. For the LWBR fuel, powder micronizing was performed in a 4-in. jet mill, which consisted of a circular grinding chamber, a vibratory powder feeder, an inlet and outlet air supply, and a milled powder collection system.

Table 3.7.2*a* lists the typical levels of surface area and particle size that were necessary for the production of high-density, high-integrity thoria and binary fuel pellets for the LWBR.

3. ***Secondary blending***. Secondary blending is performed on co-micronized thoria-urania powder batches, thereby minimizing product variability. This operation mixes powder batches to form an inspection sampling unit for the product final certification. When this operation is complete, samples are obtained from the homogenized powder. Surface area analyses are performed to verify the required activity of the powder. Blanket material blends are composed of a maximum of 12 micronizing batches for a total blend size of 100 kg. Seed material blends are composed of up to 6 micronizing batches for a total blend size of 25 kg. Both sizes are maximum units established from criticality control criteria. Blanket blending is performed in a standard industrial 2-ft^3 twin-shell blender (internally modified for criticality control), and seed blending is performed inside a 0.5-ft^3 twin-shell blender. Secondary blending follows the same levels for cleanliness that are observed in the initial (primary) blending operation.

4. ***Agglomeration***. The agglomeration process transforms the finely divided, micronized powder into a free-flowing compactible press feed, which is spherical in shape. This step resolves two major problems associated with compaction of a finely divided powder, nonuniform filling of the die and the formation of circumferential cracks in the pellets. The spherical agglomerates flow more easily and consistently into the die. Because they have a higher bulk density than micronized powder, less trapped air and associated cracks result during compaction. Agglomerates are formed by the addition of the secondary blender powder to a wax binder in solution with a solvent (oxylene). The binder-solvent solution is introduced as a spray during tumbling of the powder in a twin-shell blender. Agglomerates ranging from 0.004 to 0.25-in. diam are formed. These are subsequently granulated through a standard 25 mesh screen to produce a sphere size ranging from 0.004 to 0.030 in. diam. The output of the agglomeration process has a significant impact on the quality of LWBR fuel. The characteristics of the resultant agglomeration control subsequent processing steps and strongly influence final product characteristics. The following fuel pellet characteristics are influenced by agglomeration: granular segregation, external porosity, internal porosity, density, internal cracks, and circumferential chips (chips out of the pellet sides).

5. ***Granule drying***. Granule drying is performed on the agglomerated product after granulation to volatilize the retained oxylene from the granules in order to provide a dry press feed suitable for compaction. In this process, a batch of the agglomerated-granulated powder is

distributed into a shallow bed on drying trays and dried in a recirculating-air drying oven at a temperature (~40°C), which is sufficiently high to promote effective evaporation of the oxylene solvent. The nominal drying time for each batch is determined from the amount of retained oxylene.

6. ***Final blending***. Following drying, the agglomeration batches are finally blended together for remixing in twin-shell blenders for several minutes. For thoria blends, a 1-ft^3 blender was used. After blending, the binary powder was loaded into 5-in.- diam by 15-in.-long cans in preparation for the next step, lubricant addition. Thoria powder remained in the twin-shell blender, which also served for lubricant addition. At this point, the blended, agglomerated powder is characterized by a sieve analysis and measurement of the bulk density of the granules to control the agglomeration parameters and ensure satisfactory compaction.
7. ***Lubricant addition***. Before compaction, a dry powder lubricant (Sterotex) is added to the agglomerated powder to minimize interparticle and die-wall-to-pellet friction. The lubricant also minimizes pressing loads during pellet compaction and reduces the forces required to eject a pellet from a die cavity, thereby minimizing internal pellet stresses that tend to cause cracks and other associated pellet defects. Lubricant addition for thoria and binary compositions is performed in different types of equipment, which require different mixing parameters. However, both procedures result in comparable degrees of mixing. Addition of the lubricant to the thoria press feed is performed in a 1-ft^3 twin-shell blender following the final blending operation. For binary fuel, addition of the lubricant is performed in 5-in.-diam by 15-in.-long powder-container cans.
8. *Compaction*. The compaction process forms fuel pellets by cold pressing the feed powder. The forces of compaction establish the interparticle contacts in the powder that are necessary for pellet densification and microstructure development in the sintering operation. Compaction parameters determine the density level and particle distribution within the pellet, and these, in turn, control dimensional uniformity and pellet shrinkage during sintering. The compaction process is a very critical operation that requires close control conditions in order to prevent flaws or faults from occurring in the pressed pellet product. Such defects are not correctable in subsequent fabrication processing steps. There are several operations involved with the compaction process. Initially, the granular powder to be compacted is poured into a compacting press feed hopper. Gravity feeds the powder into a shuttle-type feed shoe, which volumetrically fills the die cavity on the forward stroke and then levels the powder charge in

the cavity on the return stroke. The powder is then compacted to a predetermined density in the die between an upper and a lower punch, and the pellet is ejected from the die and pushed away by the feed shoe in the succeeding die-fill motion. The pressed pellet is manually removed from the die table, inspected, and then loaded into a tray container (or "boat") made of Inconel or molybdenum. An Inconel boat is used for binary fuel because it is compatible with the high-temperature CO_2 pretreatment atmosphere (discussed below), while the molybdenum boat is used for thoria fuel to prevent oxidation. Figure 3.7.2*e* shows the typical geometry and finish-ground dimensions of three types of LWBR fuel pellets: seed, blanket, and thoria reflector.

9. ***Pretreatment***. Before compacted "green" (untreated) pellets are introduced into a furnace for densification (sintering), they are exposed to a thermal pretreatment to remove the Sterotex lubricant additives. For such removal to be effective, this process requires the pellets to be subjected to an environment that is controlled in terms of time, temperature, heat-up rate, and atmosphere. Thoria pellet pretreatment is performed in molybdenum boats in a CO_2 atmosphere, using a bell (batch-type) furnace at 400–450°C for about 4 h. Binary thoria-urania pellets are pretreated in a CO_2 atmosphere in a continuous electric furnace.

10. ***Sintering***. The densification or sintering process consists of heating compacted (and pretreated) fuel pellets gradually up to a maximum temperature to obtain a high-density product that meets all finished product microstructural requirements. The product density is typically 97–98% of the theoretical density. For binary fuels, sintering has the added objective of forming a homogeneous solid solution of the mixed and blended thoria and urania powder. Pellet sintering is performed inside a special furnace. For the LWBR fuel, pellets in boat trays were heated at a rate of 100–115°C/h up to a maximum furnace operating temperature of 1790°C. The pellets were sintered for a minimum of 12 h in a wet H_2 atmosphere. Such conditions are controlled by both the temperature profile (over length) of the furnace and by the stroking rate of the pellet boats through the furnace.

11. ***Pellet grinding***. The final geometric shape and size of a sintered fuel pellet are attained by a two-stage, centerless plunge grinding procedure. This operation produces pellets with a configuration which satisfies dimensional design requirements. The pellet-grinding operation is performed on conventional centerless plunge grinders. A specially designed pellet feed system accepts the sintered pellets, pushes each pellet forward along a work blade which supports it, and places it into position to be ground. When in position, the plunge grinder

regulating wheel moves toward the grinding wheel and pushes the pellet against the grinding wheel. The final shape of each pellet is determined by the shape of the grinding wheel and the steps of the regulating wheel. The latter, which control taper and chamfer size, are attained by dressing the wheel with a diamond truing tool, which traces the profile of special truing cams. This process of regulator wheel dressing, repeated when as-ground pellet characteristics begin to drift toward the limits of acceptance because of wheel wear, is a normal characteristic of commercial grinders used in the process—the only exception being that these operations are performed in a large glove box enclosure.

12. *Cleaning and drying*. Following the grinding operation, the fuel pellets are cleaned to remove remaining particulate matter in machine oil from the grinder. To ensure that no unacceptable residues are left, deionized Grade A water is used for a cleaning fluid aided by the use of ultrasonic agitation. The cleaning operation begins with the as-ground pellets being placed in specially designed, perforated, stainless-steel-covered trays. To keep grinding sludge from drying on the pellets, the trays are loaded under water, which provides buoyancy and enables the smaller, less fragile seed pellets to drop into the water-filled trays. The blanket pellets have greater size and mass and require individual handling to minimize chipping. Blanket-sized pellets are individually placed, with tweezers, into a support structure in the trays. Once the pellets are loaded into a tray, the tray is placed into a water-filled can and transported to a glove box for cleaning. Within the glove box, the trays are removed from the cans and placed into a tank of still water for a rinse before being moved to a second water-filled tank, where they are cleaned ultrasonically for several minutes. The remainder of a typical cleaning process includes another ultrasonic cleaning in a third tank followed by a water rinse in a fourth tank. Conventional commercial ultrasonic cleaners are used in this cleaning sequence. Following removal from the fourth tank, the pellets, still contained in the trays, are drained and then placed on small dollies for transport through a drying oven for several hours. During this time, the pellets are subjected to a continuous counter direction heated air flow to ensure the degree of dryness attained. The cleaning and drying processing steps for both thoria and binary fuels are the same and use the same type of ultrasonic cleaner.

13. *Inspection and evaluation*. Fuel pellets are inspected to ensure compliance with technical requirements, which include requirements for granular segregation, grain size, and nonhomogeneity. This step is accomplished by nondestructive visual examination of all pellets

and dimensional, metallographic, and chemical evaluations of sample pellets taken from each blend. The inspection and evaluation process includes the following activities:

a. Visual and dimensional inspection of all finished fuel pellets to ensure that all technical requirements are met.
b. Structural attribute inspection of random samples. This is determined by metallographic evaluation in which samples are sectioned transversely or longitudinally and then polished for evaluation of pore size, pore distribution, granular segregation, internal and corner cracks, foreign inclusions, and color.
c. Composition inspection of random samples. This involves a chemical analysis of random samples of pellets for compliance to the requirements for total and isotopic uranium content, impurities, and oxygen-to-uranium ratios.
d. Random sampling of each blend of fuel.

14. ***Degassing***. Before being loaded into fuel rods (Sect. 3.7.2.2.2), the fuel pellets are subjected to a high-temperature-vacuum degassing operation to remove any adsorbed moisture, other surface contaminants, and any residual gases within the fuel. The residual gases include mainly CO and H_2 with minor amounts of CO_2 and various hydrocarbons, which are formed during the pretreatment and sintering steps as a result of the decomposition of the binder and lubricant additives and subsequent chemical reactions of the decomposition products with the fuel and the pretreatment and sintering gases (CO_2 and H_2). The degassing operation begins with the loading of both thoria and binary pellets that have passed inspection into Inconel boats for a controlled heatup coupled with the removal of air, which results in a 3- to 4-h soak at a temperature of 970–1040°C under a pressure of 10 millitorr or less. These conditions have been found to provide pellets with very low levels of residual gas. Once degassed, pellets are loaded into tubes which are welded closed with glove box air exposure limited to a maximum of 32 h. Finally, an analysis for residual gases left after degassing is performed on samples from each fuel blend to verify that the degassing operation has indeed removed most of the gases and to certify that the degassed pellets meet the specification limits.

3.7.2.2.2 Fabrication of Fuel Rods and Assemblies

As described in the *Light-Water Breeder Reactor Program Summary Report* (Atherton October 1987), 17,290 fuel rods were assembled into the LWBR core. Each fuel rod was composed of a Zircaloy-4 seamless tube filled with oxide fuel and thoria pellets. All fuel rods were approximately 10 ft long and varied in diameter according to fuel type. Nominal diameters were 0.306 in. for seed rods, 0.571 in. for standard blanket rods, 0.526 in. for power-flattening blanket rods, and 0.832 in. for reflector rods. At the top of each rod, a plenum region provided a void volume to accommodate released fission gas and a helical coiled spring to exert pressure on the pellets to keep the stack together. As an example, the general dimensions and components of the seed rods are shown in Fig. 3.7.2*h* (Bickel et al. March 1986). The dimension specifications of all various LWBR fuel elements (pellets and rods) are given in Table 3.7.2*b* (Campbell and Giovengo October 1987).

The fabrication procedure for the LWBR fuel rods (Atherton October 1987) consisted of six major steps performed sequentially:

1. Sizing and cleaning the finished metallic components provided by suppliers. [These components consisted of tubes, end caps, and plenum hardware (spring, plenum sleeve, and plenum pin)].
2. Welding an end enclosure to the bottom end of each cladding tube to form a tube assembly.
3. Loading the fuel pellets and plenum hardware into each tube assembly to form a fuel rod assembly.
4. Welding the top end closure to seal the fuel and plenum hardware in each cladding tube to form a fuel rod. (The welding is done in a helium atmosphere to provide an inert environment inside the fuel rod.)
5. Pickling each rod to final diameter and applying a corrosion film to all surfaces.
6. Inspecting each finished fuel rod for external and internal attributes, including the integrity and proper placement of the fuel pellets.

The welding performed in Step 2 (above) is a critical procedure in processing the fuel-rod tube assemblies. For each tube assembly, gas tungsten arc welding was used to join a prepared bottom-end closure to a cladding tube. Each weld was machined and polished flush with the tube surface, and then inspected for internal defects by both radiographic and ultrasonic techniques. A pressurized helium leak-check of the welds was performed, and this was followed by measurement and visual inspection of the internal tube length before any fuel pellets were inserted.

In Step 3, before the loading of the fuel pellets, the welded tube assembly, the end-closure assembly, and plenum spring were vacuum-dried to remove surface moisture. In a glove box environment, the vacuum-degassed and inspected pellets were assembled into the required stack length. After stacking, a tube assembly end was inserted into the glove box and the fuel pellets were loaded into the tube. The loaded assemblies and their hardware were stored under vacuum in the welding equipment area until a sufficient weld lot was accumulated. The top-end-closure welding of Step 4 was performed using equipment and procedures similar to those described above for bottom-end welding. After welding, the end closures were machined and inspected ultrasonically for internal defects. To remove surface contamination, acceptable welds were rinsed in a cold nitric acid solution and transferred to the rod-processing area. Rejected welds were rewelded, and the machining and evaluation process was repeated.

Following Step 4, the rods were radiographed in motion to confirm pellet loading. The top-end closure was radiographically evaluated for weld integrity and inspected for dimensional requirements by the same procedures performed on the bottom end. The surfaces of acceptable rods were vapor-blasted to prepare for pickling to final size and corrosion testing. Remaining operations associated with Steps 5 and 6 consisted of inspections to evaluate the rod for all required attributes before final release. The corrosion film evaluation was performed after corrosion testing, the final visual inspection was performed as close to the end of the processing as possible, and the in-motion radiography for internal evaluation was performed last.

Approved and released rods were cleaned, coated with Neolube (an assembly lubricant), packaged, and then shipped to the module assembly area (Atherton October 1987).

Details of the module assembly activities, in particular, the fabrication of the fuel rod support grids for the Shippingport LWBR, have been described in detail by BAPL in various reports (notably, Bickel et al. March 1986 and Atherton October 1987).

3.7.2.3 Process Performance—Major Results

The BAPL fuel manufacturing facility fabricated about 24,000 fuel rods during the period that the Shippingport LWBR core operated (1977–1982).

In addition to providing the necessary fabrication capability, the BAPL facility for manufacturing the LWBR binary fuel incorporated features that precluded inadvertent nuclear criticality, controlled the escape of radioactive contamination, provided for nuclear material security, and minimized personnel radiation exposure. A major basis for the facility design was that the fabricated binary fuel would contain concentrations of ^{232}U <10 ppm. This resulted in a set of procedures to minimize radiation exposure and a facility which employed a system of shielded glove boxes connected by short tunnels and similar enclosures.

Not all LWBR fuel components required shielding in the BAPL fabrication facility. Since the processing of thoria powder involved only low levels of alpha radiation, the processing of thoria powder into thoria pellets was performed in hoods and exhaust-controlled containment areas relatively free from shielding.

3.7.2.4 References for Sect. 3.7.2

A list of cited references documenting the BAPL fuel fabrication for the Shippingport LWBR is provided below. This is followed by a list of sources providing additional information.

3.7.2.4.1 References Cited

Atherton, R. October 1987. *Water-Cooled Breeder Program Summary Report (LWBR Development Program)*, WAPD-TM-1600, Bettis Atomic Power Laboratory, West Mifflin, Pa.

Belle, J. et al. January 1976. *ThO_2 and ThO_2–$^{233}UO_2$ High Density Fuel Pellet Manufacture for the Light Water Breeder Reactor*, WAPD-TM-1244(L), Bettis Atomic Power Laboratory, West Mifflin, Pa.

Bickel, W. L. et al. March 1986. *The Fabrication and Loading of Fuel Rods for the Light-Water-Breeder Reactor*, WAPD-TM-1278, Bettis Atomic Power Laboratory, West Mifflin, Pa.

Bolton, S. R., A. B. Christensen, and E. J. Hallinan. March 1989. *Final Safety Analysis Report: Storage of Unirradiated and Irradiated Light-Water Breeder Reactor Fuel in Underground Dry Wells at ICPP*, INEL-WIN-107-4.7A, Rev. 1, Idaho Falls, Idaho.

Campbell, W. R. and J. F. Giovengo. October 1987. *Light-Water Breeder Reactor Fuel Rod Design and Performance Characteristics (LWBR Development Program)*, WAPD-TM-1387, Bettis Atomic Power Laboratory, West Mifflin, Pa.

Connors, D. R. et al., eds. January 1979. *Design of the Shippingport Light-Water Breeder Reactor (LWBR Development Program)*, WAPD-TM-1208, Bettis Atomic Power Laboratory, West Mifflin, Pa.

DiGuiseppe, C. P. and E. G. Johnson. July 1982. *Review of Physics Critical Experiments Using the Thoria–Fuel System (AWBA Development Program)*, WAPD-TM-1513 (Revised), Bettis Atomic Power Laboratory, West Mifflin, Pa.

Hecker, H. C. June 1979. *Summary of the Nuclear Design and Performance of the Light Water Breeder Reactor (LWBR) (LWBR Development Program)*, WAPD-TM-1326, Bettis Atomic Power Laboratory, West Mifflin, Pa.

Lamarsh, J. R. 1975. *Introduction to Nuclear Engineering*, Addison-Wesley Publishing Co., Reading, Mass., pp. 148–51.

3.7.2.4.2 Supplemental Resources

Schick, W. C., Jr. et al. September 1987. *Proof of Breeding in the Light-Water Breeder Reactor (LWBR Development Program)*, WAPD-TM-1612, Bettis Atomic Power Laboratory, West Mifflin, Pa.

Schultz, B. G., ed. May 1979. *Radiological Control Aspects of the Fabrication of the Light-Water Breeder Reactor Core (LWBR Development Program)*, WAPD-TM-1285, Bettis Atomic Power Laboratory, West Mifflin, Pa. (Note: This reference contains more detailed information on the layout of a fabrication facility for LWBR fuel.)

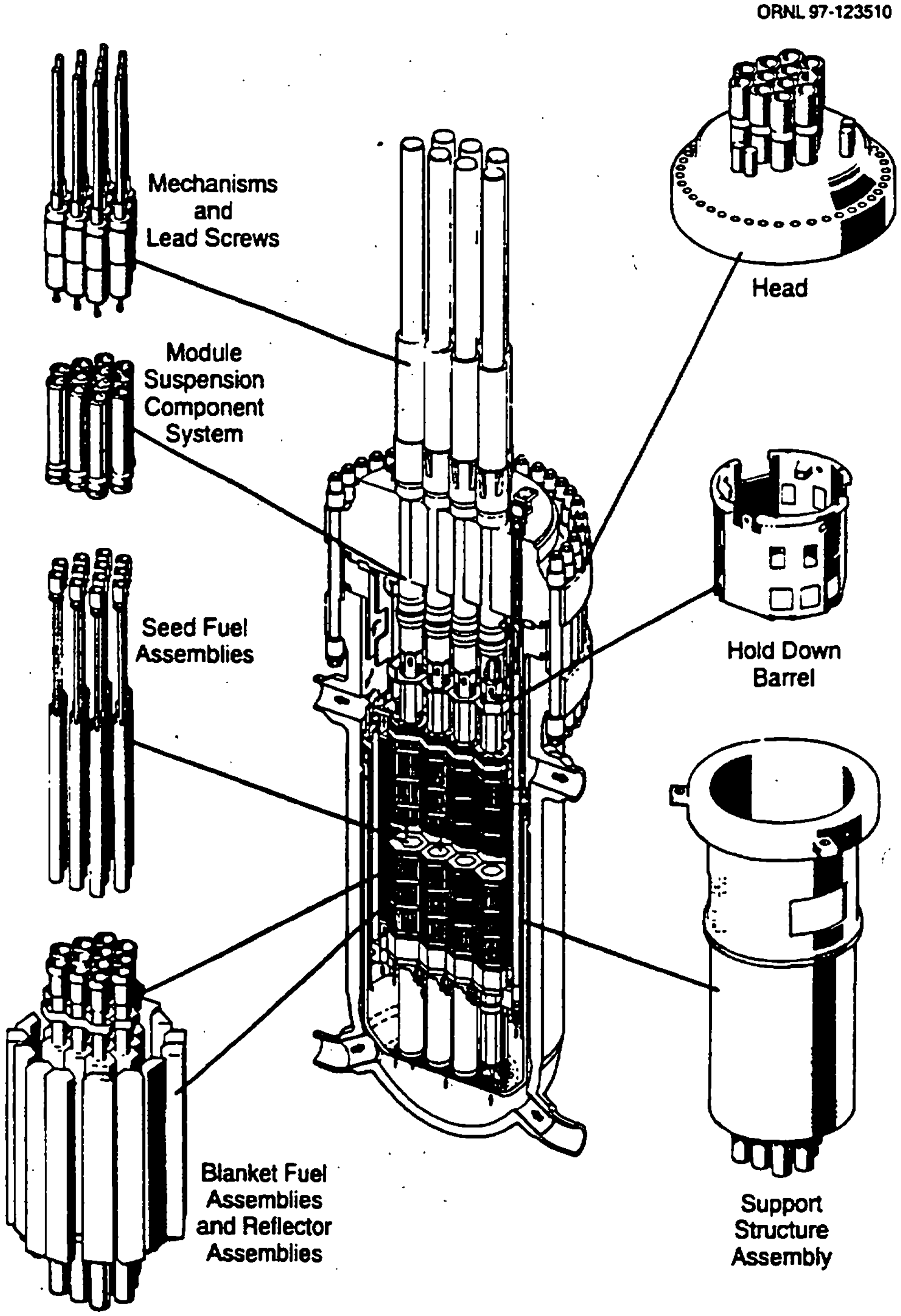

Fig. 3.7.2*a*. LWBR core in Shippingport reactor vessel. *Courtesy of Bettis Atomic Power Laboratory, West Mifflin, Pennsylvania.*

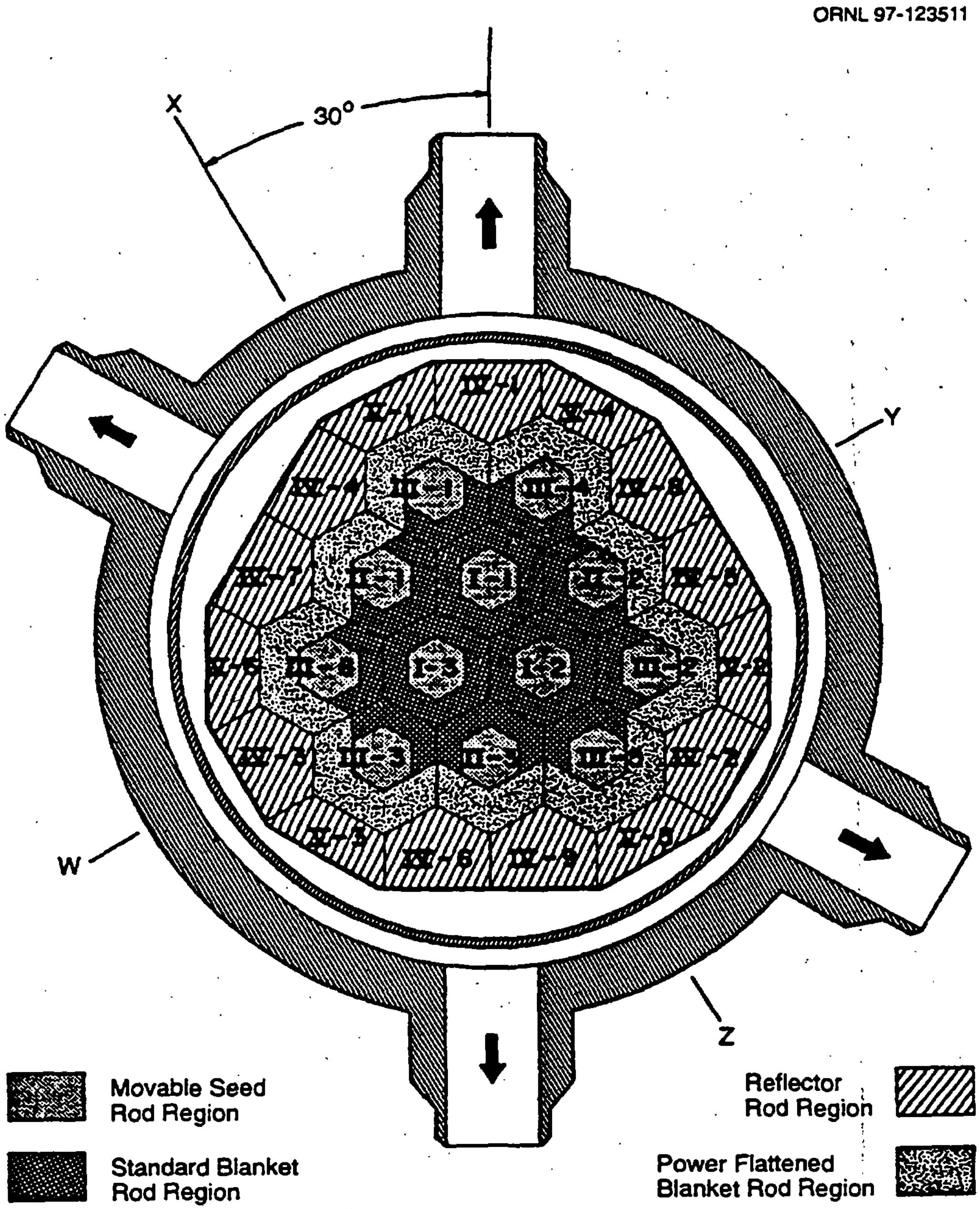

Fig. 3.7.2*b*. Cross-sectional diagram of LWBR core, showing module identification. *Courtesy of Bettis Atomic Power Laboratory, West Mifflin, Pennsylvania.*

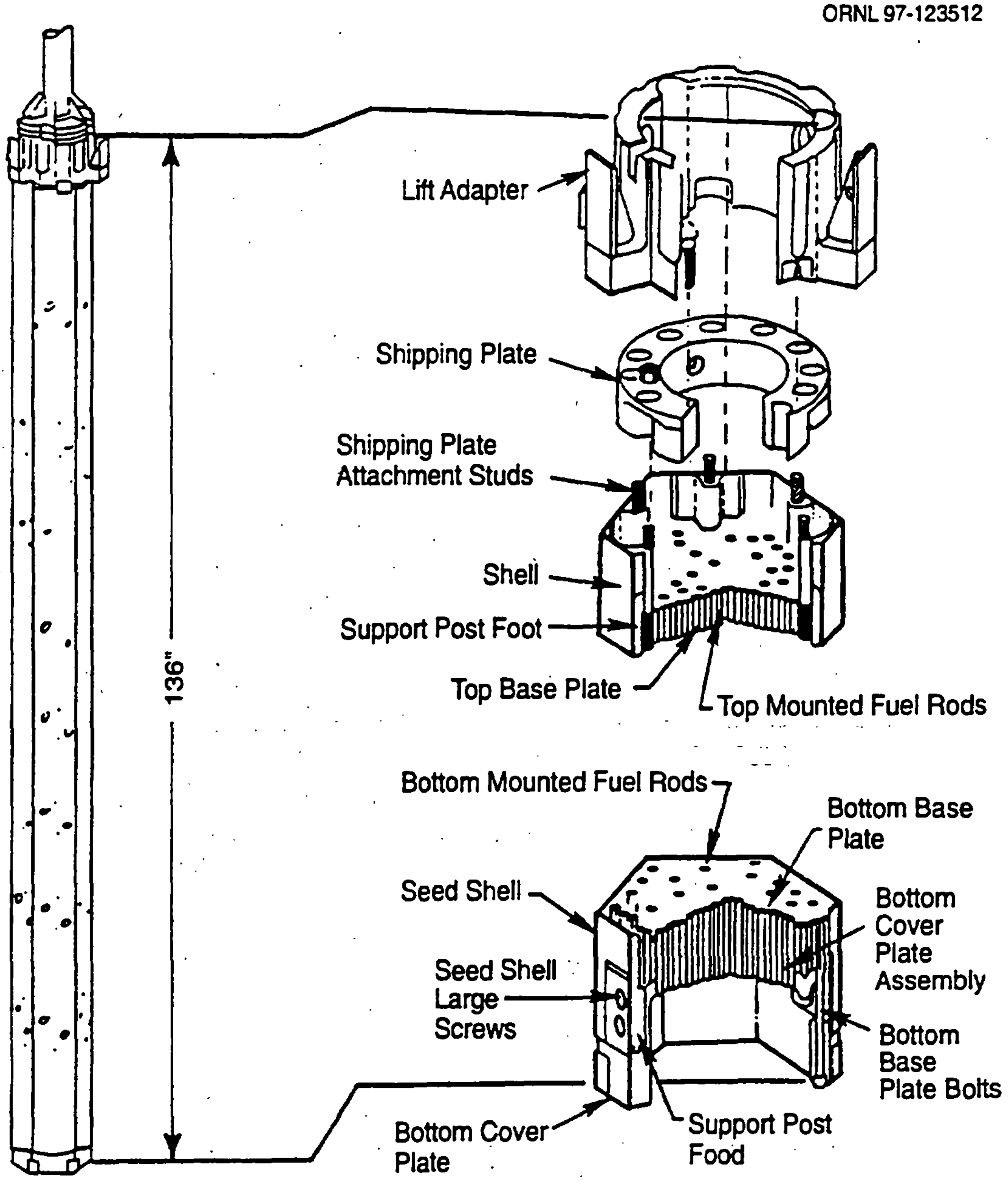

Fig. 3.7.2c. Cutaway view of an LWBR seed module. *Courtesy of Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.*

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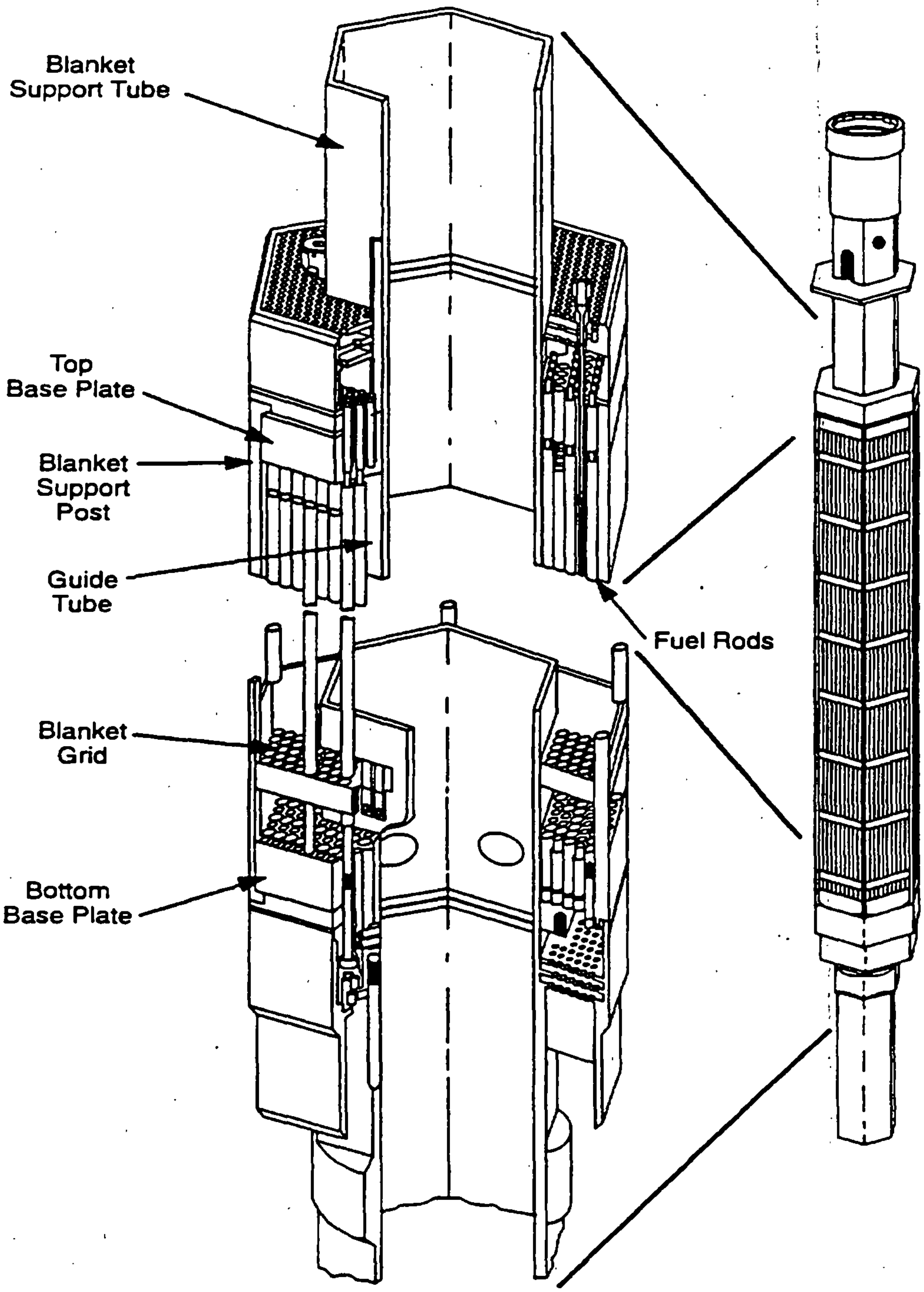

Fig. 3.7.2*d*. Shippingport LWBR blanket module.

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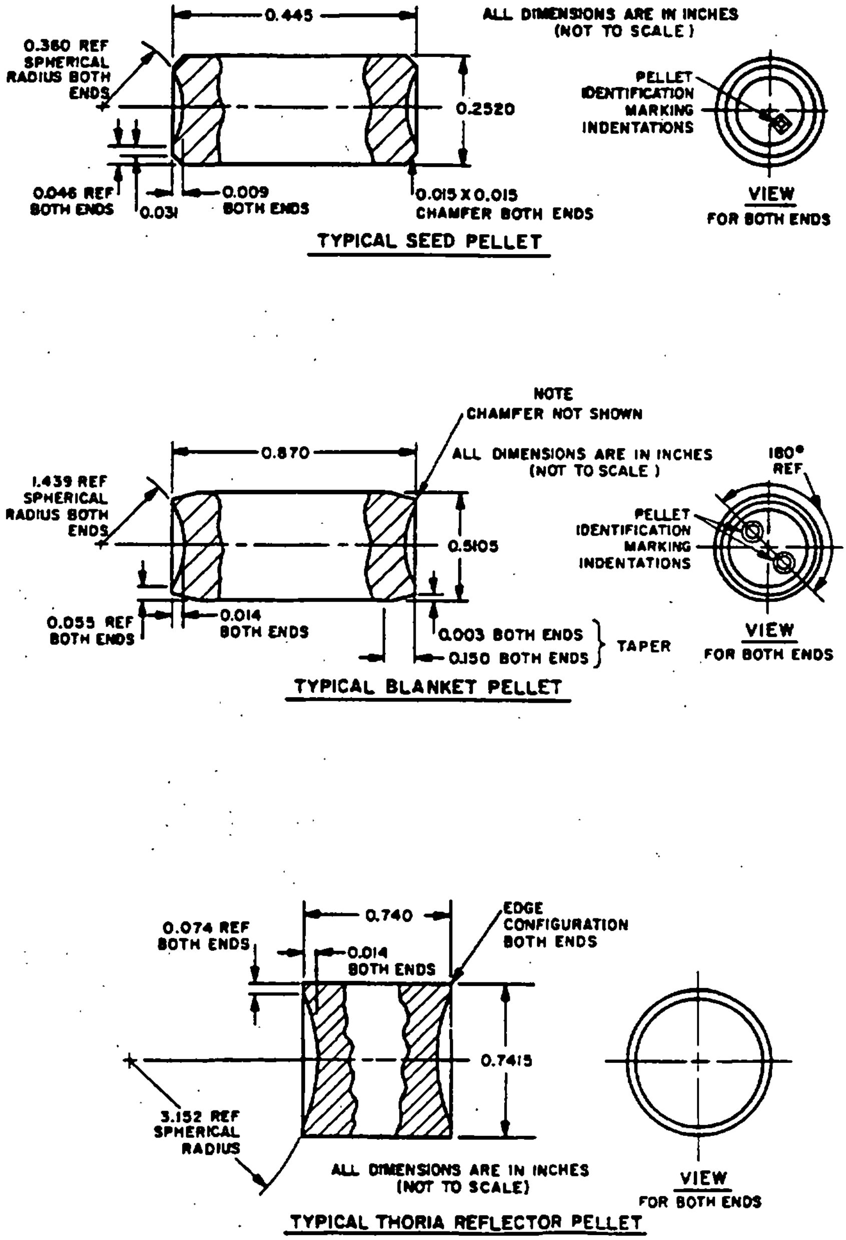

Fig. 3.7.2*e*. Typical seed, blanket, and reflector pellets showing nominal dimensions. *From Belle et al. January 1976.*

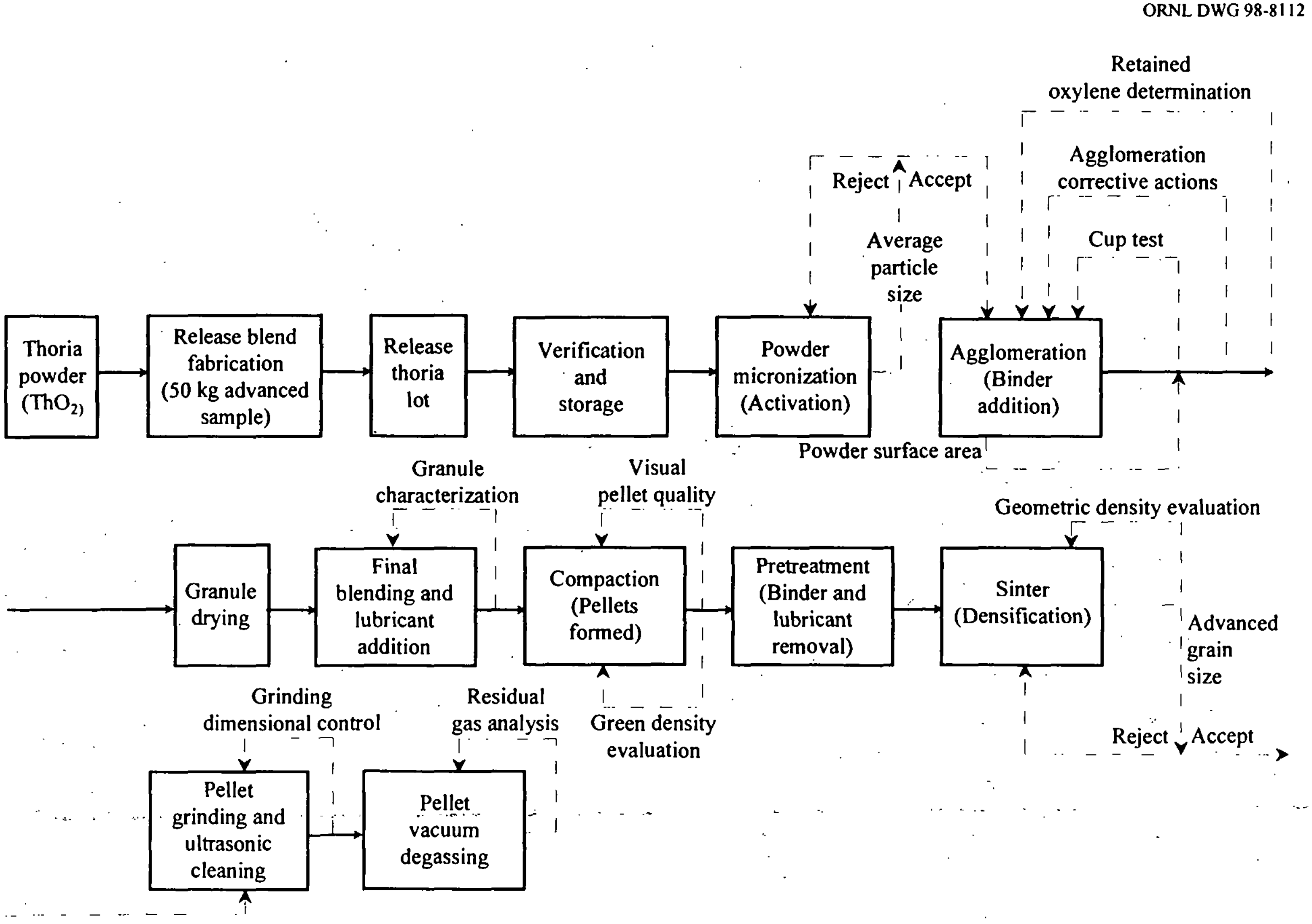

Fig. 3.7.2f. Flowchart of thoria fuel pellet fabrication. *From Belle et al. January 1976.*

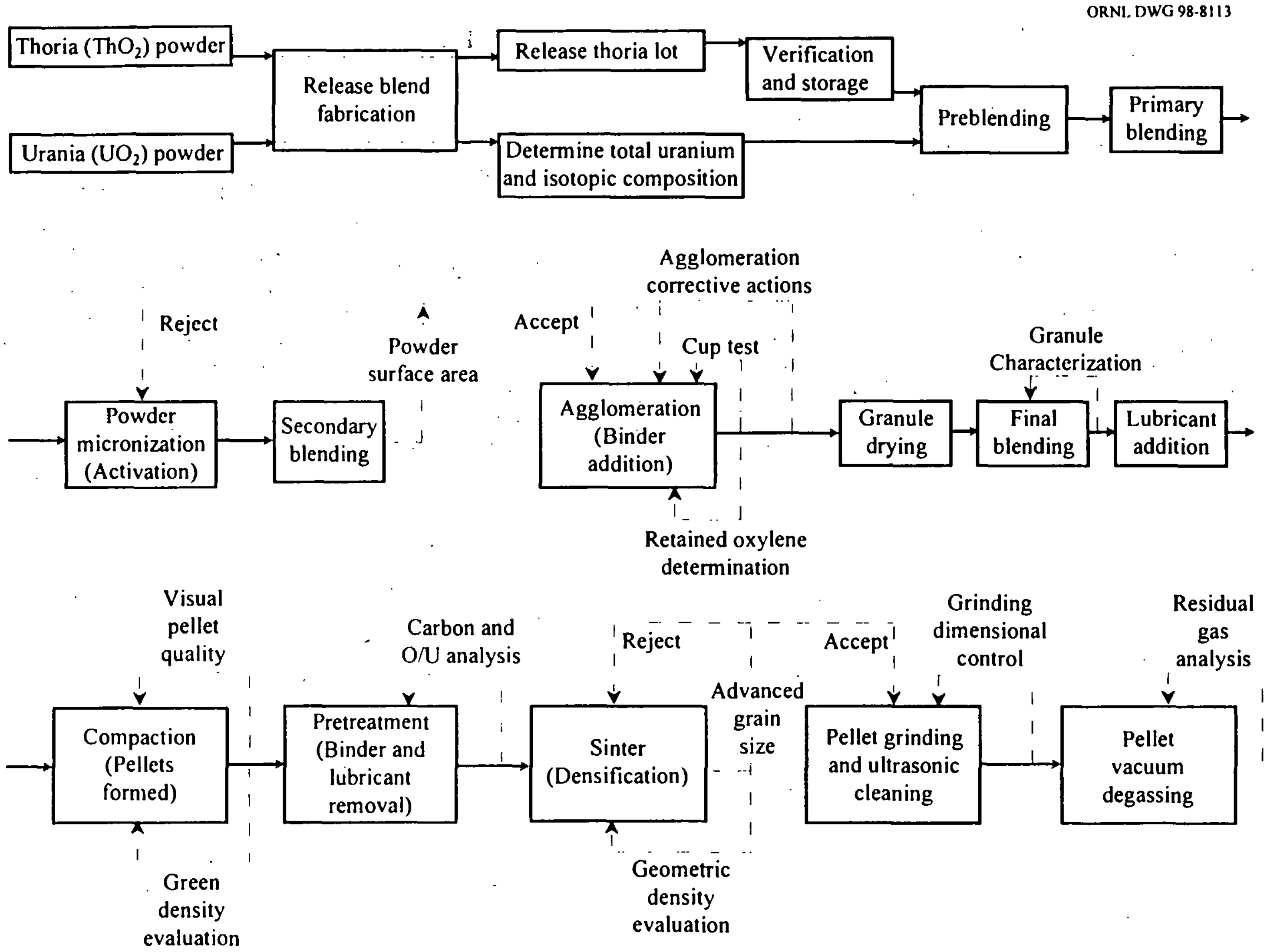

Fig. 3.7.2g. Flowchart of binary (thoria and urania) fuel pellet fabrication. *From Belle et al. January 1976.*

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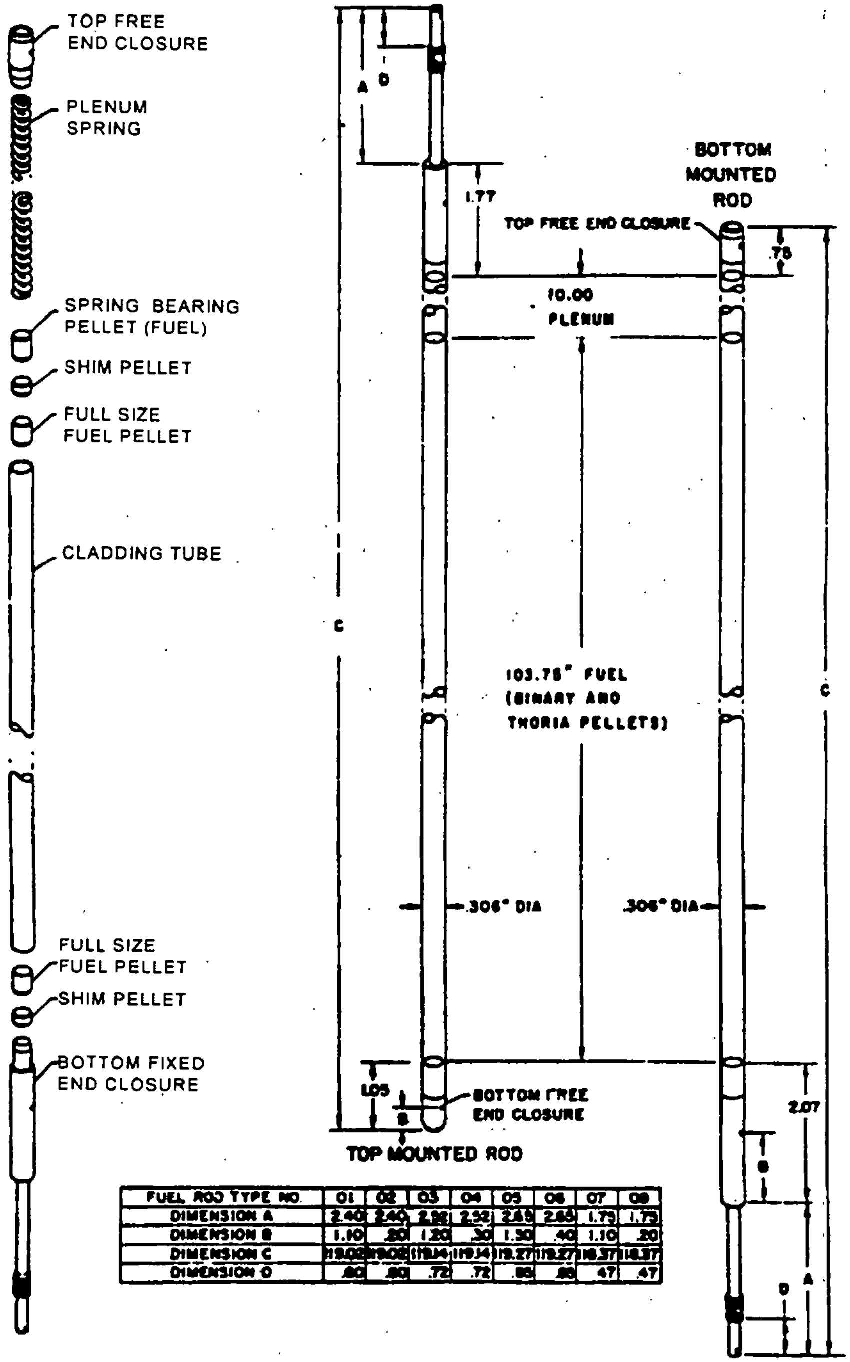

FUEL ROD TYPE NO.	01	02	03	04	05	06	07	08
DIMENSION A	2.40	2.40	2.32	2.32	2.85	2.85	1.75	1.75
DIMENSION B	1.10	.20	1.20	.30	1.30	.40	1.10	.20
DIMENSION C	119.02	119.02	119.14	119.14	119.27	119.27	118.37	118.37
DIMENSION D	.80	.80	.72	.72	.85	.85	.47	.47

Fig. 3.7.2*h*. General dimensions (in inches) and components of LWBR seed fuel rods. *From Bickel et al. March 1986.*

Table 3.7.2*a*. Typical levels of surface area and average particle size[a]

Fuel powder	Characteristic	Typical characteristics	
		As-received powder	As-micronized powder
Thoria (ThO_2)	Surface area	6.5–7.5 m^2/g	9.0–9.5 m^2/g
	Average particle size[b]	1.4–1.8 μ	0.5 μ
Binary (ThO_2–UO_2)	Surface area	4.5–6.0 m^2/g	8.0–9.0 m^2/g
	Average particle size	1.5–2.2 μ	0.5 μ

[a] From Belle et al. January 1976.

[b] Expressed in microns (μ), where 1 μ = 10^{-6} m.

Table 3.7.2*b*. LWBR fuel element dimension specifications[a,b]

Fuel element	Seed	Standard blanket	Power flattening blanket	Reflector
Zircaloy-4 cladding				
Outside diameter	0.306 ± .0015	0.5715 ± .0015	0.5275 ± .0015	0.832 ± .003
Inside diameter	0.262 ± .001	0.516 ± .001	0.475 ± .001	0.748 ± .001
Nominal wall thickness	0.022	0.02775	0.02625	0.042
Outside diameter-to-thickness ratio	13.9	20.6	20.1	19.8
Cladding heat treatment[c]	RXA	SRA	SRA	SRA
UO_2–ThO_2 fuel pellets				
Diameter	0.252 ± .0005	0.5105 ± .0005	0.4695 ± .0005	
Length	0.445 ± .020 0.615 ± .020	0.530 ± .020 0.870 ± .020 0.785 ± .020	0.870 ± .020 0.785 ± .020 0.700 ± .020	
End shoulder width	0.046 ± .008	0.055 ± .015	0.055 ± .015	
End face dish depth	0.009 ± .003	0.014 ± .004	0.014 ± .004	
Chamfer or taper				
Depth	0.015 ± .005	0.001–0.004	0.001–0.004	
Length	0.015 ± .015	0.100–0.200	0.100–0.200	
Range of individual pellet densities, % of theoretical	94.55–99.27	96.55–99.38	95.26–98.60	
Fuel–cladding diametral gap	0.0085–0.0115	0.004–0.007	0.004–0.007	
ThO_2 fuel pellets				
Diameter	0.2555 ± .0005	0.5105 ± .0005	0.4695 ± .0005	0.7415 ± .0005
Length	0.530 ± .020	0.615 ± .020	0.445 ± .020	0.740 ± .060
End shoulder width	0.055 ± .010	0.055 ± .010	0.055 ± .010	0.074 ± .010
End face dish depth	0.009 ± .003	0.014 ± .004	0.014 ± .004	0.014 ± .004
Edge configuration	0.015 ± .005 Chamfer	0.006 ± .004 Chamfer	0.006 ± .004 Chamfer	Square edge
Range of individual pellet densities, % of theoretical	95.14–99.75	93.10–99.36	95.37–99.95	93.08–99.08
Fuel–cladding diametral gap	0.005–0.008	0.004–0.007	0.004–0.007	0.005–0.008

[a] Based on Campbell and Giovengo October 1987.

[b] All dimensions are in inches, except as noted.

[c] RXA = recrystallization annealed and SRA = stress relief annealed.

3.7.3 Babcock and Wilcox Direct Fabrication of ^{233}U Fuel Elements

In the mid-1960s, as part of its Fuel Recycle Fabrication Program, the B&W fabricated ^{233}U fuel into full-sized fuel rods, which, in turn, were remotely assembled into fuel elements under water. This direct-fabrication method used unshielded glove boxes in which the fuel rod tubes were loaded with fuel powder by vibratory compaction. The details of this process were documented by B&W (Kerr, Barnes, and Ryon Feb. 1968 and Schileo February 1968) and are summarized below. The fabrication process was part of a larger experimental program that developed a pilot plant to convert recycle fuel and to fabricate a prototype fuel assembly for a power reactor. Initial fabrication of fuel elements containing ThO_2–$^{233}UO_2$ was successfully demonstrated in 1965 at the B&W Nuclear Development Center, Lynchburg, Virginia.

3.7.3.1 Process Objectives

From the conventional fabrication of ^{233}U-bearing fuels, significant personnel exposures are generally encountered from the high radiation levels of ^{233}U (and ^{232}U) decay daughter products. The B&W rod-fabrication process was carried out in a specially designed facility to permit rapid, uncontaminated fuel fabrication before the buildup of the gamma-emitting daughters of ^{233}U (and ^{232}U) to a level such that would require heavy shielding to protect fabrication workers.

3.7.3.2 Process Description and Basic Flowsheet

A summary overview flowsheet of the direct fuel-refabrication process is given in Fig. 3.7.3*a*. The method used the sol-gel process (developed by ORNL to produce high-density ThO_2–UO_2 from thorium and uranium nitrate feed), vibratory compaction of the oxide powder in Zircaloy tubing, and mechanical assembly of the fuel elements under water. Most of the fabrication activities were performed in customary glove boxes. The ^{233}U used for this demonstration contained 42 ppm ^{232}U–^{233}U and was received from ORNL in the form of a uranyl nitrate [$UO_2(NO_3)_2$] solution.

Figure 3.7.3*b* shows a general flowsheet of the specific B&W rod fabrication process. A simple glove-box line was designed for the vibratory compaction process. In a blending box, the sized fuel constituent material was received, weighed, and mixed into an oxide. The blended oxide was then placed into an adjacent glove box, which had a small vibratory feeder or shaker that loaded the blended oxide into a Zircaloy-4 fuel rod. After the loading and compaction, the fuel rod was disconnected from the shaker and weighed. The end of the fuel rod was decontaminated, capped, placed in a horizontal position, and then lowered into the welding glove box, which had a quick-release chuck used for grasping and rotating the rod. Within the glove-box line, the end caps were welded in a small automated chamber that was evacuated and filled with an inert gas. After the chamber was filled, the inert gas flow was increased, and the rods were inserted through a small opening. The gas flow was adjusted to prevent leakage of air into the welding enclosure and to maintain the purity of the atmosphere for welding the fuel rods.

For nondestructive tests, the welded fuel rods were dye-penetrant inspected; their end welds were helium leak-tested, and the rods were gamma-scanned to measure fuel-mass variation. A gamma-ray homogeneity gage, developed by B&W, was used to measure the fuel-mass variation over the length of the fuel rod. This gage used the attenuation of gamma rays passing through an absorbing medium, such as fuel material, to determine local variations in the fuel mass per unit fuel rod length.

After the fabricated fuel rods were nondestructively tested, they were ultrasonically cleaned, dried, removed from the glove-box line, and stored underwater to await remote assembly into a fuel element. As each fuel rod was removed from the line, a smear was taken to check its surface for alpha contamination.

A rail-mounted underwater assembly machine was used to assemble the fuel rods. This machine could perform three types of motion in a horizontal plane: back and forth, side to side, and circular. Additional horizontal and vertical movements for the precise positioning of each rod in a fuel element were provided and were controlled by hydraulic cylinders and adjustable stops. A hydraulic device was also used to grasp the fuel rods, to extract them from the storage bundle and then place them into a lead-lined cylinder, and to insert them into the fuel bundle.

3.7.3.3 Process Performance—Major Results

Following a preliminary checkout and an operation with ^{235}U-enriched fuel, the B&W process used 72 kg of sol-gel thoria-urania (ThO_2-$^{233}UO_2$) fuel to fabricate 37 fuel rods for part of a demonstration product fuel assembly. The urania content of this fuel was 3 wt %. Of the 72 kg of oxide handled, about 18 kg was lost in the fabrication line. The average time to process a fuel rod through the glove-box line was 1 h.

Low gamma doses were received by the operating personnel during the fuel fabrication. The total maximum whole-body dose received by an operator was 60 mrem, and the total maximum hand dose received by an operator was 170 mrem.

The results from the B&W Recycle Fuel Fabrication Program indicated that the direct method of fuel fabrication would be practical for operations with ^{233}U fuels containing higher levels of

^{232}U contamination in the fuel than the 42-ppm material that was used in these tests. About 1000-ppm ^{232}U in ^{233}U was the maximum level of impurity that was assumed that could be tolerated by the pilot-plant facility that demonstrated this fabrication scheme. For such materials, fuel- fabrication operations could be carried out in unshielded glove boxes at significantly less capital cost than in any fully shielded facility.

3.7.3.4 Reference for Section 3.7.3

Kerr, J. M., L. D. Barnes, and J. W. Ryon. February 1968. "Direct Fabrication of ^{233}U Fuel Elements," pp. 537–45 in *Proceedings of Second International Thorium fuel Cycle Symposium, Gatlinburg, Tennessee, May 3–6, 1966*, U.S. Atomic Energy Commission, Division of Technical Information, Oak Ridge, Tenn.

Schileo, G. February 1968. "An Unshielded Pilot Plant for Recycling ^{233}U," pp. 299–319 in *Proceedings of Second International Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee, May 3–6, 1966*, U.S. Atomic Energy Commission, Division of Technical Information, Oak Ridge, Tenn.

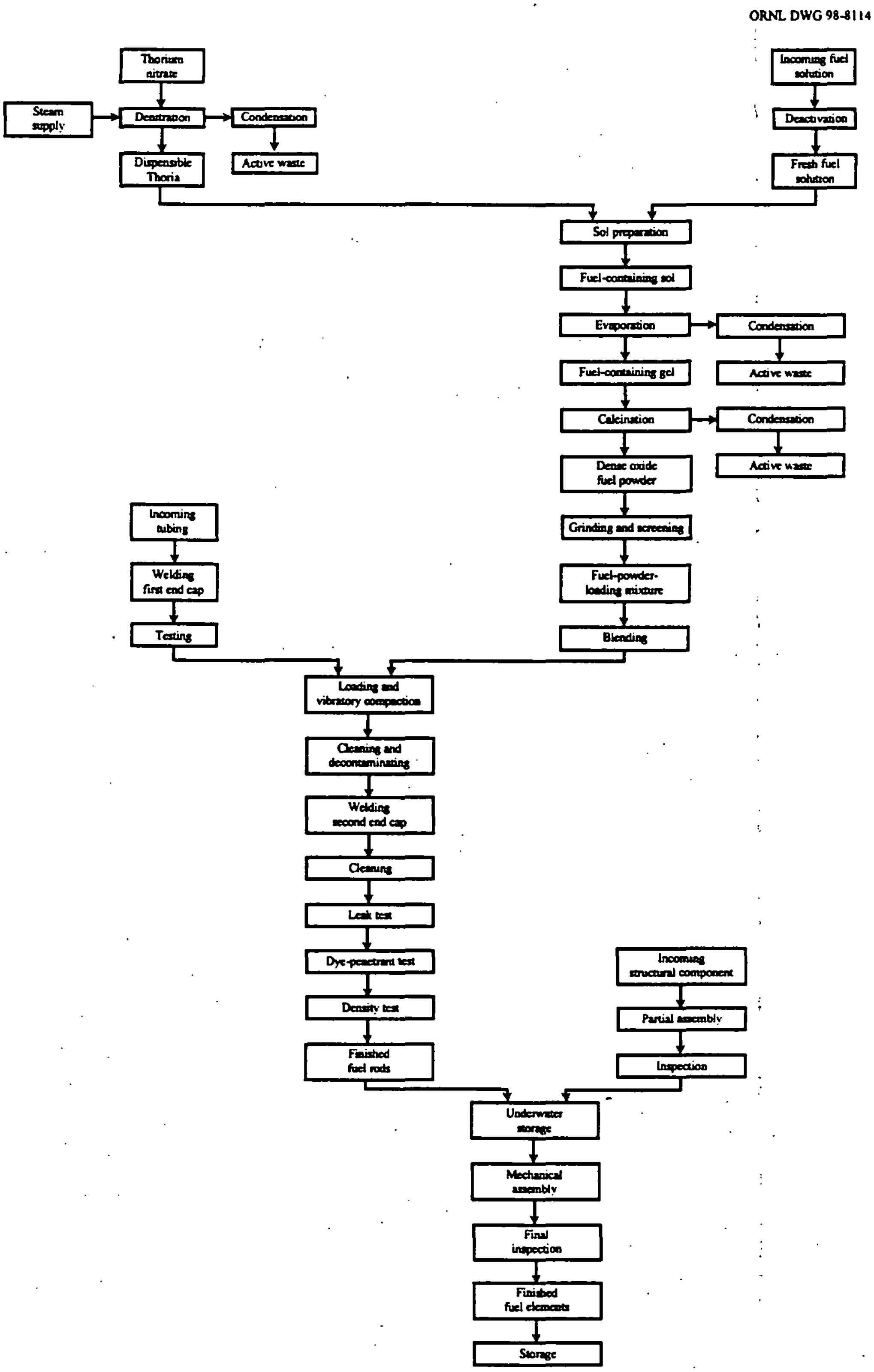

Fig. 3.7.3*a*. Flowchart of direct fuel refabrication process. *Adapted from Schileo February 1968.*

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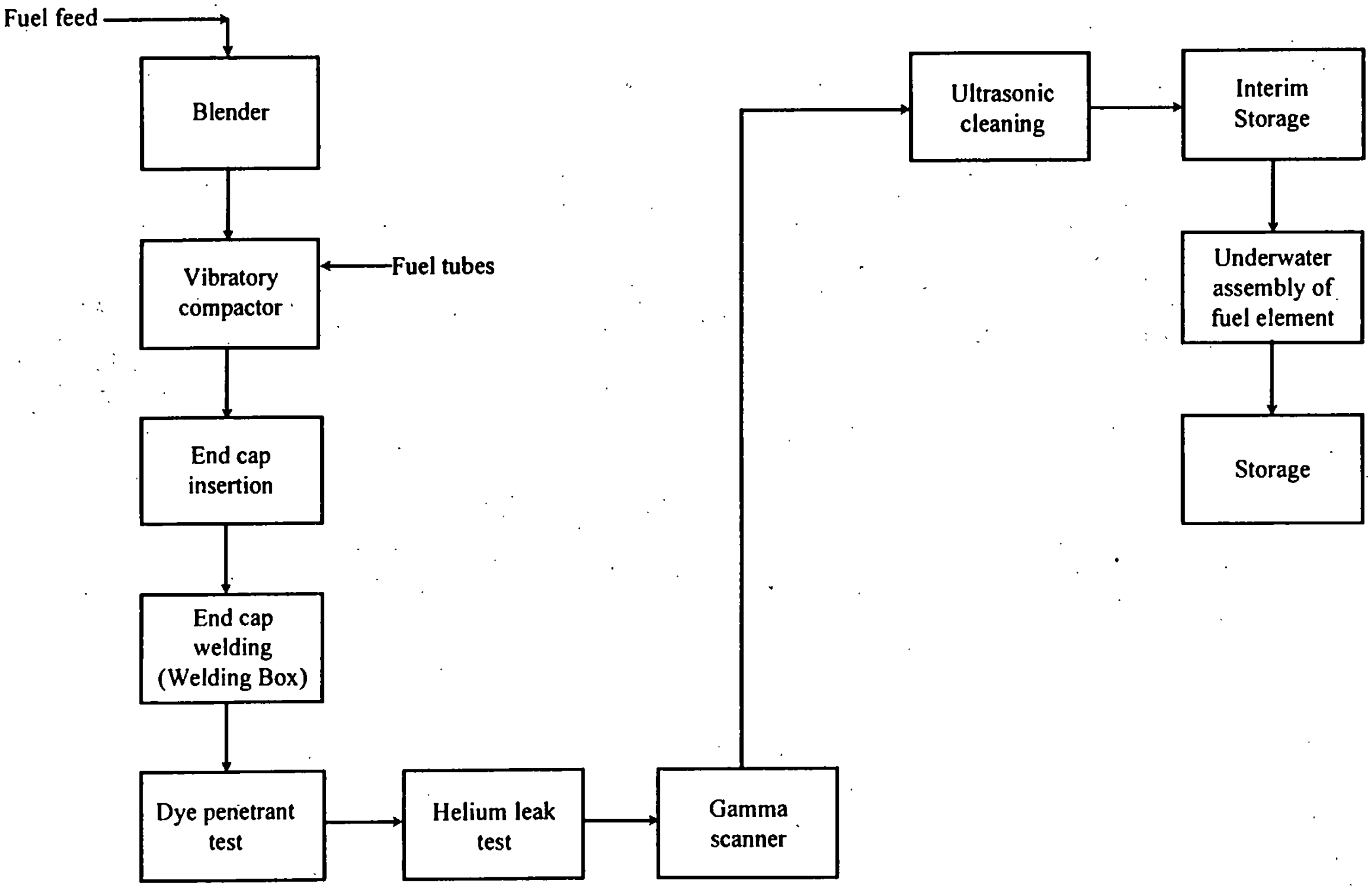

Fig. 3.7.3*b*. Flowchart of B&W rod fabrication and assembly line. *Adapted from Kerr, Barnes, and Ryon February 1968.*

3.7.4 Fabrication of Zero-Power Physics Reactor Fuel Elements

3.7.4.1 Process Objectives

During 1979–1981, ORNL, under contract with ANL–W, fabricated over 1700 fuel elements (also called packets) for use in criticality experiments in ANL's ZPPR at Idaho Falls, Idaho. This program also included recovery of ^{233}U from rejected fuel elements. Information on the activities of this program is summarized below and based on documentation prepared by the CTD of ORNL (CTD 1979, CTD 1981, and Nicol et al. May 1982).

3.7.4.2 Process Description and Basic Flowsheet

A basic flowsheet of the ZPPR fuel fabrication is given in Fig. 3.7.4*a*. The major steps involved in the ZPPR fuel fabrication included converting the purified uranyl nitrate (as solution) to U_3O_8 powder (suitable for use as fuel) and the subsequent activities of charging, sealing, decontaminating, and testing the fuel elements prior to shipment.

Because of the age of the starting uranyl nitrate and recycled oxide, purification by either SX, ion exchange, or both, was required before conversion to U_3O_8. The conversion equipment and operations were the same as those previously used and described for the LWBR Demonstration Program (Sect. 3.5.1). Fuel element production operations included preparation of the stainless steel packets (shells and lids) fabricated by ANL and shipped to ORNL. The packets were charged or loaded with $^{233}U_3O_8$ by a vibrator feeder. Groups of filled packets were then placed in an oven and heated to 250°C for 1 h to reduce moisture content. Heated packets were then removed from the oven and placed on a welding assembly, where they were sealed by fusing an end cap to the body by means of programmed welding. This was followed by leak-testing under a vacuum in an ethylene glycol solution, decontamination in an ultrasonic bath, plating with nickel to reduce direct alpha contamination, and counting for alpha contamination. These operations were performed in a line of stainless steel glove boxes. Each sealed packet with fuel then went through a series of final checks (covering U_3O_8 powder weight, internal pressure, moisture content, leak rate, surface radioactivity, dimensions, and surface flaws) before being assigned a unique identification number. After receiving an identification, each packet was packaged and placed in interim storage for shipment to the ANL ZPPR facility in Idaho.

3.7.4.3 Process Performance—Major Results

The $^{233}U_3O_8$ packet-loading program for ANL resulted in the fabrication of 1743 fuel elements, each of which contained 33 g of $^{233}U_3O_8$ converted from freshly purified ^{233}U nitrate solution. A stainless steel packet fabricated for the ZPPR experiment measured 5.08 × 7.62 × 0.64 cm. About 20 kg of ^{233}U were recovered from those fuel elements or packets that were rejected. The associated ^{232}U concentration was about 10 ppm. The uranium material balance for the ANL ZPPR Program is summarized in Table 3.7.4*a*.

The overall yield (fraction of loaded fuel elements or packets that met specifications) was 72%. Leakage caused by poor welding was the principal reason for rejection. Fusion welding of the tops onto the fuel elements was difficult because of three factors: the precision required of the tracking mechanism, the welding current changes that resulted from heat buildup in the programmer, and the length and taper of the welding rods (CTD 1981).

3.7.4.4 References for Section 3.7.4

Chemical Technology Division. 1979. "$^{233}U_3O_8$ Packet Loading for Argonne National Laboratory," pp. 90–92 in *Chemical Technology Division Annual Progress Report for the Period Ending March 31, 1979*, ORNL-5542, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Chemical Technology Division. 1981. "$^{233}U_3O_8$ Packet Loading for Argonne National Laboratory," p. 134 in *Chemical Technology Division Progress Report for the Period April 1, 1979 to March 31, 1981*, ORNL-5757, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Nicol, R. G. et al. May 1982. *Fabrication of Zero Power Reactor Fuel Elements Containing $^{233}U_3O_8$ Powder*, ORNL/TM-8140, Oak Ridge National Laboratory, Oak Ridge, Tenn.

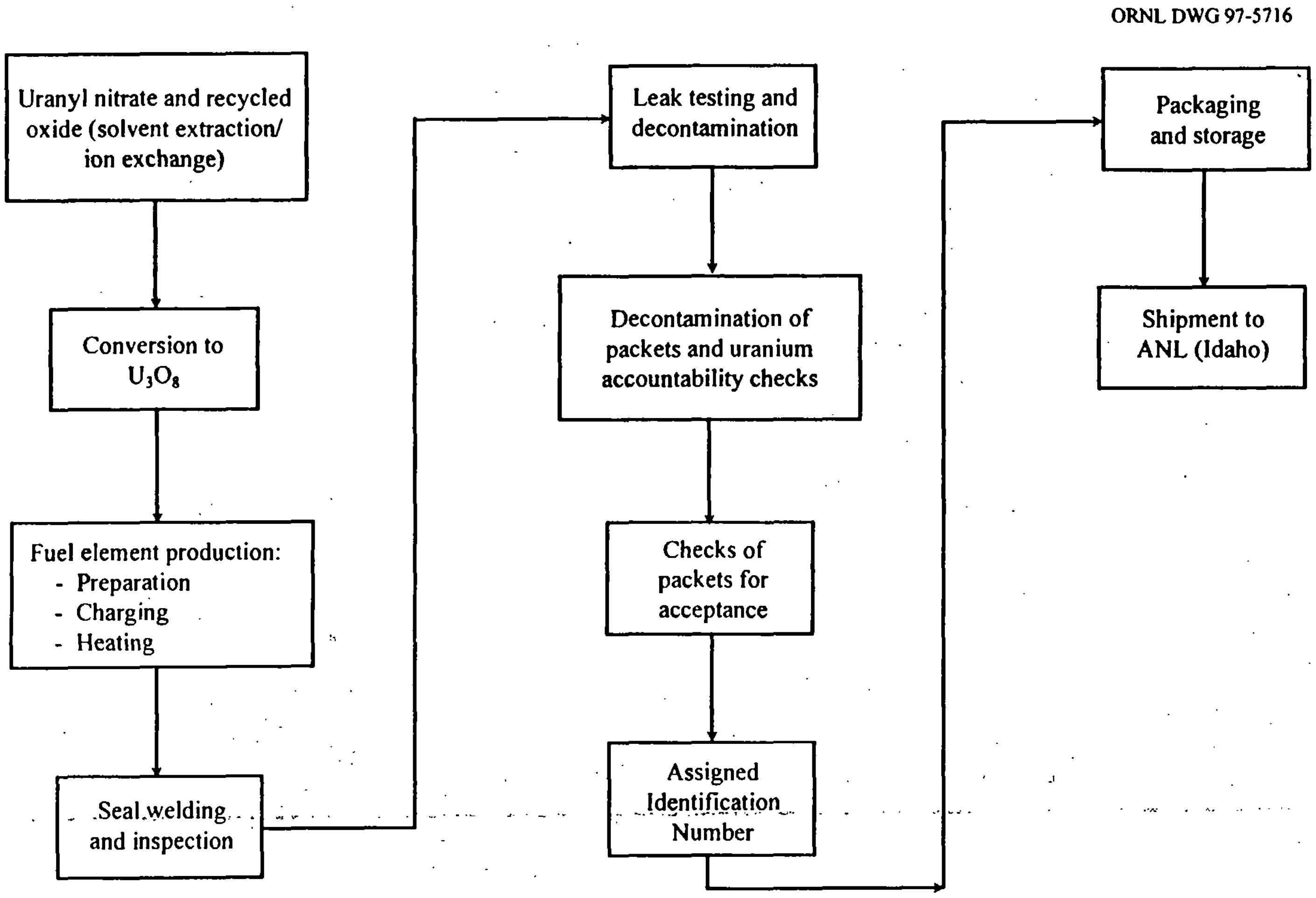

Fig. 3.7.4*a*. Flowsheet of major ZPPR fuel fabrication program activities at ORNL. *Adapted from CTD 1979, CTD 1981, and Nicol et al. May 1982.*

Table 3.7.4*a*. Uranium material balance for the ANL ZPPR program[a]
(Uranium available for use in this program)

	Total U (kg)	^{233}U (kg)
1. Initial inventory (available for use in this program)		
a. Liquid (UNH in U-storage)	55.963	54.886
Liquid ("In-process" tanks	9.472	9.285
b. Solids (as oxides in storage)	18.197	17.835
Total to account for	83.632	82.006
2. Shipments out		
a. ANL-ZPPR (Idaho)	48.690	47.722
b. Approved transfer to other programs	2.699	2.646
Total shipped	51.389	50.368
3. Waste discards		
a. From solvent extraction, ion exchange, and analytical facility	0.521	0.511
b. From oxide conversion line	0.293	0.287
Total measured losses	0.814	0.798
4. Remaining inventory		
a. Recycle oxide from program	5.367	5.262
b. Unused oxide	5.086	4.991
c. UNH solution in U-storage	18.740	18.397
d. "In-process" tanks	1.724	1.688
e. Archive samples (oxide)	0.215	0.211
Total remaining	31.132	30.549
5. Total accounted for (items 2, 3, 4)	83.335	81.715
6. Difference (item 1 minus item 5)	0.297	0.291
(% unaccounted for)	0.36	0.36

[a] Based on Nicol et al. May 1982.

3.7.5 Fabrication of Other ^{233}U Fuels

The fabrication of other ^{233}U fuels is discussed in the following sections. Such fuels include those used for criticality experiments and fuels fabricated for nuclear reactors in India, which are based on the thorium fuel cycle.

3.7.5.1 Fuel for Brookhaven Criticality Experiments

In the 1960s, a project was conducted to fabricate fuel containing ^{233}U oxide ($^{233}UO_2$) and zirconium oxide (ZrO_2) for criticality experiments at BNL. The fuel was made from uranyl nitrate [$UO_2(NO_3)_2$] that was purified at ORNL and shipped to the NFS facility in Erwin, Tennessee, for fabrication into fuel pellets. These pellets were blended with ZrO_2, sintered at 1760°C for 48 h, loaded into Zircaloy-2 tubing, and then shipped to the Nuclear Materials and Equipment Corporation (NUMEC) in Apollo, Pennsylvania, for the final seal weld on each of the rods.

In this campaign, the ^{233}U was fabricated into 1 wt % UO_2-ThO_2 and 26 wt % UO_2-ZrO_2 pellets and enclosed in Zircaloy-2 cladding tubes as 1299 blanket rods and 377 seed rods. The ^{233}U had an associated ^{232}U concentration of 38 ppm and was purified as two batches of liquid uranyl nitrate immediately prior to processing into powder form. All fuel rods were completed within 95 d of the initial solvent extraction of the nitrate. The overall uranium yield of nitrate to usable materials was over 90%, and only 14 rods were rejected in welding (all without loss of contained fuel). This material is currently stored at the RWMC at INEEL in 22 drums that are under an earthen-covered berm in the Transuranic Storage Area–Retrieval Enclosure (TSA-RE). The material in these drums has about 5.5 kg of ^{233}U (Frankhouser et al. February 1967).

3.7.5.2 Fuel Fabrication for Indian Reactors

Because India has large natural reserves of thorium and no enriched uranium, the power reactors of that nation are based on the thorium fuel cycle. The latter is initiated with natural uranium, followed by the use of self-generated plutonium with natural thorium, and, finally, the ^{232}Th-^{233}U cycle (Balakrishnan and Ganguly 1989). Summaries of various fabrication methods that have been developed and documented for fabricating ^{233}U-Th fuel for Indian reactors are provided in the following paragraphs.

India's long-term nuclear power program has envisaged different modes of the thorium fuel cycle for supporting its pressurized heavy-water reactors (PHWRs). As described in Balakrishnan and Ganguly (1989), process flowsheets have been developed for the fabrication of high-density

ThO_2-PuO_2 and ThO_2-$^{233}UO_2$ fuel pellets via the conventional "powder-pellet" route and using advanced methods that include the "pellet impregnation" and the sol-gel microsphere pelletization (SGMP) processes. Evaluations were then made of the thermophysical properties of these fuels up to the envisaged in-pile operating temperature. A six-pin Zircaloy-2-clad ThO_2-PuO_2 test fuel cluster (having 4 wt % of PuO_2) was successfully irradiated to a burnup of 18,400 MWd/MTIHM in the pressurized water loop of the CIRUS reactor, a 40-MWt research reactor located at Trombay.

The first incidence of fabricating ^{233}U-bearing fuel in India was the production of aluminum-clad Al-^{233}U alloy fuel for the Kamini research reactor. Later, the reactor physics experiments for this fuel were performed in the Purnima III critical assembly, where aluminum-plutonium alloy plates were also used. Both types of fuels were fabricated in the radiometallurgy laboratories of the Bhabha Atomic Research Centre. Ganguly et al. (October 1991) provide a detailed discussion of the fabrication of Al-^{233}U and aluminum-plutonium plate fuel for Purnima III and Kamini. Aluminum-clad Al–20 wt % ^{233}U and Al–23 wt % plutonium plate fuel subassemblies were fabricated for the critical facility and the research reactor using a flowsheet that included the following major steps:

- preparing the master alloy using aluminum and uranium or plutonium as feed materials;
- remelting and casting the fuel alloy ingots;
- rolling;
- picturing, framing, and sandwiching the fuel alloy between aluminum sheets;
- roll bonding and locating the fuel alloy core outline by X-ray radiography; and
- trimming and machining to final dimensions.

Development of this fabrication process has revealed that metallic molds produce better ingots than graphite molds. Also, the addition of zirconium during melting has been found to improve the microstructure of the aluminum-uranium and aluminum-plutonium castings and facilitate the hot rolling of the ingots. In fabricating the subassembly, the fuel plates were finally locked in aluminum spacer grooves by a novel roll-swaging technique. High-resolution X-ray radiographs and microdensitometric scans were then utilized to confirm the homogeneous distribution of the fissile material in the fuel plates. Nonbond areas were detected by blister testing and immersion ultrasonic testing of the roll-bonding fuel plates.

Experiences in the fabrication of aluminum-clad metallic uranium fuel are described by Vijayaraghavan (1989). In June 1959, the first metallic uranium fuel element was fabricated, starting from uranium ingots. Aluminum-clad metallic uranium fuel has been used in both the CIRUS reactor and Dhruva, a 100-MWt research reactor at Trombay. The Dhruva fuel is in the form of a cluster consisting of seven fuel pins as compared with the rigid single fuel element that is used for CIRUS. Uranium ingots are initially used in the fabrication of the CIRUS and Dhruva fuels, and the fuel fabrication flowsheet itself consists of the following major activities:

- vacuum melting and casting;
- hot rolling (in three stages);
- heat treatment;
- straightening;
- machining;
- decreasing, pickling, and cleaning;
- canning;
- seal welding; and
- radiography and leak testing of the final product (fuel element).

Compared with the CIRUS fuel, the fuel for the Dhruva reactor requires a uranium metal rod of smaller diameter, a higher length-to-diameter ratio, and different configurations of fins on aluminum sheaths and cluster assembly. As a result, such differences have required development work in optimizing some of the production parameters for this fabrication process.

3.7.5.3 References for Sect. 3.7.5

Listed are the references cited in Sect. 3.7.5. This is followed by a list of additional resources that provide more detailed information on the fabrication of other ^{233}U fuels.

3.7.5.3.1 References Cited

Balakrishnan, K., and C. Ganguly. 1989. "Thorium Utilization in Indian Power Programme," pp. 125–38 in *Proceedings of a Symposium on Nuclear Fuel Fabrication, NUFFAB '88, Bombay, India, December 12–14, 1988*, Trans Tech Publications, Aedermannsdorf, Switzerland.

Frankhouser, W. L., et al. February 1967. *Fabrication of Fuel Rods Containing ^{233}U Pelletized Oxide Fuels*, WAPD-TM-588, Bettis Atomic Power Laboratory, West Mifflin, Pa.

Ganguly, C., et al. October 1991. "Fabrication Experience of Al-^{233}U and Al-Pu Plate Fuel for the Purnima III and Kamini Research Reactors," *Nuclear Technol.*, 96(1), 72–83.

Vijayaraghavan, R. 1989. "Experiences in the Fabrication of Aluminum Clad Metallic Uranium Fuel," pp. 329–46 in *Proceedings of a Symposium on Nuclear Fuel Fabrication, NUFFAB '88, Bombay, India, December 12–14, 1988*, Trans Tech Publications, Aedermannsdorf, Switzerland.

3.7.5.3.2 Supplemental Resources

Bhagwat, A. M., et al. August 1993. *Radiological Safety Experience in the Fabrication of Alloy Plate Fuels Bearing ^{233}U/Pu, Nuclear Technol.*, 103(11), 246–56.

Sood, D. D., and V. N. Vaidya. 1989. "Experience in BARC on the Preparation of Gel Microspheres of Uranium, Thorium, and Plutonium Fuels," pp. 245–56 in *Proceedings of a Symposium on Nuclear Fuel Fabrication, NUFFAB '88, Bombay, India, December 12–14, 1988*, Trans Tech Publications, Aedermannsdorf, Switzerland.

4. HANDLING GUIDELINES FOR ^{233}U-BEARING MATERIALS

This section includes a discussion of the major areas associated with the handling of ^{233}U-bearing materials. Major requirements are described for the following areas that impact ^{233}U material handling: (1) radiation protection practices, (2) shielding materials and techniques, (3) control of radon emissions, (4) off-gas filtration, (5) confinement in ^{233}U material processing, (6) special chemical hazards, (7) packaging materials and techniques, (8) storage requirements, (9) nuclear materials accountability, (10) transportation, (11) safe plant operations, and (12) worker training and certification. The separate subsections that follow are devoted to each of these topics. Major references that provide more detailed information on each of these topics are also listed. Throughout the discussion of these topics in Sect. 4, the present tense is used to indicate that the activities described are currently being performed in facilities that contain ^{233}U-bearing materials.

There are two major areas for which the handling requirements for ^{233}U materials are significantly different from those of most other radioactive materials: (1) special radiation protection practices needed as a result of the increased gamma dosage with time to exposed personnel and (2) the presence of radioactive radon (^{220}Rn) in the off-gas emissions from a facility containing ^{233}U-bearing materials. Section 4 is a discussion of the special handling guidelines that are needed to address these two major radiological concerns.

4.1 RADIATION PROTECTION PRACTICES

The radiation hazards posed by ^{233}U and ^{232}U, their radioactive daughters, and other radionuclides present in ^{233}U-bearing material are considered in this chapter. Since the insult posed to man from exposure to the radiation from ^{233}U and ^{232}U is measured in terms of dose, some basic principles of dosimetry are discussed. The techniques for external and internal radiation protection are then covered. Special precautions are needed for the radiation protection of workers from ^{233}U-bearing materials. These are discussed in Sect. 4.1.3 following discussions of the basic principles of radiation dosimetry (Sect. 4.1.1) and the basic techniques for external radiation protection (Sect. 4.1.2). Uranium-233 is a fissile material, and a criticality accident can result in excessive doses. Nuclear criticality safety and control are discussed in Sect. 4.1.5.

4.1.1 Radiation Dosimetry

Radiation dosimetry is the branch of science that deals with the theory and application of the principles and techniques involved in the measurement and recording of radiation doses. Its practical aspect is concerned with the use of various types of radiation instruments with which measurements are made (Shleien 1992). Dosimetry is essential for quantifying the incidence of various biological changes as a function of the amount of radiation received (dose-effect relationships), for comparing different experiments, for monitoring the radiation exposures of individuals, and for surveillance of the environment (Turner 1986).

Quantities and Units Used in Radiation Dosimetry

Exposure. Radiation exposure is expressed in terms of the unit, roentgen (R). A *roentgen* is defined as the amount of ionization of either charge produced in air by gamma or x-rays, i.e.,

$$1\ \mathrm{R} = 2.58 \times 10^{-4}\ \mathrm{C/kg}$$

Exposure is defined only for electromagnetic radiation in air.

Absorbed dose. *Absorbed dose* is defined as the energy absorbed per unit mass. The traditional unit of absorbed dose is the rad, defined as 100 erg/g. The International System of Units (SI) unit is the gray (Gy). A gray is equal to 1 J/kg, or 100 rad.

Dose equivalent. For the same absorbed dose in tissue delivered at the same rate, some types of radiation (e.g., alpha particles, neutrons) produce greater biological effects than others (e.g., photons, electrons). The different biological effectiveness of different types of radiation is incorporated in the dose equivalent. The dose equivalent, H, is defined as the product of the absorbed dose, D, and a dimensionless quality factor, Q, which depends on the linear energy transfer (LET):

$$H = QD.$$

For purposes of radiation protection, the quality factor (Q) is assumed to be 1 for photons and electrons and 20 for alpha particles. The values for neutrons vary from 5 to 20 depending on their energy. When the absorbed dose is expressed in terms of rads, the dose-equivalent unit is the rem (roentgen equivalent man). With the absorbed dose expressed in gray, the SI dose-equivalent unit is called the sievert (Sv), where 1 Sv = 100 rem.

4.1.2 Techniques for External Radiation Protection

The objective of external radiation protection is to protect individual radiation workers by optimizing the external dose equivalent and preventing exposure above the administrative and regulatory limits. External radiation protection is an important issue when dealing with ^{233}U and ^{232}U because of the highly energetic 2.6-MeV gamma rays from the ^{232}U radioactive daughter, ^{208}Tl. To a lesser extent, neutron doses can be of concern depending on the impurity radionuclides present in the ^{233}U-bearing material and the chemical form of the material (e.g., fluoride compounds in which α-n reactions can occur).

The exposure of personnel to external radiation may be controlled using one or any combination of the following three techniques (Cember 1983):

1. minimization of exposure time,
2. maximization of distance from the radiation source, and
3. shielding the radiation source.

Time. As general rule, the following relationship is valid:

$$\text{Dose rate} \times \text{time} = \text{total dose.}$$

Hence, reduction in worker exposure time will result in less dose. Operations involving ^{233}U-bearing material need to be planned carefully to reduce worker exposure time to the extent practicable.

Distance. Radiation exposure decreases with increasing distance from a radioactive source. Hence, the use of techniques to make operations semiremote and to keep the distance of workers as far away as practicable from the radiation source while performing work will result in dose reductions.

Shielding. The use of shielding is a very important method for reducing doses to personnel, especially when handling or storing ^{233}U, because of the highly energetic 2.6-MeV photons released by ^{208}Tl (a radioactive daughter of ^{232}U). Lead shields and barite concrete are commonly used materials for gamma shielding. The amounts or thicknesses of shielding material to be used depend on the source activity, geometry, and matrix. Expected exposure rates for actual conditions should be determined on a case-by-case basis using a combination of radiation measurements and computer programs that project radiation shielding requirements.

4.1.3 Special Precautions for Radiation Protection from ^{233}U-Bearing Materials

As indicated in Sect. 2, a major problem with ^{233}U is that some neutron-irradiated thorium is transformed into another uranium isotope, ^{232}U, which has a decay product, ^{208}Tl, which emits a highly energetic (2.6-MeV) gamma ray when it decays. Depending upon the concentration of the ^{232}U isotope, this gamma emission can produce an intense radiation field that can hinder and complicate the handling of ^{233}U-bearing materials and require these materials to be stored inside shielded vaults. This feature can also require the construction of special-purpose, remote facilities for the fabrication of ^{233}U fuel.

As discussed in Sect. 4.1.2, exposure of facility personnel to external radiation from radiation sources is generally controlled by techniques associated with optimizing exposure times, distances from the radiation sources, and shielding of the sources. (The features and requirements associated with the shielding of ^{233}U-bearing materials are discussed in Sect. 4.2.) However, application of considerations of time and distance to spills and general periodic housekeeping involving ^{233}U requires some modification from most approaches generally taken. Experience from handling ^{233}U-bearing materials indicates that, for example, spills involving these materials need to be cleaned up quickly (with minimal delay) followed by an immediate evacuation of personnel. In addition, material residues containing ^{233}U on process equipment need to be removed periodically. Because of the rapid ingrowth of harmful radiation from the decay products of the associated ^{232}U isotope, delayed responses to the cleanup of ^{233}U materials are to be avoided. Delayed housekeeping and cleanup activities will lead only to increased exposures to cleanup personnel when they finally enter the area of contamination.

4.1.4 Techniques for Internal Radiation Protection

Internal radiation protection is concerned with the control of intakes of radionuclides into the body. This is accomplished by keeping contamination in radiologically contaminated areas ALARA and using engineering and administrative controls to prevent the accidental deposition of radioactive material on or within the body.

There are three ways by which radioactive material may gain entry into the human body (Cember 1983):

1. Inhalation—by breathing radioactive dust and gas;
2. Ingestion—by drinking contaminated water, eating contaminated food, or by tacitly transferring radioactivity to the mouth; and

3. Absorption—through the intact skin or through wounds.

To prevent the entry of radioactive material into the body or deposition of contamination on skin, the radioactive source(s) must be enclosed or confined, or the environment has to be controlled by limiting access of workers or the public to areas where radioactive sources are kept or areas where contamination occurs.

4.1.4.1 Confinement

The simplest type of confinement and enclosure is achieved by limiting the handling of radioactive materials to well-defined, separated areas within a laboratory and by subisolating units such as trays. In cases where the potential for airborne contamination exists or where radioactive gases might be present, a ventilated hood is used. When the potential for personnel contamination is high or when a ventilation system for ventilated hoods is not available, glove boxes are used. The main function of a glove box is to isolate the contaminants from the environment by confining it to an enclosed volume. In operations involving ^{233}U-bearing materials, the glove boxes are designed to provide gamma shielding to reduce personnel exposure to the high-energy gamma rays associated with ^{208}Tl.

4.1.4.2 Environmental Control

Environmental control of hazards from radioactive contamination is achieved through proper design of the confinement systems, rooms, buildings, and facilities where radioactive material is used or stored. Good administrative controls are also essential. Proper procedures and work processes must be implemented. Ingress and egress of personnel and material from radiation areas must be carefully monitored to prevent the possible spread of contamination outside radiation areas. Decontaminability of working surfaces, floors, walls, piping; the means for monitoring for contamination; and a well-designed and functional ventilation system are very important in physical facilities where contamination exists or can occur.

4.1.4.3 Personnel Protection

Personnel protection can be provided by requiring radiation workers to wear appropriate protective clothing and respiratory protection devices (as necessary when airborne hazards are encountered) when performing work in radiation areas.

Protective clothing minimizes the potential for contamination to get on or in a worker's body. The types of protective clothing used may include laboratory coats, coveralls, caps, gloves, shoes, and shoe covers. The choice of protective clothing to be worn for a job depends on the type of job and types and levels of hazards. This determination is made by radiation protection and health and safety personnel. Protective clothing is always assumed contaminated after its use and is left in the radiation areas, where it is then either packaged for disposal or sent for laundering.

Respiratory protection is required when a person is likely to be exposed to a high concentration of airborne radioactivity. The type of respiratory protection used depends on the nature and levels of contaminants. These are two classifications of respiratory protection in radiological applications: filter type and supplied air masks. The choice of appropriate respiratory protection devices is made by the radiation protection and health and safety personnel.

4.1.4.4 Surface Contamination Limits

Contamination is the presence of undesirable radioactivity. *Undesirable* can be in the context of health or for technical reasons. For radiation protection, only the health aspects of contamination are considered. There are two categories of surface contamination: fixed and removable. Generally, fixed contamination cannot be transmitted to personnel, and the main hazard that results is the external radiation. The hazard from removable contamination is that it can spread and be transferred to the skin or be ingested. Removable contamination can also be resuspended and inhaled. The limits for both fixed and removable contamination are provided in 10 CFR Part 835, "Occupational Radiation Program" (U.S. DOE Dec. 14, 1993). In some cases, more restrictive site-specific limits for surface contamination are implemented.

4.1.4.5 Internal Exposure Monitoring

Monitoring for internal exposures includes prospective monitoring, retrospective monitoring, and dose assessments (Rich 1998). Prospective monitoring is performed to verify the integrity of radioactive material confinement systems and to detect accidental releases of radioactive material into the environment. Prospective monitoring would also indicate possible intakes of radionuclides by workers. Retrospective monitoring is aimed at measuring radioactive material in the body and in excretion collected from workers with known or suspected intakes, that is, in-vitro and in-vivo bioassay. Dose assessments (internal dose estimates) are then performed using bioassay data.

4.1.5 Personnel Radiation Experience (Kilorod Facility)

Personnel radiation experience from handling ^{233}U-bearing materials was obtained during the operations of the ORNL Kilorod Facility, the major operations of which are described in Sect. 3.7.1. Exposure of Kilorod Facility workers to radiation at the 38-ppm ^{232}U level was far below permissible limits.

A summary of personnel exposures from the Kilorod Project (Haws et al. August 1965) is provided in Tables 4.1*a* and 4.1*b*. Total body exposure of all personnel is reported for each of three quarterly periods of operation in Table 4.1*c*. Film-badge and pocket-meter exposures are reported for both supervisors and different process workers. Table 4.1*b* reports total-body radiation exposures for various operations involved with specific major Kilorod processes: denitration (feed material preparation), sol-gel (sintered solid preparation), and fuel-rod fabrication. Estimated radiation dose rates to operating personnel for various levels of shielding and ^{232}U content in fuel-element manufacturing are provided in Table 4.1*c*.

4.1.6 Nuclear Criticality Safety and Control

As previously indicated in Sect. 2.4, nuclear criticality safety of ^{233}U-bearing materials is maintained by a combination of material mass, geometry, and concentration controls. Criticality safety of ^{233}U is also maintained by limiting the neutron interaction with other fissionable materials within or adjacent to ^{233}U operations or storage. As discussed in Sect. 4.11, administrative controls, along with technical practices, are used to prevent accidental criticality. At facilities that use fissionable materials like ^{233}U, criticality safety programs are primarily directed at the avoidance of nuclear criticality accidents. Because the possibility of such accidents exists with life-threatening consequences, the implementation and use of detection systems, advanced planning, practice in planned emergency responses, and verification of readiness are mandated.

A ^{233}U criticality accident may lead to an excessive radiation dose. Consequently, a means of alerting personnel and a procedure for their prompt evacuation or other protective actions to limit their exposure to radiation are provided. To meet these objectives, two major systems are required for alleviating the consequences of a ^{233}U criticality accident: one for criticality accident alarms and another for emergency planning and response (commonly referred to as emergency preparedness). For each of these systems, a set of standard procedures were developed by the ANS and then accredited by the ANSI.

4.1.6.1 Criticality Alarm Systems

Requirements for criticality accident alarm systems are documented in ANSI/ANS-8.3-1997 (ANSI/ANS 1997*a*). This standard provides guidance for establishing and maintaining an alarm system to initiate personnel protective actions in the event of inadvertent criticality. The standard is applicable to all operations involving fissionable materials, including ^{233}U-bearing materials, in which inadvertent criticality can occur and cause personnel to receive unacceptable exposure to radiation. Requirements for criticality alarms covered in the standard include those affecting basic alarm system features, design criteria, tests, and employee training.

4.1.6.1.1 General Principles and Coverage

General principles and coverage specified in ANSI/ANS-8.3-1997 (ANSI/ANS 1997*a*) for criticality alarms that pertain to ^{233}U-bearing materials include the following:

- The purpose of a criticality alarm system is to reduce the risk of a criticality accident to personnel.
- Evaluation of risks from criticality accidents has led us to recognize that hazards may result from false alarms and subsequent interruption of facility operations and relocation of personnel.
- Equipment used in processing areas from which immediate evacuation is required are designed so that leaving that equipment will not introduce significant risk.
- The criteria for determining when a criticality alarm system needs to be installed is specified by applicable local site standards as well as by ANSI/ANS-8.3-1977.
- For a facility criticality evaluation, individual areas are considered unrelated and applicable to ^{233}U-bearing materials when: (1) no uncontrollable transfer of materials can occur between those areas, (2) the minimum separation between material in adjacent areas is 10 cm, and (3) the areal density of fissile material averaged over each individual area is less than 50 g/m^2.
- A criticality alarm system is installed in those facility areas where personnel would be subject to an excessive radiation dose. For this purpose, the maximum fission yield integrated over the duration of the accident does not exceed 2.0×10^{19} fissions. The basis for a different yield is documented.
- In areas in which criticality alarm coverage is required, a means is provided to detect a criticality accident and to signal that prompt protective action is required.

4.1.6.1.2 Criticality Alarm System Features

The ANSI/ANS-8.3-1997 standard (ANSI/ANS 1997*a*) specifies the following major features for a criticality alarm system:

- The signals from such an alarm system are uniform, distinctive from other alarms, and indicate a response of prompt evacuation or other protective actions.
- The signal generators of the alarm system are automatically and promptly actuated upon detection of a criticality accident. As required by emergency procedures, the signal generators continue to function after actuation, even if the radiation falls below the alarm point.
- For areas where personnel protective action is required following the detection of a criticality accident, the number and placement of criticality alarm signal generators are adequate to notify personnel promptly throughout those areas.
- Audio generators are designed to produce a total sound pressure level of at least 75 decibels (dB), but not less than 10 dB above the ambient noise level of each area for which audio coverage is to be provided. To avoid injury, audio generators do not produce an A-weighted sound level in excess of 115 dB at an individual's ear.
- In areas with very high audio background or mandatory hearing protection, criticality alarm systems incorporate the use of visual signals.
- Measures are taken to maximize criticality alarm system dependability by
  - — Avoiding false alarms through the use of redundant detector systems.
  - — Using portable instruments in special situations to augment an installed criticality accident alarm system. These situations include alarm system maintenance or testing, evacuation drills, and activities in areas not usually occupied by personnel.
  - — Installing emergency power supplies for alarm systems or portable instruments in process areas in which activities continue during power outages.
  - — Ensuring that the alarm system design has adequate sensitivity (discussed below).

4.1.6.1.3 Alarm System Design Criteria

Major design criteria are specified in the standard ANSI/ANS-8.3-1997 (ANSI/ANS 1997*a*) for a nuclear criticality alarm system. These include:

- *Reliability*. The system design minimizes the effects of nonuse, deterioration, power surges, and other adverse conditions and ensure reliable actuation of the criticality alarm signal and avoidance of false alarms. System components do not require frequent servicing, lubrication, or cleaning.

- *System vulnerability*. The alarm system components are located or protected to minimize damage from extreme conditions (e.g., fire, explosion, corrosive atmosphere, etc.). Major components are labeled.
- *Seismic tolerance*. The criticality alarm system remains operational following a seismic shock from an earthquake.
- *Failure warning*. The alarm system provides a visible or an audible warning signal to indicate system malfunction or the loss of primary power.
- *Response time*. The system design ensures that the criticality alarm signal is produced within 0.5 s of detector recognition of a criticality accident.
- *Detection capability*. The alarm system responds immediately to the minimum accident of concern. In areas where the material is processed or handled with only nominal shielding, the minimum accident is assumed to deliver the equivalent of an absorbed dose rate in air of 20 rad/min at 2 m from the reacting material. The basis for a minimum accident of concern is documented.
- *Detector sensitivity*. The system design ensures that alarm actuation occurs as a result of a minimum duration radiation transient of 1 ms. The alarm trip-point is set high enough such as to minimize the probability of an alarm from sources other than criticality and low enough such as to detect the minimum accident of concern.
- *Detector spacing*. The spacing of detectors is consistent with the selected alarm trip-point and specified detection capability. The location and spacing of detectors serve to minimize the effect of shielding caused by massive equipment or materials.

4.1.6.1.4 Alarm System Testing

Requirements in ANSI/ANS-8.3-1997 (ANSI/ANS 1997*a*) for tests, inspections, checks of criticality alarm systems cover the following:

- *Initial tests*. Initial system tests, inspections, and checks verify that the alarm system fabrication and installation were made according to design specifications.
- *Special tests*. Special tests and inspections are adequate to demonstrate system operability and are performed following modifications, repairs, or events that may affect system performance.

- *Response to radiation*. System response to radiation are periodically tested and measured to confirm continuing instrument performance. Tests are performed at least monthly, and records of these test must be maintained. Portions of this testing may be automated by system designs that incorporate self-checking features.
- *Periodic tests*. The entire alarm system is tested periodically and must establish that criticality alarm signals are functional throughout all areas where personnel would be subject to an excessive radiation dose. Each signal generator is tested annually.
- *Corrective action*. Without unnecessary delay, corrective action is taken when tests reveal inadequate performance.
- *Test procedures*. System test procedures minimize both false alarms and inadvertent initiation of emergency response. Following a test, an alarm system is returned immediately to normal operation.
- *Records*. To provide information on system operability and identify sources of failure, records of tests and corrective action for each criticality alarm system are maintained.

4.1.6.1.5 Employee Awareness and Training

To familiarize employees with criticality alarm system requirements, posted instructions, training, and criticality alarm drills are required by ANSI/ANS-8.3-1997 (ANSI/ANS 1997*a*). Instructions regarding response to criticality alarm signals are posted at strategic locations within areas requiring alarm coverage. Specific requirements and guidance for the training of facility employees, the training of visitors, and the conduct of criticality alarm drills are provided in the standard ANSI/ANS-8.19-1996 (Administrative Practices for Nuclear Criticality Safety) (ANSI/ANS 1996).

4.1.6.2 Emergency Planning and Response for Criticality Accidents

Where criticality alarm systems are installed, emergency procedures are established and maintained. Requirements for emergency planning and response to a criticality accident are documented in ANSI/ANS-8.23-1997 (ANSI/ANS 1997*b*). This standard provides guidance for emergency planning and response to a nuclear criticality accident for facilities outside reactors that process, store, or handle fissionable materials, including ^{233}U-bearing materials. The standard assumes that a criticality alarm system that complies with the previously described standard ANSI/ANS-8.3-1997 (ANSI/ANS 1997*a*) is in place. In addition, the emergency planning and response standard is not general in scope but focuses on those elements of planning and response needed specifically for a criticality accident. Requirements for emergency planning and response covered in the standard include those affecting personnel responsibilities, emergency-response planning, evacuation, rescue and stabilization, and training.

4.1.6.2.1 Responsibilities

Separate responsibilities for criticality emergency preparedness are given in standard ANSI/ANS-8.23-1997 (ANSI/ANS 1997*b*) for management and technical staff. Management establishes or provides the following:

- an emergency response plan;
- staff with relevant expertise;
- evacuation zones and routes;
- personnel assembly stations and personnel accounting;
- equipment and instrumentation for criticality accident response;
- training to ensure adequate readiness for criticality accident response;
- capability to perform radiological dose assessments in response to criticality accidents;
- communication system for coordinating site emergency activities;
- nuclear accident dosimeters, both personnel and fixed units, as specified in the standard ANCIEN-1969(R1981) (ANSI/ANS 1981);
- criticality alarm system equipment, as specified in the standard ANSI/ANS-8.3-1997 (ANSI/ANS 1997*a*); and
- documented procedures for activating emergency response when needed.

Responsibilities for a technical staff cover planning and emergency response. For planning, the technical staff:

- Identifies potential criticality accident locations and define immediate evacuation zones.
- Evaluates and characterizes potential criticality accidents.
- Determines instrumentation and equipment requirements for emergency response activities.
- Participates in the planning, conduct, and evaluation of emergency response drills.

During an emergency response, the technical staff:

- is available to advise and assist the emergency coordinator in responding to a criticality accident.
- conducts a radiological dose assessment appropriate for a criticality accident.

4.1.6.2.2 Emergency Response Planning

As required by standard ANSI/ANS-8.23-1997(ANSI/ANS 1997*b*), emergency response planning includes preparing a documented evaluation, providing appropriate equipment for responding to a criticality accident, and developing an emergency response plan.

The evaluation describes the bounds of a credible accident, an estimated fission yield, and an estimated likelihood of criticality recurrence. As a result of the evaluation, an immediate evacuation zone is established along with a maximum level of acceptable absorbed dose at its boundary.

Protective clothing and equipment is provided for personnel responding to a criticality accident. As standard ANSI/ANS-8.23-1997 (ANSI/ANS 1997*b*) indicates, such clothing and equipment may include the following:

- respiratory protection equipment,
- anticontamination suits,
- both high- and low-range gamma radiation detection equipment,
- neutron detection equipment.
- communications equipment, and
- personnel-monitoring devices (e.g., pocket dosimeters).

Monitoring equipment to determine if further evacuation is needed and to identify exposed individuals is provided at personnel assembly stations.

An emergency response plan is established and maintained if an evaluation indicates that a criticality accident from ^{233}U-bearing materials is creditable. The plan provides guidance to all personnel for responding to a criticality accident and may be activated on even a perception that a criticality accident is either developing, is occurring, or has occurred. The emergency response plan includes the following:

- functions of response personnel,
- recommended protective actions,

- equipment needed for criticality accident response, and
- identification of potential criticality accident locations and appropriate facility descriptions.

The plan also includes provisions for

- providing an emergency coordinator and coordinating with emergency organizations expected to provide emergency response assistance;
- assembly and accountability of personnel;
- activating emergency response;
- responding to concurrent emergencies (e.g., fire, personnel injury, security incidents);
- identifying exposed personnel, determining their radiation dose, and providing appropriate medical care;
- evaluating both radiological and other consequences of a criticality accident; and
- determining when emergency conditions no longer apply.

4.1.6.2.3 Evacuation

Requirements in standard ANSI/ANS-8.23-1997 (ANSI/ANS 1997*b*) for evacuating personnel include the following:

- *Personnel in the immediate evacuation zone*. During an evacuation, all personnel within the immediate evacuation zone evacuates immediately by planned routes to established assembly stations.
- *Monitoring in adjacent areas*. Radiation levels are monitored in occupied areas adjacent to the immediate evacuation zone after initiation of a criticality emergency response.
- *Monitoring at assembly stations*. Radiation levels are monitored periodically at assembly stations after initiation of a criticality emergency response.
- *Evacuation of nonemergency response personnel*. If the dose rates of personnel in the adjacent areas and at the assembly stations exceed 100 mrem/h, then nonemergency response personnel are evacuated from those areas.
- *Exits*. Sufficient exits from the immediate evacuation zone are provided to enable immediate evacuation of personnel. The latter takes precedence over contamination control or security considerations.
- *Identification of assembly stations*. Assembly stations are clearly labeled for identification.
- *Evacuation route planning*. Evacuation routes are planned to minimize risks from all potential hazards, including chemical, industrial, as well as radiation.

4.1.6.2.4 Reentry, Rescue, and Stabilization

The facility emergency coordinator is responsible for authorizing and coordinating reentry, rescue, and stabilization activities in response to a criticality emergency.

Reentry activities include:

- Provisions for continuous radiation monitoring and minimizing risks to personnel.
- Only individuals trained in emergency response.
- Preliminary radiological surveys that indicate acceptable exposure levels.
- A planned method for disabling any system that still may be critical. The method is implemented so as to minimize hazards to the reentry team.

If a personnel rescue is necessary, the activities for this effort

- is planned to address continuing or recurring criticality.
- does not expose rescuers to life-threatening radiation doses.
- is performed by more than one trained person if reentry into the immediate evacuation zone is required.

Requirements for achieving and ensuring a stabilized condition following a criticality accident include:

- The technical staff determines if the system is subcritical and advise management of the safe conditions for personnel and of methods to ensure stabilization of affected equipment.
- Methods for ensuring stabilization of ^{233}U materials may include
  - — placing the material in a favorable geometry,
  - — diluting the material below a critical concentration, and
  - — using a sufficient supply of neutron absorbers to maintain subcriticality.

4.1.6.2.5 Training, Exercises, and Evacuation Drills

Facilities that contain ^{233}U-bearing materials develop and annually provide a training program for responding to a criticality accident in accordance with the Criticality Training Standard ANSI/ANS-8.20-1991 (ANSI/ANS 1991). The criticality training program must be annually reviewed to ensure that appropriate changes or modifications are incorporated. This training program ensures the following objectives:

- Facility personnel who respond to a criticality accident alarm are able to recognize the alarm and know the facility layout, evacuation routes, location of personnel assembly stations, and personnel accountability and monitoring methods.
- Technical staff who respond to a criticality accident know their specific duties and responsibilities.
- Emergency response personnel who respond to a criticality accident know their specific duties and responsibilities, which include procedures, facility layout, and characteristics of a criticality accident.
- Reentry team personnel receive annual training on reentry procedures and facility hazards.
- Visitors are briefed on their responsibilities in responding to a criticality alarm or accident.

To reinforce emergency training and test capabilities of the emergency organizations and communication system, a criticality-accident-response exercise is conducted annually. Such exercises may include evacuation drills and have the following features:

- include a realistic simulated criticality-accident scenario with defined objectives for testing and reinforcing,
- be planned and controlled by individuals not directly participating in the exercise,
- include the participation of emergency response personnel, and
- a postexercise be followed by critique involving observers, planners/controllers, and representative participants.

Preannounced evacuation drills are conducted annually and include all personnel who work routinely within the immediate evacuation zone. These drills do not include false alarms. Drill response tests cover the same evacuation practices as used for a criticality accident.

4.1.7 References for Sect. 4.1

Listed below are the references cited in Sect. 4.1. This is followed by a list of additional resources that provide more detailed information on radiation protection practices for workers handling ^{233}U-bearing materials.

4.1.7.1 References Cited

American National Standards Institute/American Nuclear Society. 1981. *American National Standard Dosimetry for Criticality Accidents*, ANSIN13.3-1969 (R1981), American Nuclear Society, La Grange Park, Ill.

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Table 4.1*a*. Summary of whole-body exposure of all Kilorod personnel[a]

Personnel identification	Whole-body exposure (mrem)											
	3rd quarter 1963				4th quarter 1963				1st quarter 1964			
	Film badge Dc[b]		Pocket meter		Film badge Dc[b]		Pocket meter		Film badge Dc[b]		Pocket meter	
	Total	Average weekly	Range of daily values	Maximum weekly	Total	Average weekly	Range of daily values	Maximum weekly	Total	Average weekly	Range of daily values	Maximum weekly
Denitrator operators A	100[c]	15	0–25	35	340[d]	26	0–15	30				
Sol-gel operators												
B	220	17	0–100[e]	120[e]	240	18	0–20	30	310	24	0–40	100
A	100	15	0–25	35	(See denitrator above)				270	21	0–90[e]	130[e]
C	10	0.8	0–20	35	120	9	0–20	20	160	12	0–30	55
Rod fabrication												
operators	150	12	0–20	40	250	19	0–10	30	350	27	0–30	55
D	230	18	0–60	60	290	22	0–15	45	270	21	0–30	75
E	310	24	0–25	55	200	15	0–20	35	220	17	0–30	60
F	170	13	0–30	50	120	9	0–10	35	160	17	0–15	30
G												
Supervisors												
R	70	5	0–15	25	50	4	0–10	20	60	5	0–20	30
S	140[f]	11	0–20	35	20	7	0–5	5	60	5	0–15	25
T			0–40	40	80	6	0–15	75	70	5	0–20	20

[a] Based on Haws et al. August 1965.

[b] Dc = dose to the critical organ; in this case, the whole body. [This parameter is used in reference to the cadmium (Cd) disc filter placed in the film badge. Any radiation penetrating the Cd disc is measured as the dose the wearer received.]

[c] Worked first half of quarter in Cell 4 and last half at denitrator.

[d] Worked 7 weeks at denitrator and 6 in Cell 4.

[e] This high value believed to be result of dropping of meters. Operator did no unusual task during this week.

[f] Assigned to another project for the first four weeks in the quarter.

Table 4.1*b*. Whole-body radiation exposures per operation for the Kilorod Program[a]
(Source: Dc values from film badges)[b]

Process	Operation	Whole-body exposure (mrems/week)			
		3rd quarter (1963)	4th quarter (1963)	1st quarter (1964)	Average
Denitration	All operations	15	24[c] (7-week operation)	Shutdown	20
Sol-gel	Blending	22	9[c]	20	17
	Operations at crucible table	29	12[c]	25	22
Sol-gel total		51	21	45	39
Rod fabrication	Jaw crushing and sampling	3.2	5.1	7.3	5.1
	Ball milling	2.1	3.2	4.6	3.2
	Blending (powder)	5.3	8.4	12.0	8.4
	Compacting	16.0	20.0	19.0	18.0
	Scanning	4.8	3.0	3.4	3.4
	Transferring rod for scanning	0.5	0.4	0.5	0.4
	Welding	6.5	4.5	6.0	5.5
	Ultrasonic cleaning	2.2	1.6	2.1	1.9
	Leak testing and weighing	2.5	1.7	2.3	2.1
	Turco cleaning; smearing and loading into carrier	4.4	5.4	6.5	5.4
	Supervising	19.0	12.0	14.0	14.0
Rod fabrication total		66.5	65.3	77.7	67.4

[a] Based on Haws et al. August 1965.

[b] Dc values are doses measured to the critical organ, in this case the whole body.

[c] From sum of pocket-meter values.

Table 4.1*c*. Estimated radiation dose rates to operating personnel as a function of shielding and ^{232}U content for fuel element manufacture (Kilorod Project)[a]

(Glove box line producing 97 wt % ThO_2–3 wt % $^{233}UO_2$ by sol-gel and vibratory compaction; ^{233}U purified by solvent extraction)

Type of operation	Scale (kg oxide/d)	Shielding as equivalent of lead of shadow shield	Average post-purification time in sol-gel process average (d)	Average post-purification time in rod fabrication (d)	Weekly radiation dose rate to operators (mrem)		^{232}U content (ppm in ^{233}U)
					Hands	Body	
Kilorod facility	10	2	15	19	100	20	40
Batch facility	10	2	15	19	500	100	200
	10	2	7.5	12	500	100	500
	10	0	7.5	12	50	100	50
Semicontinuous facility	100	2	4.5	6	500	100	600
	100	0	4.5	6	50	100	50

[a] Based on Haws et al. August 1965.

4.2 SHIELDING MATERIALS AND TECHNIQUES

This section discusses the shielding requirements for ^{233}U-bearing materials. Separate discussions are provided on the proper materials and techniques needed to shield workers handling ^{233}U materials.

Like all radiation sources, ^{233}U-bearing materials need to be managed such as to keep the occupational radiation exposure associated with their storage, processing, and handling ALARA. The ALARA concept was developed by the NCRP as a measure to ensure the continuation of effective radiation-protection programs and practices that have kept exposures for monitored workers well below established limits. ALARA is also an essential requirement of radiation protection programs at all DOE sites.

Radioactive-shielding requirements for ^{233}U-bearing materials are strongly dependent on the concentration of the associated contaminant radionuclide ^{232}U and its daughter products. As previously discussed, ^{233}U materials also contain ^{232}U, whose decay products include alpha emitters and strong gamma emitters. The quantities of ^{232}U present with ^{233}U determine the radiation-shielding requirements for ^{233}U-bearing materials. The ^{232}U decay chain daughter product ^{208}Tl emits a 2.6-MeV gamma ray, which often requires massive shielding to protect workers—especially if the ^{232}U concentration is significant. Uranium-233 materials may contain concentrations of the ^{232}U impurity in concentrations sufficient such as to require special handling facilities (hot cells with gamma shielding) because of high radiation levels (see Sect. 4.1).

Because of the high radiation levels associated with the contaminant isotope, ^{232}U, radiation shielding of most ^{233}U-bearing material is generally handled by the design of the custodial facility. However, if the amount of material is sufficiently low, the packaging itself may provide sufficient shielding to satisfy requirements for ALARA conditions.

4.2.1 Radiation from ^{233}U-Bearing Materials

Often ^{233}U materials must be handled in shielded enclosures because of the hazard from their high external radiation. The exposure of workers to external radiation fields from ^{233}U materials depends upon several factors:

- surface area of the material source,
- distance from the source,

- self-shielding as a result of material density and geometry, and
- presence of external shielding.

Major nuclear characteristics of ^{232}U and ^{233}U, along with the isotopes of their decay chains, are discussed in Appendix B.

4.2.2 Radiological Characteristics

The combined nuclear characteristics of ^{233}U and ^{232}U account for some unique characteristics for systems containing ^{233}U-bearing materials. If ^{233}U is chemically purified to remove selected products from the decay chain of ^{232}U, the ^{233}U, with significant concentrations of ^{232}U, can be processed and converted into desired forms in gloveboxes and other enclosures without significant radiation exposure to workers. It takes time (days to weeks) for the gamma-emitting products of the ^{232}U decay chain to build up to high enough concentrations such that they require thick radiation shielding to protect workers. If significant (5 ppm or more) ^{232}U contamination remains in the system, radiation levels will build up with time and can dominate the radiation field of the processing activity. An example of the buildup and decay of ^{233}U with a high concentration (100 ppm) of ^{232}U impurities is provided in Fig. 4.2*a* (Forsberg and Krichinsky January 1998). This case shows both alpha activity and gamma exposure rate at 1 ft as a function of time calculated for 1 kg of ^{233}U (with 100 ppm of ^{232}U). The ^{233}U-bearing material is assumed to be a loose-pour powder of a density of 1.5 g/cm^3 that is contained in a 3-in.-diam by 6-in.-high can with 20-mil-thick steel walls. Four sets of peaks are illustrated in Fig. 4.2*a*. One set is from the alpha buildup and subsequent decrease of the decay products of ^{232}U. A second set shows the alpha buildup and subsequent decrease of the decay products of ^{233}U. A graph summarizing the alpha activity from both of the ^{232}U and ^{233}U curves is also shown. Finally, a fourth graph shows the variation of gamma-ray exposure rate with time since the uranium was purified. The latter curve indicates peaks in gamma exposure at 10 years and at 32,000 years following purification, and between these peaks a minimum dosage occurs at about 500 years following purification (Forsberg et al. Sept. 30, 1998).

4.2.3 Shielding Materials

While self-shielding and stainless steel containers provide a small reduction in the external radiation field of ^{233}U materials, the primary shielding materials used to protect workers and the public are lead and concrete. The basic physical and chemical characteristics of these shielding materials is provided in Table 4.2*a* (La Londe, Jr. and Janes 1961; Linde 1998; and Stewart 1988). As indicated previously, the amount of shielding material needs depends primarily on the amount of ^{232}U present in the ^{233}U inventory. Figure 4.2*b* shows the thickness of lead shielding that is needed to reduce worker dose from 1 kg of 35-d aged ^{233}U to 2 mrem/h at a distance of 1 m (Arnold 1962). Further discussion on exposure impacts from ^{233}U-bearing materials is given in Sect. 4.1.

A shielding parameter that is a useful indicator of external radiation exposure is the mean gamma-ray attenuation coefficient (μ). The reciprocal of the mean gamma-ray attenuation coefficient is the thickness of lead that would be required to reduce the external dose rate at a distance of 1 m from a point source in air to 5% of its unshielded value.

Table 4.2*b* lists the mean gamma-ray attenuation coefficients in lead and concrete for the radionuclides of the ^{233}U and ^{232}U decay chains (ANSI/ANS 1997 and Unger and Trubey May 1982). While these coefficients do not account for any shielding provided by the source itself, they are, nevertheless, useful indicators of whether external exposure would be an important concern for materials containing these isotopes. For example, external exposure is a much greater concern for ^{232}U and its short-lived decay products than for ^{233}U, primarily because the major decay products of the ^{232}U decay chain (namely, ^{212}Bi and ^{208}Tl) emit high intensities of high-energy photons (gamma rays), but ^{233}U emits only low intensities of low-energy photons (see Tables B.2 and B.4 of Appendix B). This conclusion is supported in part by the much lower mean gamma-ray attenuation coefficients for lead and concrete for the important ^{212}Bi and ^{208}Tl decay products of ^{232}U compared with the values listed for ^{233}U and its decay products. The higher attenuation coefficients for ^{233}U and its decay products indicate that self-shielding by a finite source would reduce the external dose by large factors.

Diluting ^{233}U with DU may help reduce shield-thickness requirements for ^{233}U materials. However, while the added uranium mass provides an additional degree of self-shielding, it can pose a substantially larger mass (and volume) to be shielded, which can effectively increase the overall shielding mass (Bereolos et al. April 1998).

Another useful shielding parameter is the mass attenuation coefficient, which is the ratio of the attenuation coefficient (μ) to the density (ρ) of the shielding material. Table 4.2*c* (ANSI/ANS 1997 and White May 13, 1952) gives the mass attenuation coefficients for photons of various energies in five different types of shielding materials, including uranium. For each material listed, the coefficients reported take into account the total affects of shielding attenuation from Compton scattering and absorption, photoelectric absorption, and pair production (Evans 1972). For the

2.6-MeV gamma radiation emitted by the ^{232}U decay daughter, ^{208}Tl, Table 4.2*c* shows a minimum value of the total mass attenuation coefficient for lead shielding.

4.2.4 References for Sect. 4.2

A list of cited references documenting the shielding requirements for ^{233}U-bearing materials is provided below. This is followed by a list of sources providing additional information.

4.2.4.1 References Cited

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Unger, L. M., and D. K. Trubey. May 1982. *Specific Gamma-Ray Dose Constants for Nuclides Important to Dosimetry and Radiological Assessment*, ORNL/RSIC-45, Rev. 1, Oak Ridge National Laboratory, Oak Ridge, Tenn.

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Blizard, E. P., and L. S. Abbott, eds. 1962. *Reactor Handbook*, Volume III, Part B ("Shielding"), Interscience Publishers, New York.

ORNL DWG 98-3897

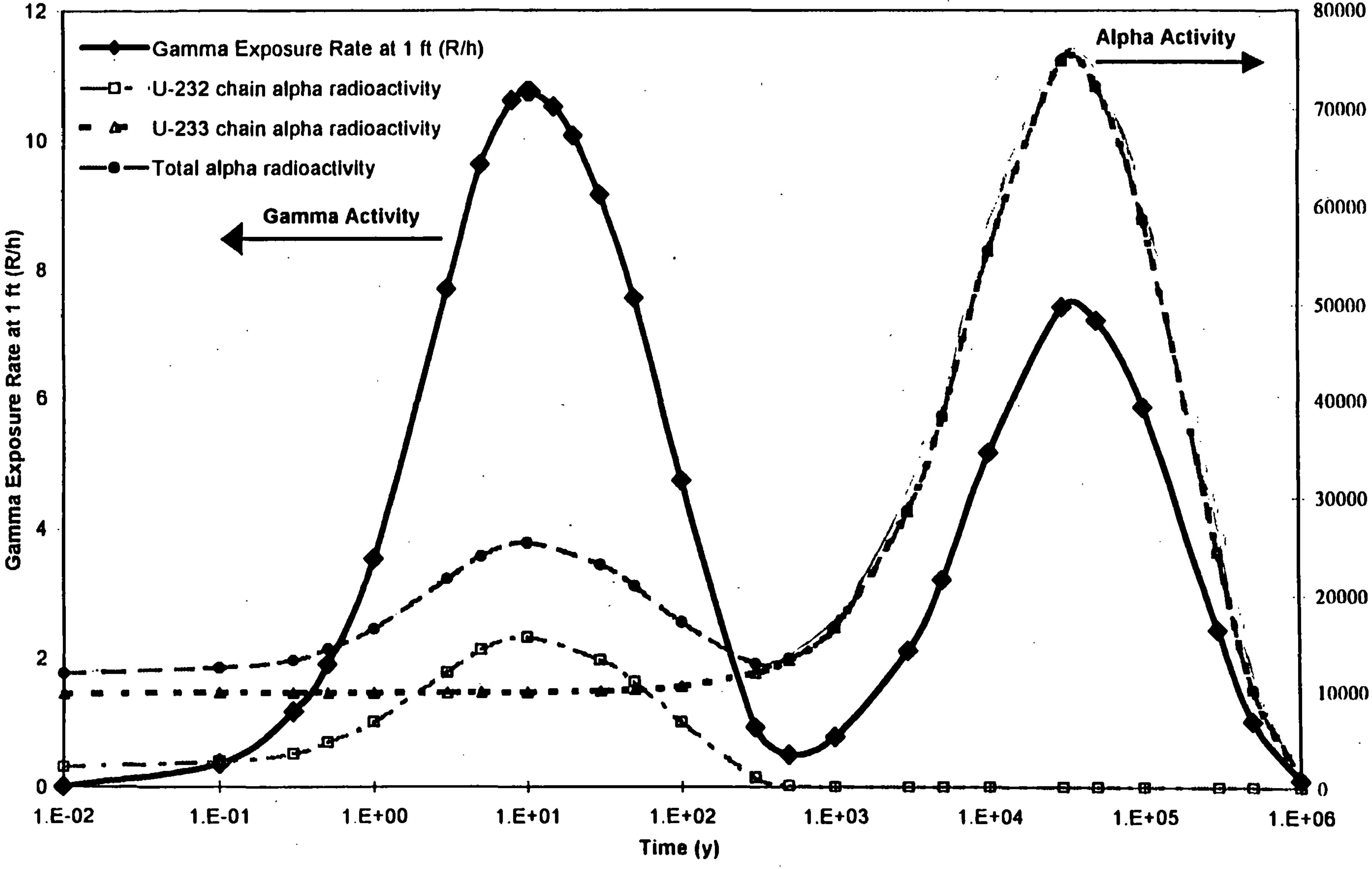

Fig. 4.2*a*. Alpha activity and gamma exposure rate at 1 ft as a function of time calculated for 1 kg ^{233}U (with 100 ppm ^{233}U) as a loose-pour powder (1.5 g/cm^3) contained in a 3-in. diam by 6-in. tall can with 20-mil-thick steel walls. *Courtesy of Forsberg and K[illegible]nsky January 1998.*

ORNL DWG 98-3898

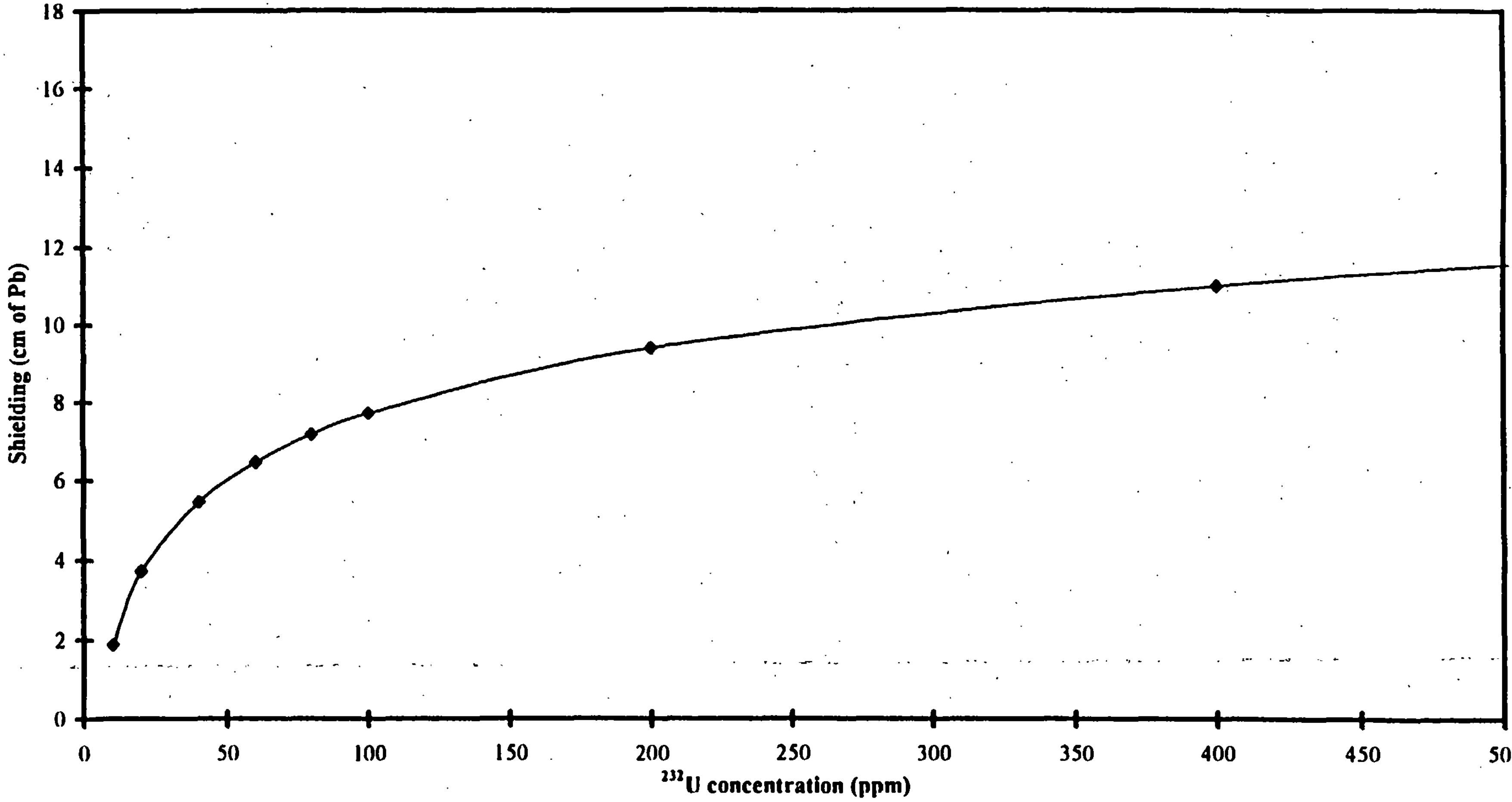

Fig. 4.2*b*. Lead shielding required for 1 kg of ^{233}U with various concentrations of ^{232}U. (Thickness needed to reduce worker dose from 1 kg of 35-d aged ^{233}U to 2 mR/h at a distance of 1 m.) *Adapted from Arnold 1962.*

Table 4.2*a*. Major physical and chemical characteristics of concrete and lead[a]		
Characteristic (units)	Concrete	Lead
Atomic mass (g)	Varies	207.2
Chemical formula	Varies[b]	Pb
Linear expansion coefficient (10^{-6} °C^{-1})	4–7	29.3
Specific heat (cal/g °C)	0.156	0.031
Specific gravity[c]	2.1–6.0	11.35
Tensile strength (kg/m^2)	77,300–443,000	12,700–16,100
Thermal conductivity (cal/s· cm°C)	0.002	0.083

[a] Sources: La Londe, Jr., and Janes 1961; Linde 1998; and Stewart 1988.

[b] Examples for shielding include serpentine (MgO–SiO_2), limonite ($2Fe_2O_3 \cdot 3H_2O$), Barytes ($BaSO_4$), Ilmenite (FeO–TiO_2), Magnetite (Fe_3O_4), and Hematite (Fe_2O_3).

[c] At 20°C. A typical average is 2.35.

Table 4.2*b*. Mean gamma-ray attenuation coefficients in concrete and lead for radionuclides of the ^{233}U and ^{232}U decay chains

Decay chain	Radionuclide	Attenuation coefficient (μ, cm^{-1})	
		Concrete[a]	Lead[b,c]
^{233}U	^{233}U	180	705.0
	^{229}Th	2.1	103.7
	^{225}Ra	28	304.4
	^{225}Ac	12	472.6
	^{221}Fr	3.5	11.522
	^{217}At	0.23	1.378
	^{213}Bi	0.47	2.094
	^{213}Po	0.56	1.002
	^{209}Tl	0.11	0.705
	^{209}Pb	[d]	[d]
	^{209}Bi	[e]	[e]
^{232}U	^{232}U	212	716.7
	^{228}Th	131	731.9
	^{224}Ra	2.6	8.124
	^{220}Rn	0.20	1.534
	^{216}Po	0.16	0.965
	^{212}Pb	0.34	11.112
	^{212}Bi	0.39	1.042
	^{212}Po	[d]	[d]
	^{208}Tl	0.08	0.555
	^{208}Pb	[e]	[e]

[a] Based on a plot of data for the mass attenuation coefficients of gamma radiation with coherent scattering for ordinary concrete, which are reported in Table B.1 (Appendix B) of ANSI/ANS-6.4-1997 (ANSI/ANS 1997). Also based on an assumed density of 2.35 g/cm^3 for ordinary concrete.

[b] Based on Unger and Trubey May 1982.

[c] This is the mean gamma-ray attenuation coefficient. For lead, the reciprocal of this value gives the thickness (cm) required to reduce the external gamma dose-equivalent rate at a distance of 1 m from a point source in air to 5% of its unshielded value.

[d] Not a gamma emitter.

[e] Stable.

Table 4.2*c*. Total mass attenuation coefficient (cm^2/g) for photons of various energies in selected materials

Photon energy (MeV)	Material[a]				
	Air[b]	Concrete[c]	Lead[d]	Uranium[d]	Water[d]
0.01	4.55E+00	2.66E+01	8.46E+01	1.18E+02	4.72E+00
0.015	1.45E+00	8.30E+00	8.33E+01	4.02E+01	1.50E+00
0.02	7.12E-01	3.65E+00	7.18E+01	5.76E+01	7.36E-01
0.03	3.35E-01	1.22E+00	2.35E+01	3.19E+01	3.55E-01
0.04	2.39E-01	6.12E-01	1.05E+01	1.43E+01	2.58E-01
0.05	2.03E-01	3.94E-01	5.73E+00	7.79E+00	2.21E-01
0.06	1.85E-01	2.96E-01	3.55E+00	4.73E+00	2.03E-01
0.08	1.66E-01	2.13E-01	1.66E+00	2.22E+00	1.83E-01
0.10	1.55E-01	1.78E-01	5.46E+00	1.26E+00	1.71E-01
0.15	1.36E-01	1.43E-01	1.92E+00	2.49E+00	1.51E-01
0.20	1.23E-01	1.27E-01	9.42E-01	1.20E+00	1.37E-01
0.30	1.07E-01	1.08E-01	3.78E-01	4.76E-01	1.19E-01
0.40	9.53E-02	9.63E-02	2.20E-01	2.73E-01	1.06E-01
0.50	8.69E-02	8.77E-02	1.52E-01	1.85E-01	9.67E-02
0.60	8.04E-02	8.10E-02	1.19E-01	1.42E-01	8.94E-02
0.80	7.06E-02	7.10E-02	8.66E-02	9.87E-02	7.86E-02
1.00	6.35E-02	6.38E-02	7.03E-02	7.79E-02	7.06E-02
1.50	5.16E-02	5.20E-02	5.23E-02	5.62E-02	5.76E-02
2.00	4.43E-02	4.48E-02	4.56E-02	4.83E-02	4.93E-02
3.00	3.57E-02	3.65E-02	4.13E-02	4.35E-02	3.96E-02
4.00	3.07E-02	3.19E-02	4.16E-02	4.38E-02	3.39E-02
5.00	2.75E-02	2.90E-02	4.30E-02	4.55E-02	3.02E-02
6.00	2.52E-02	2.70E-02	4.45E-02	4.71E-02	2.77E-02
8.00	2.22E-02	2.45E-02	4.71E-02	5.01E-02	2.42E-02
10.00	2.04E-02	2.31E-02	5.03E-02	5.31E-02	2.21E-02
15.00	1.80E-02	2.15E-02	5.67E-02	6.00E-02	1.94E-02
20.00	1.69E-02	2.11E-02	6.25E-02	6.60E-02	1.80E-02
30.00	1.63E-02	2.11E-02	7.09E-02	7.54E-02	1.70E-02
40.00	1.60E-02	2.13E-02	7.73E-02	8.20E-02	1.67E-02
50.00	1.61E-02	2.17E-02	8.17E-02	8.65E-02	1.67E-02
60.00	1.62E-02	2.22E-02	8.55E-02	9.06E-02	1.68E-02
80.00	1.66E-02	2.30E-02	9.07E-02	9.61E-02	1.70E-02
100.00	1.69E-02	2.37E-02	9.45E-02	1.00E-01	1.73E-02

[a] For purposes of estimating the corresponding linear attenuation coefficient [μ(cm^{-1})] of these materials, the following densities should be used:

- air: 1.21 × 10^{-3} g/cm^3 (at 20°C)
- concrete: 2.35 g/cm^3
- lead: 11.35 g/cm^3
- uranium: 18.95 g/cm^3
- water: 1.00 g/cm^3

[b] Based on 20°C as reported in White May 13, 1952.

[c] Based on information reported for coherent scattering in ANSI/ANS-6.4-1997 (ANSI/ANS 1997) except for data associated with photon energies exceeding 30 MeV, which are based on White May 13, 1952.

[d] Based on information reported in White May 13, 1952.

4.3 RADON CONTROL

This section discusses measures taken in the control of radon emissions from ^{233}U-bearing materials. Specific attention is given to the process for absorbing and removing ^{220}Rn from ^{232}U decay. An overall basic radon control system is discussed, and this discussion is followed by a description of the features of the equipment used.

4.3.1 Discussion

Off-gases from ^{233}U operations are passed through systems designed to eliminate both the inert radon gas and particulates contaminated with other radioisotopes before their discharge to the environment. HEPA filters can be used for capturing suspended particles; however, these will have no effect on radon or other inert gases passing through such a system. Methods considered to be viable for ^{220}Rn reduction and for other inert radioactive gases include decay during retention and adsorption onto activated charcoal or other suitable material. Discussion of filtration for particulates and noxious gases is discussed in Sect. 4.4.

Ackley (April 1975) reviewed radon filtration concepts and identified a mathematical treatment of adsorber design using activated charcoal. Ackley derived an application of gas-chromatography mechanics from publications by others which described the holdup and decay of radioactive noble gases onto activated charcoal. The result of this approach was an equation set designed to allow the prediction of radon removal in an air stream using a combination of known and estimated parameters.

Factors that affect radon adsorption from a flowing stream of gas onto charcoal include (a) the properties of the charcoal used such as granularity, material type, and porosity; (b) the concentration of water or other competing molecules in the gas; (c) the rate of movement of the gas through the charcoal; and (d) the half-life of the radon isotope being evaluated. The number of *radon-affinitive* adsorber sites in activated charcoal is expected to be extremely large, with published values on the order of 6×10^{21} cm^{-3} (Blue, Jarzemba, and Fentiman 1995). The collective term *adsorber sites* is used to describe the overall adsorptive capacity of charcoal and is empirically related to the number of atoms, or molecules, that can be retained within a fixed volume of charcoal. Given such a large number of available sites and the high specific activity of ^{220}Rn, the effect of input concentration on adsorption capability should be small over a very broad range of concentration.

More recently, Coleman (March 1999) performed experiments to evaluate the effectiveness of activated charcoal for the removal of ^{220}Rn in process off-gas from the MSRE at ORNL during remediation tasks. A series of bench-scale tests were performed at linear flow rates of 20, 35, 47, and 65 ft/min with an input concentration of ^{220}Rn on the order of 10^4 pCi/L in air. In addition, two tests were performed at the MSRE facility by flowing helium through an auxiliary charcoal bed, in which a deposit of ^{233}U and ^{232}U was located. The MSRE tests were performed specifically so that the filtration effectiveness could be evaluated with a relatively high concentration of ^{220}Rn. In fact, the input concentration during these facility measurements was about 10^{10} pCi/L. The charcoal used for the tests was coconut-based Calgon Carbon polychlorinated biphenyl (PCB)-6 × 16 with a 6 × 16 mesh sizing and a density of 0.41 g/cm^3.

A summary of tenth-value layers (TVLs) determined during the study is listed in Table 4.3*a* and shown graphically in Fig. 4.3*a* as a function of flow velocity. As given, the TVL is the thickness of charcoal that reduced the concentration of ^{220}Rn by a factor of 100. Note that the adsorptive effectiveness of the charcoal was not affected by the concentration of ^{220}Rn used, and the two measurements collected at 35 ft/min indicated an unexpected reduction in filtration effectiveness at that velocity. The reason for this finding was not discussed, but it could presumably have been caused by a flow condition specific to the sample geometry used during the experiments. To calculate the concentration reduction factor for a filter design using these data, the following equation can be used:

$$R = R_0\left(\frac{1}{10}\right)^{\frac{x}{T}},$$

where R_0 is the concentration of ^{220}Rn input to the charcoal bed, T is the TVL at the velocity of interest, x is the thickness of charcoal in the direction of flow, and R is the concentration at the output.

As a comparison, the method presented by Ackley (April 1975) was used to estimate ^{220}Rn TVL values for some of the flow rates measured by Coleman (March 1999). The results indicated that the calculated values did not match very well with those that were measured. For example, the TVLs that would be predicted using Ackley's model at flow velocities of 20, 35, and 65 ft/min would be about 3, 5, and 9 in., respectively, indicating a relatively constant increase of TVL with velocity. Conversely, the experimentally measured values at these same flow rates were about 4, 6, and 4 in. and did not follow a linear pattern. It should be mentioned that the chromatographic data referenced in Ackley (April 1975) could easily be altered by the selection of different data sets and, as such, could alter the comparison of calculated to measured data.

4.3.2 Filter Design

Coleman (March 1999) discussed a charcoal filter design that had been proposed to capture ^{220}Rn during remediation operations at the MSRE. Although this design is specific to applications at the facility, the same logic could be used when evaluating a filter for other purposes. As an example case, the proposed design and associated evaluation are included herein as a general guide of some of the parameters that should be considered.

A design schematic for the proposed housing is shown in Fig. 4.3*b* for reference. The design is that of a charcoal column in the shape of a right-circular cylinder having a diameter of 17 in. and a length of 3 ft. For this design, a flow rate through the filter of 1 ft^3/min would be expected to produce an average linear velocity of 0.63 ft/min. An important consideration for any filter design is the spatial uniformity of flow velocity across the face of the unit. For a granular bed, such as one made of charcoal pellets, the flow will typically be nondiffuse at the entrance. In most cases, the flow will become uniform across the bed by natural diffusion, but it could also be necessary to add flow barriers which prevent tunneling, or short-circuiting, from occurring.

4.3.2.1 Filtration Effectiveness

Off-gas and suspended residuals would presumably be delivered through a particulate filtration system and then be passed through a charcoal filter for removal of ^{220}Rn. To evaluate the example filter bed, the measured TVL values were used to estimate the expected decontamination factor as a function of input flow velocity. The results of these intermediate calculations are listed in Table 4.3*a*. Review of the results indicate a relatively constant TVL of about 4 in. at flow rates ranging from 20 to 65 ft/min, with a single exception occurring at a flow rate of 35 ft/min. For reasons unknown, the TVL at this velocity was about 50% larger than at the other measured rates. This could have been because of any number of reasons, but the most probable one was that some type of flow-pattern transition was occurring at this velocity inside the 4.8-cm-diam, charcoal-filled tube. Since this effect could not be explained, a TVL value of 6 in. would apparently be a conservative point when analyzing the effectiveness of a proposed filter. Using this value and calculating a reduction factor for 3 ft of charcoal give a result of 1 × 10^{-6}.

4.3.2.2 Filter Capacity

Coleman (March 1999) also evaluated the expected capacity, or lifetime, of a charcoal filter by considering its adsorptive capacity, which was asserted to be a direct function of the adsorber site density of the material. In addition, the effect of humidity on capacity and performance was also briefly discussed.

Based on data presented by Watson et al. (1988) and Gray and Windham (1987), Blue, Jarzemba, and Fentiman (1995) determined that a reasonable estimate for the number of adsorption sites in activated charcoal would be about 6×10^{21} cm^{-3}. This value was based on measurements of ^{222}Rn adsorption using U.S. Environmental Protection Agency (EPA) measurement canisters. Unfortunately, the specific type of charcoal used when determining this factor was not given. However, coconut-based forms are common for this application.

Considering the 55-s half-life of ^{220}Rn, there will be 2.9×10^{12} atoms per Ci of the isotope. According to Blue, Jarzemba, and Fentiman (1995), the adsorptive ability of a charcoal volume will decrease with the number of available sites, but no appreciable effect will be expected until the number of sites expended comes within two orders of magnitude of the total number originally available. The overall effectiveness of the proposed filter can be approximated by assuming that all ^{220}Rn entering the system will be adsorbed within the first inch of charcoal. This is a somewhat conservative assumption, since all radon entering the bed will certainly not be adsorbed within the first inch.

Applying this concept to the filter design described in Sect. 4.3.2.1, a 1-in.-thick layer of charcoal within the cylinder would equate to a total number of available adsorber sites before operation of about 1×10^{25}. Assume now that the adsorptive ability for the entire filter bed would begin at about the time that the number of adsorption sites in the first 1-in. layer were depleted by 1%, or down to 9.9×10^{24} sites. For this to occur, a total of about 1×10^{23} sites would need to be exhausted. Since there would be one radon atom for each site, this would equate to a total adsorbed activity of about 3×10^{10} Ci. Rounding down gives a total estimated capacity, before the onset of degradation, of about 10^{10} Ci. Note that this is the amount of adsorbed activity that would begin to degrade the overall effectiveness of the proposed filter. The overall filtration effectiveness would be expected to decrease past this point, but the effectiveness would still be expected to remain relatively high for quite some time.

4.3.2.3 Effects of Humidity

The previous analysis of capacity did not account for adsorption sites being depleted by means other than radon. According to Coleman (March 1999), a primary concern for a charcoal bed when filtering air is the competition for sites by water molecules. Humid conditions should be avoided since operation in dry atmospheres would alleviate concerns for the effect of water on the charcoal bed. Since such avoidance is not always possible, proper consideration needs to be given to water effects when predicting filter performance. It should be noted that most of the measurements previously discussed were collected at a room temperature of about 70°F and a relative humidity range of 30 to 60%.

At standard temperature and pressure, there would be about 4 μg of water for every cm^3 of air when the relative humidity is 50% which equates to about 10^{17} molecules of water per cm^3. Unlike ^{220}Rn, which will exhaust sites following decay because its daughter products are not mobile, water will be continually adsorbed and desorbed until a steady-state condition is reached. According to Blue, Jarzemba, and Fentiman (1995), 50% relative humidity in air at standard conditions will result in about 5×10^{20} sites per cm^3 of charcoal being occupied by water molecules after steady state has been reached. Considering that there are about 6×10^{21} cm^{-3} total sites available, this equates to about 10% potentially being depleted by the water at 50% relative humidity.

Operation with moist air at higher temperatures, where the absolute humidity could be higher, could potentially degrade adsorptive ability significantly. Note, however, that even under conditions of saturation humidity, radon will still compete for sites and that the filtration ability for radon will not be reduced to zero by the presence of water. As an example of this effect, Pojer et al. (1990) demonstrated by laboratory measurements that the adsorptive ability of charcoal for ^{222}Rn was reduced by about a factor of 3 when the relative humidity was increased from 15 up to 90% at a room temperature of 35°C. As a point of comparison, it was also demonstrated during the study that a change in relative humidity from 20 up to 50% decreased the effective performance by less than 20% at a room temperature of about 20°C.

4.3.3 References for Sect. 4.3

A list of cited references documenting radon control requirements for ^{233}U-bearing materials is provided below. This is followed by a list of sources providing additional information.

4.3.3.1 References Cited

Ackley, R. D. April 1975. *Removal of Radon-220 from HTGR Fuel Reprocessing and Refabrication Off-Gas Streams by Adsorption (Based on Literature Survey)*, ORNL-TM-4883, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Blue, T. E., M. S. Jarzemba, and A. W. Fentiman. 1995. "Steady-State Response of a Charcoal Bed to Radon in Flowing Air with Water Vapor," *Health Physics* 68(6), 809–16.

Coleman, R. L. March 1999. *Use of Activated charcoal for ^{220}Rn Adsorption During Remediation of the Uranium Deposit in the Auxiliary Charcoal Bed at the Molten Salt Reactor Experiment Facility*, ORNL/TM-13733, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Gray, D. J., and S. T. Windham. 1987. *EERF Standard Operating Procedure for Rn-222 Measurement Using Charcoal Canisters*, EPA 520-5-005, EPA Office of Radiation Programs, Montgomery, Ala.

Pojer, P. M., et al. 1990. "Performance of a Diffusion Barrier Charcoal Adsorption ^{222}Rn Monitor Under Conditions of Varying Humidity and Temperature," *Health Physics* 58(1), 13–19, Pergamon Press, Elmsford, N.Y.

Watson, J. E., et al. 1988. "Survey of ^{222}Rn in North Carolina Homes," *Health Physics* 55, 71–75, New York.

4.3.3.2 Supplemental Resources

Benedict, M., T. H. Pigford, and H. W. Levi. 1981. *Nuclear Chemical Engineering*, 2d ed., McGraw Hill, New York.

ORNL DWG 98-8103

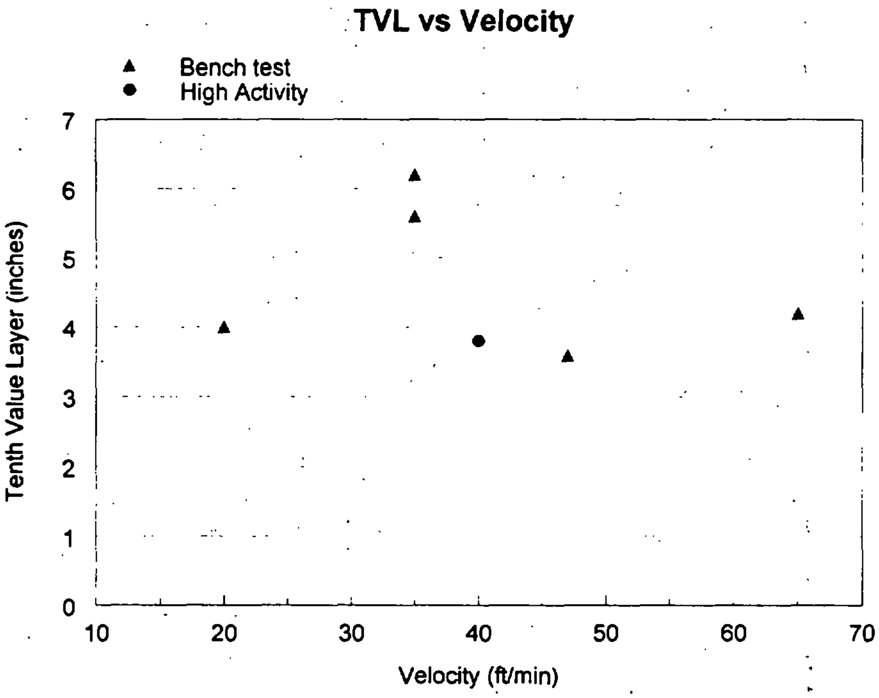

Fig. 4.3*a*. Plot of measured TVL values vs flow velocity. *From Coleman March 1999.*

ORNL DWG 98-8104

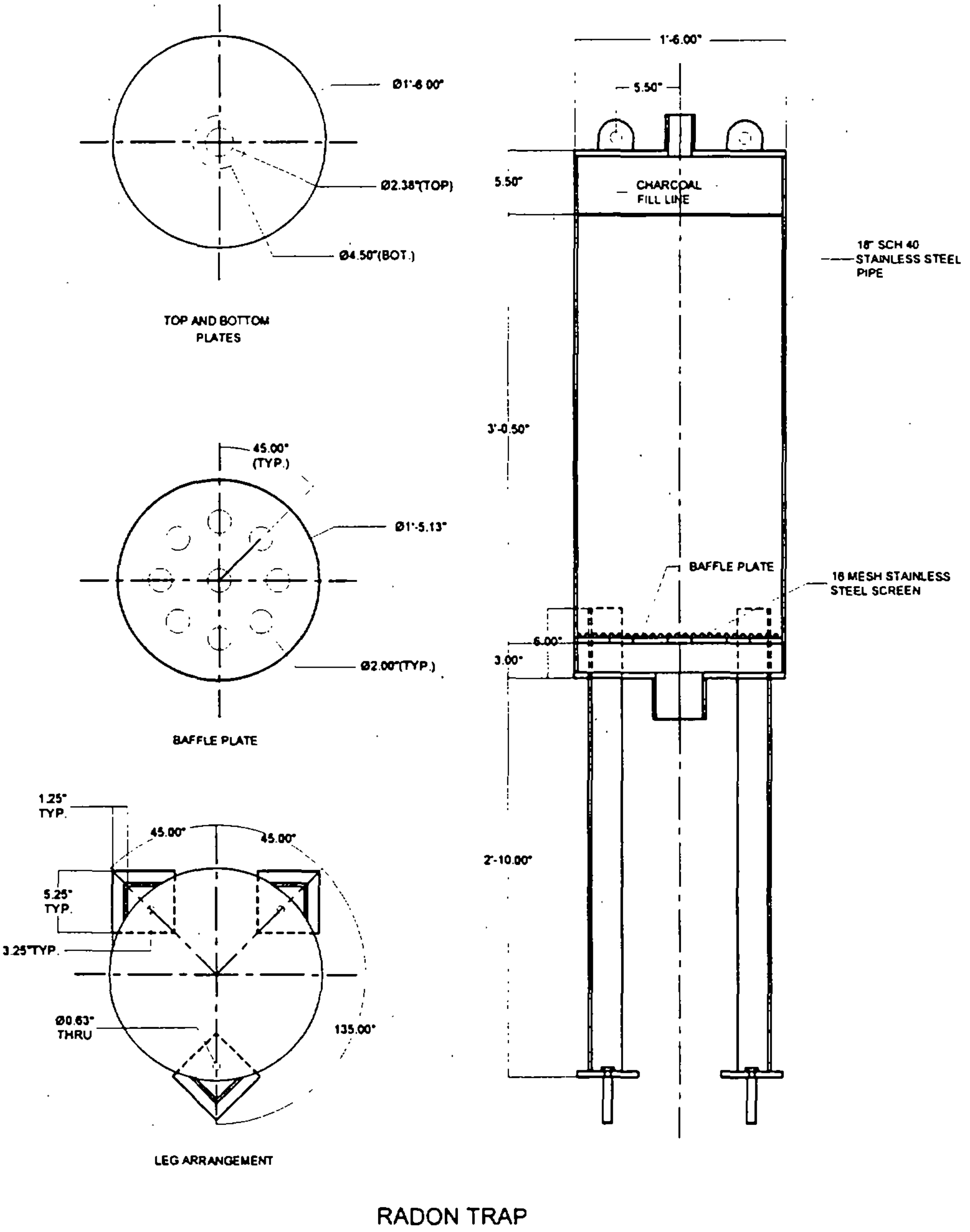

Fig. 4.3*b*. Schematic of a proposed charcoal filter to be used during uranium remediation operations. *From Coleman March 1999.*

Table 4.3*a*. Summary of measured tenth-value layers (TVL) for ^{220}Rn passing through activated charcoal[a]

Relative input concentration[b]	Flow velocity (ft/min)	TVL (in.)	Reduction factor[c]
Low	20	4.0	1.0E-09
Low	35[d]	5.6	3.7E-07
Low	35[d]	6.0	1.0E-06
High	40	3.8	3.4E-10
Low	47	3.6	1.0E-10
Low	65	4.2	2.7E-09

[a] Based on Coleman March 1999.

[b] Data collected with either a low (bench-scale) ^{220}Rn concentration or a high ^{220}Rn concentration.

[c] Predicted reduction factor for the proposed filter design (i.e., a 3-ft-long column of Calgon Carbon PCB-6 × 16 activated coconut-based charcoal).

[d] Two separate measurements were collected at a velocity of 35 ft/min to confirm the larger TVL value.

4.4 OFF-GAS FILTRATION

This section discusses the off-gas filtration system needed in the processing of ^{233}U-bearing materials. The basic principles and requirements for an off-gas filtration system are discussed, and this is followed by a description of the equipment used.

The concentration of ^{232}U in low-quality ^{233}U impacts the requirements of off-gas systems for processing ^{233}U-bearing materials. In its decay chain (Fig. 2.1*c*, Sect. 2.1), ^{232}U decays through several isotopes to the noble (and inert) gas ^{220}Rn, which eventually decays to ^{208}Tl, a radionuclide that emits a 2.6-MeV gamma ray. As an inert gas, ^{220}Rn can pass through commonly used HEPA filters and then decay to ^{208}Tl. To prevent this from happening in a process system, the off-gas system must contain charcoal beds, delay lines, filters, or other special equipment to hold the radon in the system until it decays and attaches to a solid material that can be removed from the off-gas with a HEPA filter (Forsberg et al. Sept. 30, 1998).

4.4.1 Off-Gas Filtration System Features for Radon Removal

An off-gas treatment system is designed to remove radioactive particles from the gas stream(s) [or off-gas(es)] generated by a production process. This discussion addresses off-gas treatment systems in those processes involving ^{233}U-bearing materials. Off-gas equipment will clean a process gas before releasing it to a common ventilation system. Off-gases are quenched, filtered, scrubbed, and vented through HEPA filtration. Typical contaminants removed by off-gas systems include ^{220}Rn, water vapor, NO_x, SO_x, and particulates. The particulates are sometimes returned to the process. The specific control of ^{220}Rn is discussed in Sect. 4.3.

A typical off-gas system consists of filters to collect radioactive particles and auxiliary equipment to condition the off-gas in order that it will not be harmful to the filters. Figure 4.4*a* shows such a system consisting of an entrainment separator, deep-bed filters, a steam heater, pocket filters, blower, and a stack (Hylton Dec. 11, 1952).

A chamber packed with a separator and having a 1-ft^2 (930 cm^3) cross section serves to collect liquid entrained in the off-gas. The deep-bed filters serve to collect solid particles. These are packed with glass fiber and are located downstream from the separator. Beyond the deep-bed filters is a steam heating chamber to prevent any off-gas condensate from collecting on a multistage set of pocket filters. The latter filters have layers of different size filter media in series to remove any particles that escape the deep-bed filters. The end of the system has a blower that discharges the remaining off-gas via a stack to the atmosphere.

In practice, an off-gas system is a component of a facility ventilation system. An example of such a system is provided in Fig. 4.4b, which shows the ORNL Building 3019 interconnections between the process off-gas and the cell ventilation system of the pilot plant (Horton et al. March 1972).

4.4.2 Off-Gas Filtration System Features for Nuclear Fuel Reprocessing

The reprocessing of ^{233}U-bearing fuels also involves the treatment of other off-gases besides ^{220}Rn. Off-gas systems for ^{233}U fuel reprocessing are discussed in detail in other sources (Aßmann et al. 1982 and Benedict 1981). Such systems deal with the treatment of fission product off-gases. When ^{233}U fuels are dissolved in acid, gaseous fission products are liberated into the off-gases. In addition, aerosols in the form of droplets are formed. Significant constituents of the off-gases may include nitrous oxides and aerosols along with the radioactive isotopes of iodine, ruthenium, krypton, cesium, strontium, xenon, radon, and tritium. Such gaseous contaminants are liberated into the off-gas partly during the cutting open (shearing) of the fuel elements and partly during the phase in which those elements are dissolved in acid (Aßmann et al. 1982).

4.4.3 References for Section 4.4

A list of cited references documenting the requirements for off-gas filtration of ^{233}U-bearing materials is provided below. This is followed by a list of sources providing additional information.

4.4.3.1 References Cited

Aßmann, H., et al. 1982. "Reprocessing of Spent ^{232}Th–^{233}U Fuels," pp. 276–351 in *Gmelin Handbook of Inorganic Chemistry*, 8th ed., Supplement Vol. A4, "Uranium, System 55," Sect. 2.4, Springer-Verlag, New York.

Benedict, M., T. H. Pigford, and H. W. Levi. 1981. *Nuclear Chemical Engineering*, 2d ed., McGraw-Hill, New York.

Forsberg, C. W., et al. Sept. 30, 1998. *Disposition Options for Uranium-233*, ORNL/TM-13553, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Horton, R. W., et al. March 1972. *Safety Analysis: LWBR Support Program in Building 3019 Pilot Plant*, ORNL/TM-3567, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Hylton, C. D. Dec. 11, 1952. *Separation of ^{233}U in the ORNL Pilot Plant*, ORNL-1425, Oak Ridge National Laboratory, Oak Ridge, Tenn.

4.4.3.2 Supplemental Resources

Hartman, H. F., et al. Sept. 14, 1984. *Final Safety Analysis Report for the Consolidated Edison Uranium Solidification Program (CEUSP) Facility*, ORNL/ENG/INF-83/2, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Rich, B. L., et al. June 1988. *Health Physics Manual of Good Practices for Uranium Facilities*, EGG-2530, Idaho National Engineering Laboratory, Idaho Falls, Idaho. (Table 5.1 of this reference provides a summary of filter characteristics.)

ORNL DWG 98-8117

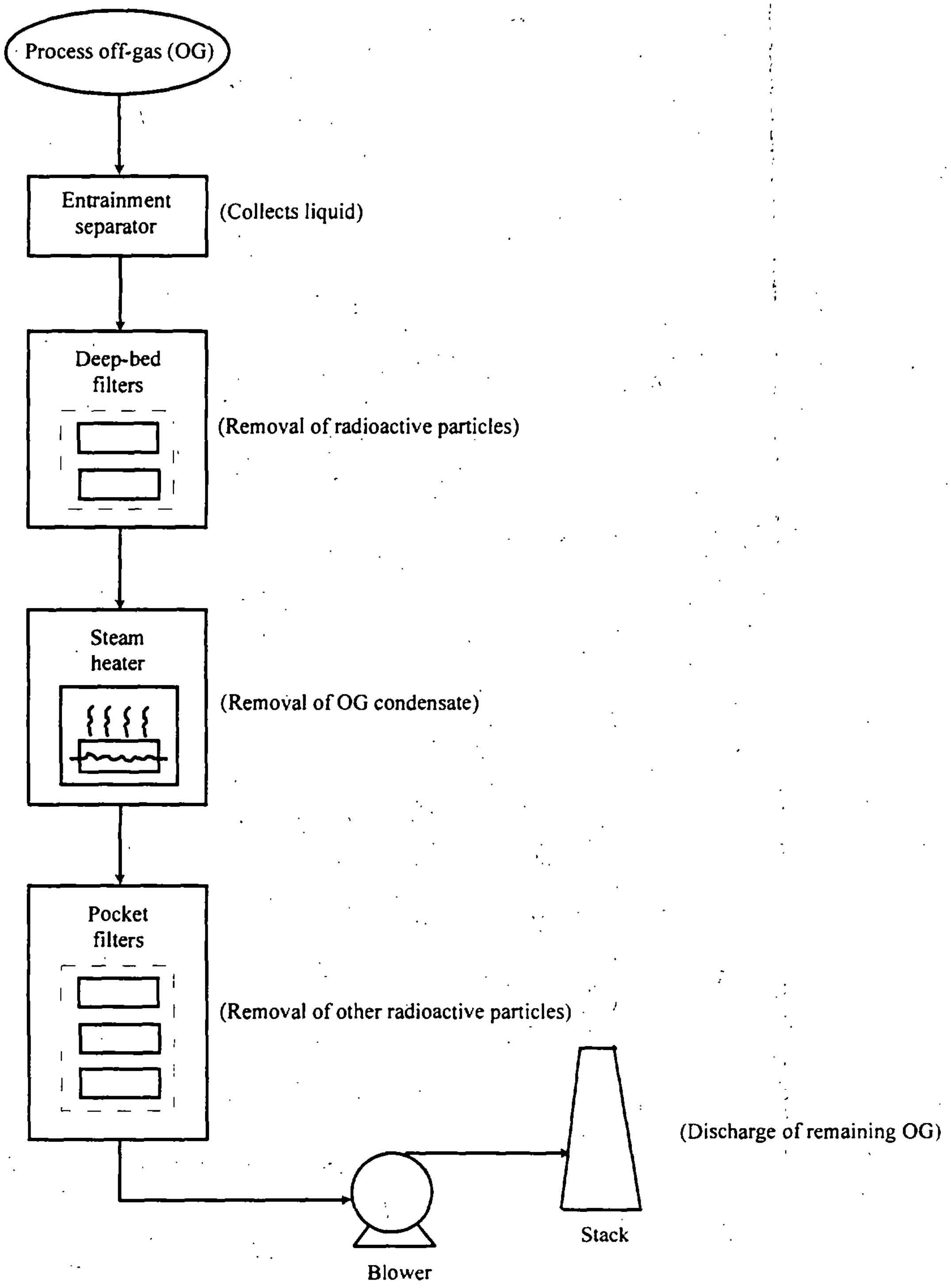

Fig. 4.4*a*. Typical off-gas treatment system.

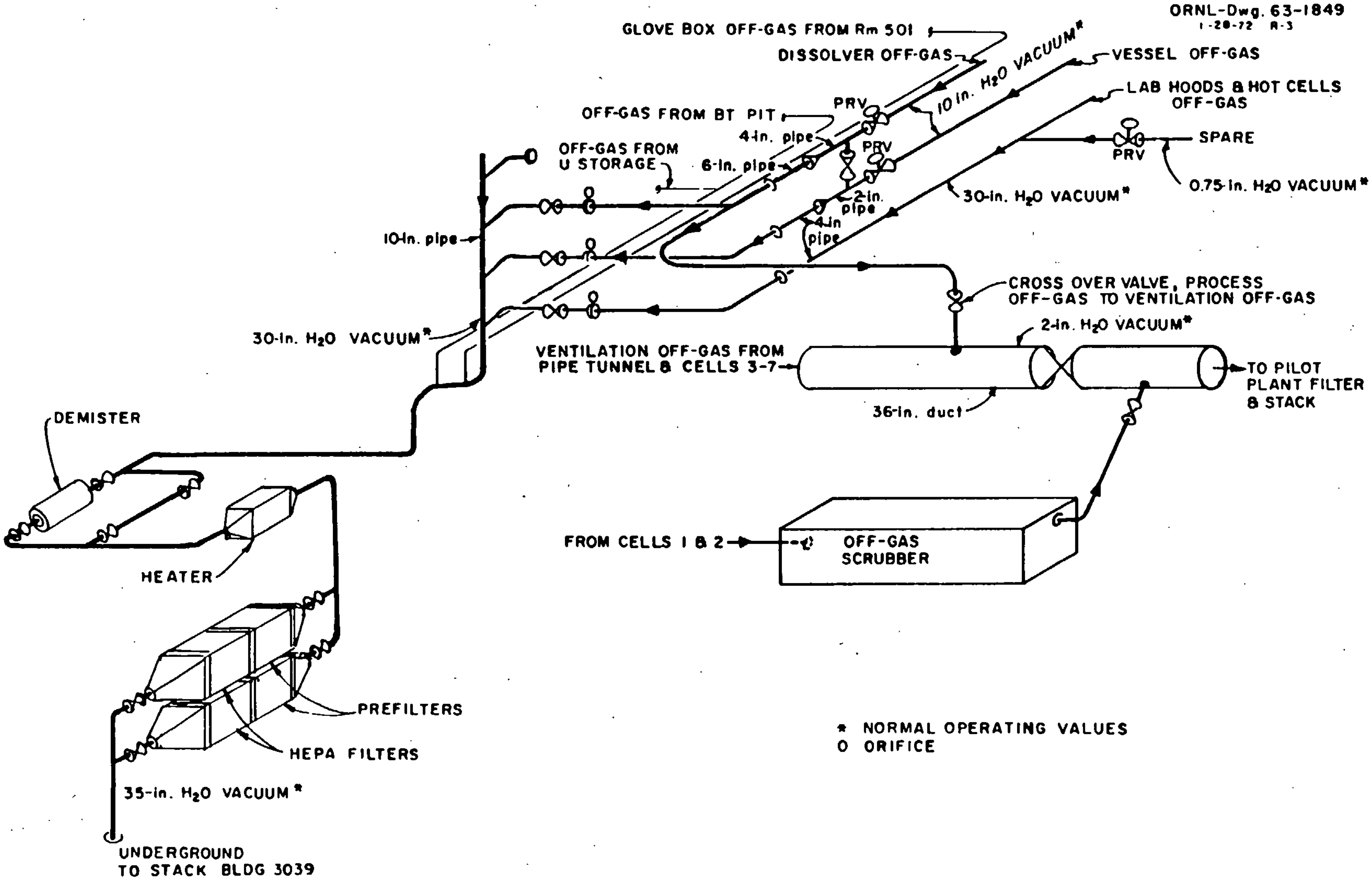

Fig. 4.4*b*. ORNL Building 3019 interconnections between process off-gas system and Pilot Plant cell ventilation system. *From Horton et al. March 1972.*

4.5 GENERAL CONTAINMENT PRINCIPLES AND REQUIREMENTS

As indicated in the tables of Sect. 2, the specific activity (radioactivity per unit mass) of ^{233}U is about 4500 times greater than ^{235}U and approximately 15% of that for ^{239}Pu. This difference would suggest that the confinement requirements for ^{233}U would lie between those for these two fissile materials and perhaps closer to ^{239}Pu than ^{235}U. In addition, the shielding requirements for ^{233}U-bearing materials are complicated by the presence (and degree of concentration) of the associated ^{232}U radionuclide. As indicated in Sect. 2, the presence of ^{232}U and its decay products contribute additional radioactivity. In fact, most of the penetrating beta-gamma radioactivity associated with ^{233}U-bearing materials results from the decay daughters of ^{232}U.

The high specific activity of ^{233}U (and that of ^{232}U) results from the emission of high-energy alpha particles. As a result of momentum conservation, the parent nuclides associated with these decay emissions respond to the ejection of the alpha particles by recoiling. This phenomenon is referred to as "alpha recoil." For materials having concentrations of ^{232}U that are greater than 10 ppm, the net effect of the alpha recoil is a migration of the radioactive parents. It is against this background of alpha recoil that confinement concepts have evolved.

4.5.1 General Containment and Confinement Concepts

In the nuclear fuel processing industry, containment and confinement have different and sometimes confusing meanings. Containment generally refers to the container holding bulk radioactive material. Movement of the bulk material is severely constrained within the boundary of the container itself. For example, many of the tanks and vessels at a nuclear fuel processing plant are designed to contain bulk radioactive materials. The vessels themselves are further enclosed within a shielded concrete room or process cell. The process cell serves as a back-up to confine any releases of the radioactive material from its containment vessels should they occur for whatever reason.

Confinement, on the other hand, is associated with contamination—radioactive material in undesired places. Confinement constrains the migration of radioactive material from a bulk material container. The confinement boundary is usually larger and the anticipated radioactive material encountered is less. For example, radioactive material is contained in a process vessel and the process vessel is located in a confinement space to handle any deliberate or accidental release of material. Furthermore, at a nuclear fuel processing plant, the building surrounding the concrete process cell serves to confine any migratory material from the process cells. Confinement can be thought of as a boundary to restrict the migration of small amounts of radioactive materials. By design, containment and confinement methods overlap.

4.5.2 Levels of Confinement

For a facility handling ^{233}U-bearing materials, multiple confinement areas, arranged in series, are often used. In this scheme, each area has a separate physical structure and ventilation system. Area requirements for the proper confinement of ^{233}U-bearing materials can be divided into primary, secondary, and tertiary levels. In general, primary confinement surrounds the radioactive material, secondary confinement surrounds the primary, tertiary confinement surrounds the secondary, etc.

Primary confinement consists of a barrier or set of associated barriers that have the most intimate contact with the radioactive material. In a nuclear fuel processing facility for ^{233}U-bearing materials, primary confinement areas can include shielded process cells, process vessels, and sealed enclosures such as storage wells, laboratory hoods, and glove boxes. The rooms surrounding the primary confinement areas constitute secondary confinement and enclose the primary areas to receive and control any contamination released from them. Secondary confinement areas may also include vaults containing a tank or the outer wall of a double-walled tank. Tertiary confinement areas serve as barriers that enclose secondary areas to receive and control any contamination that may be released from them. Examples of tertiary confinement systems include a building shell that contains a room with a single-walled tank of radioactive material or a room containing ^{233}U-bearing material in a double-walled tank.

The different levels of confinement need to be as independent as possible. However, required secondary and tertiary barriers may exist in a common form (such as a roof slab) provided the barrier can withstand the effects of relevant design-basis accidents. Major requirements for the primary, secondary, and tertiary containment systems of ^{233}U material facilities are summarized below.

- Primary confinement includes process cells, glove boxes, laboratory hoods, storage containers, process piping, and storage tanks used in the facility. As appropriate, the primary confinement spaces are compartmentalized to isolate high-risk areas and minimize the effects of design-basis accidents.

- Secondary confinement generally includes the facility's operating compartments and associated ventilation systems. This confinement system also houses any process cells or glove boxes or other enclosures.
- Tertiary confinement will typically be the building shell housing the facility's operation area and its associated ventilation system(s).

The degree of confinement required at a nuclear fuel processing facility where ^{233}U-bearing materials are handled depends on the quantity, physical form, chemical characteristics, and radiological characteristics of those materials that potentially could be released. In general, ^{233}U-bearing materials are stored in containers that are enclosed in specially design buildings. Material handling processes includes all equipment that contacts bulk radioactive materials. Depending upon the facility, such equipment may include storage containers, collection tanks, process vessels, pumps, valves, and glove boxes. Maintenance and inspection of material handing systems should be done without breaching confinement schemes. In general, material handling processes maintain barriers between an operating, limited-access area, and general-access area. Such equipment may include the walls and ventilating systems of the facility-operating area. The mode of secondary confinement has sufficient passive-relief capacity such as to use in the event of a large leak from the primary-confinement area. A tertiary confinement system for material handling may be optional, depending on the major facility operation. This system includes all equipment that maintains the barrier between the general-access area(s) and the outside of the building housing them. Such equipment may include the outside walls and roof of the building and building ventilation system.

4.5.3 Confinement Ventilation Concepts

In the nuclear fuel processing industry, all radioactive materials are controlled or confined by physical barriers to occupy spaces designed to protect the health and safety of the workers and the public. One widely used method is that of confinement ventilation, which includes specially controlled airflows, the use of negative-pressure enclosures, and high-efficiency filters to control the migration of radioactive materials. In a properly designed nuclear fuel processing facility, the actual or potential migration of any radioactive material is controlled by confinement ventilation, which directs airflow from areas of no contamination toward areas of higher contamination. The airflow is then treated as necessary and HEPA filtered and monitored before release to the atmosphere.

For a specific facility containing ^{233}U-bearing materials, the number and arrangement of confinement ventilation systems and their required design features and characteristics need to be determined on a case-by-case basis, consistent with a facility's major function and process-design specifications. Such determination must meet the objective of either preventing or limiting the release of radionuclides and shielding the high-radiation emitters from the ^{232}U decay chains during normal facility operation, anticipated operational occurrences, and postulated accidents. By design, air flows from areas of lower contamination hazards into those with higher contamination hazards, thus facilitating access to most areas with minimal risk. Before the air is released to the environment, it must be filtered and monitored to ensure that any residual contamination is well below acceptable, safe levels for public exposure (Mansfield 1998).

4.5.4 Confinement and Ventilation in ^{233}U-^{232}U Processing

Confinement is DOE's preferred method for protecting the public and workers from exposure to hazardous substances like ^{233}U-bearing materials. To meet this objective, confinement encompasses both the physical structures in which a material like ^{233}U resides and the associated ventilation systems designed to protect workers and the public from inhalation exposure to ^{233}U by maintaining radiological confinement to designated areas. The objective of material confinement is to provide a physical barrier. Ventilation systems for such radioactive materials are designed to perform two major functions: (1) draw air from areas of lower radiological contamination to areas of higher contamination and (2) provide a means of filtration before atmospheric discharge.

4.5.5 Confinement Ventilation Requirements

The high specific activity of ^{233}U (and that of ^{232}U) promotes the evolution of gaseous decomposition by-products from contaminants such as water and plastics. Such by-products include potentially explosive gases (e.g, hydrogen) that must be diluted and removed by a reliable ventilation system. This system must also retain an inert radioactive gas that is a by-product of the ^{232}U decay chain, ^{220}Rn, whose characteristics are discussed in Sect. 2.3 and whose control and filtration are discussed in Sects. 4.3 and 4.4, respectively. The retention of ^{220}Rn is crucial for ^{233}U-bearing materials having concentrations of ^{232}U greater than 10 ppm and for conditions in which purging of evolved radon is facilitated by gas flow through the bulk of the ^{233}U-bearing material. However, for dormant ^{233}U material storage, ^{220}Rn evolution must be considered in the ventilation-system design. Ventilation systems for ^{233}U-bearing materials are also needed for dissipating the heat generated by highly energetic alpha decay emissions.

Special consideration must be given to the design of ventilation systems for ^{233}U materials stored as UF_6, which have a significant vapor pressure. Chemically, as well as radiologically, hazardous UF_6 readily decomposes to release the toxic and corrosive gases F_2 and HF. These gases can quickly deteriorate improper ventilation and filtration equipment.

Ventilation requirements are less severe for ^{233}U-bearing materials stored in high-integrity packages. These may include "special-form" canisters or packages {as defined in accordance with 49 CFR Part 173 [U.S. Department of Transportation (DOT) Oct. 1, 1998]} that have two corrosion-resistant, certified-welded layers of metal containers. As long as their integrity is established, such special-form canisters or packages can be considered reliable for containing alpha particles, recoiling parent radionuclides, radon, and radiolytically generated gases.

4.5.6 Effective Glove-Box Design Concepts

Glove boxes for handling ^{233}U-bearing materials are environmentally sealed enclosures usually made of stainless steel and having large panes of glass or transparent rigid plastic to view inside. Workers using rubber gloves attached to openings in the box can safely handle hazardous ^{233}U materials from the outside by inserting their hands into the gloves and manually performing manipulations. In some cases, it is necessary to provide radiation shielding to either or both the glove box or rubber gloves depending on the radiation field present.

A comprehensive review of the use of glove boxes in handling radioactive materials is provided by C. J. Barton (1979). This reference discusses the major factors associated with the general design of glove boxes and associated auxiliary equipment used to handle hazardous materials. These include:

- air monitoring;
- controlled-atmosphere enclosures for nontoxic materials;
- controlling personnel exposure to radiation;
- doors and air locks;
- fire, heat resistance, and criticality control;
- glove materials and design;
- housekeeping and waste disposal;
- initial operation procedures;

- leak testing;
- materials of construction;
- monitoring for escape of alpha activity;
- ports and port closures;
- pressure measurement and control;
- safe operating procedures;
- ventilation, filter, and exhaust systems; and
- window materials.

Nuclear criticality safety aspects of working with fissionable materials, including ^{233}U, in glove boxes are described in Shuck (August 1959) and include two major methodologies: always-safe-geometry (shape) and always-safe-mass. The latter method involves keeping the mass of fissionable material in a glove box or in an interconnected series of glove boxes below the minimum mass level required to produce a chain reaction, regardless of its shape or environment. The always-safe-geometry concept refers to observing limits on the containment and dispersion of the fissile material in the glove box along with its geometric shape. Employment of the always-safe-geometry method of avoiding nuclear criticality is usually needed only in production-type operations where large amounts of materials are present (Barton 1979).

For fuel fabrication work with ^{233}U materials, double-gloving is recommended (Shuck August 1959). Using lead-lined gloves is also effective against strong penetrating radiation emitted by the daughter products of ^{232}U.

As an example, ORNL Radiological Protection Procedure (RPP) RPP-347, *Radiochemical Glovebox Safety* [Lockheed Martin Energy Research Corp. (LMER) Mar. 30, 1995*a*], documents the current ORNL radiological safety requirements for operations carried out in radiochemical glove boxes and the surveillance and inspection program for such containers. This procedure also indicates that glove box designs satisfy the requirements of RPP-128, *Radiological Design Requirements for New Facilities and Modifications to Existing Facilities* (LMER Nov. 14, 1995).

The design of glove boxes for handling ^{233}U materials is strongly based on the ^{233}U criticality limits, as discussed in Sect. 2.4. The criticality requirements and limits for ^{233}U-bearing materials limit the mass of material that can be handled in a given batch, and these, in turn, limit or restrict the size of the work area in a particular region of confinement.

4.5.7 References for Sect. 4.5

A list of cited references documenting the confinement and containment requirements for ^{233}U-bearing materials is provided below. This is followed by a list of sources providing additional information.

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4.6 SPECIAL CHEMICAL HAZARDS

This section is intended to outline special chemical hazards that may arise during processing or storage because of the nature of relatively high activity of ^{233}U but which generally do not appear in processing of more commonly encountered isotopic mixes of uranium. It is not intended to cover inherent hazards in processes which happen to be applied to ^{233}U, nor are radiation damage of materials of construction discussed.

Chemical hazards unique to ^{233}U are a consequence of the relatively high radioactivity of ^{233}U (or the ^{232}U which may accompany it). At the activity level of ^{233}U, radiochemical processes may produce hazardous or active species at rates which merit consideration, while those same processes occur only to a negligible extent in natural or even ^{235}U enriched uranium and are thus commonly disregarded. It is difficult to generalize, but the topic can perhaps best be treated by discussion of some examples.

4.6.1 Radiolytic Generation of Gases

Radiation of the uranium compound or of nearby materials can produce chemical changes, including radiation damage and radiolytic generation of gases. The net generation of gas is a balance between production and destruction. Sometimes the reverse reactions (consuming the radiolytically produced gas) are so large such as to render the reaction moot, as is typically the case for uranium oxides. In other cases, gas formation is a well-known phenomenon. In the decay chain for ^{233}U, the decay energy is largely alpha, whereas most available radiolysis information is for material exposed to gamma or x-ray exposures. The effects of alpha, beta, gamma, and neutron irradiation can be much different.

H_2O radiolyzes to form H_2, H_2O_2, and O_2. In liquid water, this process tends to self-limit as the recombination reactions balance the decomposition reaction at moderate partial pressures of H_2. The steady-state pressure can be strongly dependent upon other species present in the solution (Allen May 1952 and Hochnadel May 1952). The H_2, of course, could form flammable mixtures with air or O_2, though it will not spontaneously ignite at room temperature but requires an ignition source.

Both NH_3 and NH_4^+ salts have been demonstrated to radiolyze in beta or gamma fields (Orlov et al. 1988) and probably do so also upon alpha exposure. H_2 and N_2 are observed as the primary reaction products. Unlike the case for H_2O, the reverse reactions are insignificant until fairly high pressures are reached (Ausloos, ed. 1968). H_2 is, of course, flammable on mixing with air or O_2. In ^{233}U experience, UF_6 trapped on activated charcoal (which was also impregnated with NH_4F) was observed to produce H_2 and N_2 by radiolysis.

Several instances have been observed of the radiolytic generation of F_2 from ^{233}U-bearing materials. After shutdown of the MSRE, the frozen fuel salt was observed to generate F_2 (though this is most likely because of fission product radiation and only to a minor degree to the uranium decay series, since one alpha-induced radiolysis test yielded no obvious gas generation) (Williams, Del Cul, and Toth January 1996). UF_6 has been observed to decompose under its own (primarily alpha) radiation field, generating reduced uranium fluorides (e.g., UF_5) and F_2. This phenomenon has been observed in the gaseous and solid states and also for UF_6 complexed with sodium fluoride. In the gas phase, net decomposition can be essentially completely suppressed by the presence of a low-partial pressure of F_2. Such a suppression of decomposition is not evident in radiolysis of condensed phases containing UF_6 (Trowbridge August 1995).

4.6.2 Potential Hazards

Radiolytic production of reactive gases can have a number of potentially detrimental effects. The simplest pressure rise can be a problem if large quantities of radiolyzing material are stored in a sealed container of limited volume and if the reverse reactions are insufficient such as to stop the pressure buildup before vessel limits are exceeded. In such cases, venting at a rate or frequency sufficient such as to prevent buildup of detrimental pressures can resolve this problem. Another contemplated solution is inclusion of a chemical getter for the generated gas. The chemical characteristics of the radiolysis product gases would, of course, need to be considered in performing the venting. For example, F_2 would generally be chemically trapped or scrubbed from the vented gas stream, and, when venting H_2, consideration would have to be given for the flammability of the gas (e.g., avoiding ignition sources, diluting below flammability limits, or venting under circumstances where no harm could occur were there an accidental ignition). Radon would accompany the vented gas if other isotopes of uranium with radon in their decay chain were present (e.g., ^{232}U with its ^{220}Rn daughter), so provision would have to be made for that as well.

Any oxidizers produced (O_2, F_2, etc.) could pose reactivity concerns if suitable fuel were present, particularly if the pressure were allowed to build to significant levels.

Halogens (e.g., F_2 and Cl_2) generated in the presence of moisture (including not only liquid water but also humidity or hydrated material) will form strong acids, which may then attack construction materials at a more rapid rate than does the parent halogen.

Other, more exotic, secondary effects have been observed. In one instance (in the MSRE), radiolytic fluorine slowly migrated to an activated charcoal bed (ACB), upon which it was trapped. Low-temperature fluorinated charcoal is thermodynamically unstable and has (infrequently) been known to decompose with near-explosive characteristics (Del Cul et al. October 1997 and September 1998).

The instances cited here by no means constitute a comprehensive listing of potential direct or indirect chemical effects in ^{233}U handling, storage, or processing. Similar materials (certainly other halide salts, other forms of water or hydrates, and other hydrogen-containing species) can be expected to exhibit some degree of radiolytic breakdown. The specific system under consideration should be evaluated for vulnerability to such effects.

4.6.3 Gaseous Uranium Compounds

One specific concern with uranium compounds compared to plutonium and other fissile materials is the potential for conversion to gaseous uranium compounds in the presence of halides and certain other chemicals. This can potentially create unique modes of ^{233}U transport and unique hazards.

An example of this is the experience at the MSRE. The ^{233}U was trapped as UF_4 in a solid solution of lithium fluoride and beryllium fluoride. Radiolysis created free fluorine that reacted with the UF_4 to produce UF_6. In this case, radiolysis and chemical kinetics created conditions that would not be predicted by classical thermodynamics. The $^{233}UF_6$ migrated into the off-gas system. Some of the UF_6 plated out in the off-gas system while the remainder of the UF_6 was trapped on a charcoal bed. This created safety concerns about the potential for (1) accidental nuclear criticality since the off-gas system was not designed for fissile materials and (2) exothermic chemical reactions between the fluorine and charcoal bed. Corrective actions removed the $^{233}UF_6$ from the off-gas system.

In any system with radiation and halogens that can create volatile uranium compounds, special attention is required to assure that in the long-term volatile uranium compounds that can transport the uranium are not created.

4.6.4 References for Sect. 4.6

A list of cited references documenting the special chemical hazards of ^{233}U-bearing materials is provided below. This is followed by a list of sources providing additional information.

4.6.4.1 References Cited

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4.6.4.2 Supplemental References

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4.7 PACKAGING MATERIALS AND TECHNIQUES

This section is a discussion of suitable materials and techniques for properly packaging ^{233}U-bearing materials. Types of suitable packaging materials are described, and then a summary description of proper techniques is presented.

4.7.1 Types of Packaging Materials

The inventory of ^{233}U is stored in a variety of chemical and physical forms and in various packaging configurations. A detailed example is given in Table C.6 in Appendix C, which summarizes the packaging configuration at ORNL Building 3019.

The unirradiated LWBR fuel stored at INEEL consists of ceramic fuel pellets, which provide the primary level of containment for the $^{233}UO_2$-ThO_2 oxide. The physical packaging provides additional levels of containment. The packaging at the RWMC consists of Zircaloy-clad fuel rods, stainless-steel rods closed with an O-ring plug, polyvinyl chloride (PVC) bags of pellets, or polyethylene bottles of pellets. These units are placed inside steel 2R containers that have been coated with a rust-resistant paint and closed with a lightly oiled pipe cap. The 2R containers are put into an epoxy-coated steel lid sealed with an elastomer seal ring. Each 2R container is located in the center of its respective drum surrounded by layers of fiberboard packing. The drums are then packed inside a lead- or steel-shielded overpack, which is then stored inside a steel building on a concrete pad. This combination of physical barriers presents an effective level of containment for the ceramic pellet (Shappert 1998).

4.7.2 DOE Packaging and Storage Standard

Packaging provides a principal barrier for isolating stored material from the environment. As such, it is designed to maintain mechanical integrity, including closure, during anticipated handling and storage operations. General issues surrounding the package relate to materials of construction, internal package atmosphere, identification and, closure. The storage package for metals and powders consists of a minimum of two nested, leaktight containers to isolate the stored materials from the environment and to prevent the release of contamination. This two-container system is also acceptable for monoliths and ceramic oxides. However, the storage system for monoliths may consist of a minimum of one container. For ceramic oxides, the integrity of the ceramic form may replace one of the package barriers.

The general requirements for containers used in packaging are corrosion resistance, adequate mechanical strength, permanent identification, leaktightness, and contamination-free. Additionally, the design should consider nondestructive assay (NDA) requirements for material control and accountability (MC&A), anticipated storage conditions, and potential handling accidents. The inner container must be sized such that it fits in the outer container with clearance for closure. The outer container must be sized to fit in the storage configuration. Additional optional containers are also allowed (U.S. DOE December 1998).

4.7.3 References for Sect. 4.7

A list of cited references documenting the packaging requirements for ^{233}U-bearing materials is provided below. This is followed by a list of sources providing additional information.

4.7.3.1 References Cited

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4.7.3.2 Supplemental Resources

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4.8 STORAGE REQUIREMENTS

This section is a description of ^{233}U storage requirements. It includes discussions of required storage facility characteristics and viable storage options. These discussions are followed by a summary of the DOE standard criteria for packaging, transporting, and storing ^{233}U-bearing materials. The officially published interim DOE standard for the storage of ^{233}U-bearing materials is provided in the report, *DOE Standard—Criteria for Preparing and Packaging Uranium-233-Bearing Materials for Safe Long-Term Storage* (SAFT-0067) (U.S. DOE December 1998). A full copy of this document is provided in Appendix A.

4.8.1 Storage Facility Characteristics

A facility used for the storage of ^{233}U should address the unique characteristics of the material and include nuclear criticality safety, confinement of radioactive materials, radiation shielding, and safeguarding special nuclear material (SNM). Requirements for safeguards are discussed in Sect. 4.9.

4.8.1.1 Nuclear Criticality Safety

Because a principal safety consideration for the safe storage of ^{233}U is eliminating the possibility of the material reaching a configuration that would result in criticality, criticality avoidance is a prime priority in safety considerations in the design and operation of a ^{233}U storage facility. The principal facility function is to provide an array that is criticality safe under normal circumstances. Additionally, the packages and facility must be engineered, constructed, controlled, and monitored to avoid the occurrence of accidental criticality for all credible natural-phenomena events such as fires, flooding, earthquakes, and tornadoes. Because criticality safety is considered to be the dominant safety concern in the design and operation of a ^{233}U storage facility, the vault area should be designed with consideration of water sources such as fire sprinklers. Coexisting combustible materials should be minimized or eliminated from the facility to minimize the potential for fires and the need for fire-suppression systems.

A majority of the ^{233}U in inventory consists of mixtures of ^{233}U and ^{232}U or mixtures whose properties are dominated by the ^{233}U and ^{232}U content. Uranium-233 has substantially different nuclear criticality properties than two other SNMs, ^{235}U and plutonium. Therefore, facilities designed for ^{235}U and plutonium may not be acceptable for comparable activities involving ^{233}U from a nuclear criticality safety standpoint.

The criticality safety requirements for storage and handling of ^{233}U-bearing materials must conform to the criticality safety requirements of DOE Order 420.1 (U.S. DOE Oct. 13, 1995). Criticality safety evaluations document that storage and handling activities remain subcritical during all normal and abnormal events. Criticality safety evaluations are performed for operations (under normal conditions) within any facility containing ^{233}U in excess of the limits specified in DOE Order 420.1 (U.S. DOE Oct. 13, 1995) or as specified in site-specific nuclear criticality safety program policies and procedures. Special care should be exercised in validating calculation methods supporting criticality safety evaluations because of the paucity of data in the intermediate energy regime which may be important for some ^{233}U-bearing matrices under specified operational conditions.

4.8.1.2 Confinement of Contamination

The material form, material containers, or containment vessels serve as the principal barrier for confinement of contamination. Depending on the material storage system, the facility itself may serve as another confinement barrier. The combination of the material storage system and the storage facility represents a defense-in-depth safety confinement system.

The matrix of the material and/or the inner container provide the first barrier against spread of contamination; the outer container and the tube vaults provide additional barriers. The packaging is designed to maintain mechanical integrity, including its seal, during normal handling. However, this package is not expected to provide protection from all perils, such as major fires and earthquakes; design of the facility and of the storage array are expected to address these considerations (see Appendix A, U.S. DOE December 1998).

The facility where ^{233}U-bearing material is stored provides a physical barrier to the release of contamination. The integrity of the storage facility shall be maintainable through all normal operations, anticipated operational occurrences, and any design-basis accidents (DBAs) the barrier is required to withstand. The particular DBAs that the storage facility is required to withstand is determined on a case-by-case basis. The DBAs to be considered include external events (e.g., severe natural phenomena and man-made events) and internal events (e.g., container overpressurization). The adequacy of these confinement systems to effectively perform their required functions shall be demonstrated by the safety analysis. Requirements governing the safety analysis process include the applicable portions of DOE Orders 420.1 (U.S. DOE Oct. 13, 1995), 5480.21 (U.S. DOE Dec. 24, 1991), 5480.22 (U.S. DOE Feb. 25, 1992), and 5480.23 (U.S. DOE

Apr. 10, 1992). The need for ventilation systems for confinement should be based on the results of the safety analysis.

4.8.1.3 Radiation Shielding

Owing to the presence of ^{232}U in ^{233}U inventories, radiation shielding is required to attenuate the 2.6-MeV photon emitted by the ^{232}U daughter, ^{208}Tl. Depending on the material form and material storage system used, the facility itself may serve as a radiation shield. The regulations pertaining to occupational radiation protection as specified in 10 CFR Part 835 (U.S. DOE Dec. 14, 1993), "Occupational Radiation Protection" must be met. A general discussion of ^{233}U shielding is given in Sect. 4.2.

Uranium-233 and its associated sister isotope, ^{232}U, present much more severe external radiation hazards than any of the naturally occurring uranium isotopes. Massive biological shielding is required where high concentrations of ^{232}U occur. This shielding protects personnel from the 2.6-MeV gamma emission of ^{232}U daughter product ^{208}Tl. The occupational radiation exposure should be kept ALARA, and radiation protection be provided as specified in 10 CFR Part 835 (U.S. DOE Dec. 14, 1993). Dose rates are dependent on the source (e.g., activity, geometry, and matrix), shielding, and source-to-detector configuration, so expected dose rates for actual conditions should be determined on a case-by-case basis.

Except for spontaneous fission, neutrons are not directly produced during the radioactive decay of any of the uranium isotopes or the sequential decays. However, alpha-neutron reactions, in which alpha particles react with low-Z isotopes such as ^{6}Li, ^{7}Li, ^{9}Be, ^{10}B, and ^{19}F (and to a lesser extent ^{27}Al and ^{28}Si) generate neutrons. Depending on the material storage system used, the facility itself may serve as a shield (see Appendix A, U.S. DOE December 1998).

Additionally, the occupational radiation exposure must be kept ALARA. In defining ALARA, the NCRP states that "ALARA is simply the continuation of good radiation-protection programs and practices which traditionally have been effective in keeping the average and individual exposures for monitored workers well below the limits." The NCRP "did not intend that application of the ALARA principle be raised to such extremes so as to restrict unnecessarily the use of radiation in the occupations of commerce and medicine and consequently preclude its employment when there are countervailing benefits to be gained."

4.8.2 Storage Options

Different options for the storage of nuclear materials imply different policies and multiple process options. As described and discussed in Forsberg et al. (Sept. 30, 1998), there are three long-term storage options for ^{233}U-bearing materials:

- store as is,
- isotopically dilute to nonweapons-usable ^{233}U (i.e., <12 wt % ^{233}U) for future use as nonweapons-usable metal, and
- isotopically dilute to critically safe ^{233}U (i.e., <0.66 wt % ^{233}U with no other fissile nuclides) as a waste.

Three technologies have been identified for isotopically diluting ^{233}U materials: (1) dry-powder blending, (2) dry-melt blending, and (3) aqueous-nitrate blending. Each technology has specific advantages and disadvantages.

4.8.2.1 Dry-Powder Blending with Sintering

In the dry-powder blending process (ORNL July 19, 1995), ^{233}U oxide is mixed with DU oxide (both in fine powder form) and pressed into pellets, which are sintered (by heating to a high temperature) to produce a ceramic-type material. Solid diffusion during the sintering step isotopically mixes the ^{233}U with the DU. The ^{233}U in the resulting product cannot be separated from the ^{238}U by chemical or physical means except by the use of existing uranium isotope separation technology. A schematic flowsheet of the process is shown in Fig. 4.8*a*.

The ^{233}U to be processed is removed from the storage wells and transported in a shielded carrier to the processing hot cell. A bagless loading procedure was used for contamination control. The material is processed in limited-size batches for criticality control. Inside the hot cell, the material is inventoried for accountability control. After inventory, the containers are opened, and the contents are removed. Many of the containers, such as the CEUSP monoliths, require equipment to cut open the container and to drill into or otherwise extract the contents. After any large chunks are removed from the containers, they are crushed into granules before the material is sent to a ball mill to be powdered. Any of the oxide forms in which the uranium is stored (e.g., UO_2 and U_3O_8) can be used. Metallic uranium and nonoxide uranium are converted to oxide (U_3O_8) by heating in a furnace under an air atmosphere before the blending operation. The nominal processing rate is 1.2 kg of fissile uranium per day, assuming an operation of three shifts per day and a 4-h cycle per batch. The batch size is chosen to be 200 g to ensure criticality control. However, the processing rate could be increased by installing parallel systems. Material in the feed other than uranium oxides, such as cadmium and gadolinium oxides or thorium oxide, will remain with the uranium oxide throughout the process and be present in the final product.

Blending begins by adding a weighed amount of ^{233}U oxide powder with a predetermined quantity of DU oxide (U_3O_8) powder in a mixing vessel. Depleted uranium oxide for blending is prepared outside the hot cell. The powder is mixed by rotating the mixing vessel in a tumbling apparatus for a prescribed length of time. To aid in the subsequent pellet-making process, an organic binder is added and blended with the powder during the mixing operation.

An automatic press is used to cold-press the mixed oxide powder. Blended powder is fed into a cavity and pressed by a piston. The ensuing pellets are limited to a mass of 57 g or less and a maximum diameter or height of 3 cm, and the nominal fissionable material in each pellet do not exceed 1 g. The pellets are then ejected from the cavity into a sintering tray.

The uranium oxide pellets are placed in a sintering oven and heated to a temperature that is sufficient such as to vaporize the organic binder and to heat the pellets to effect sintering. The pellets shrink as the volatile material is driven off. The finished pellets will be approximately 90% of theoretical density of the mixed oxide. (For UO_2, 90% theoretical density is 9.86 g/cm^3.) After they are sintered, the pellets are allowed to cool and are then transferred to an area for nondestructive analysis to verify the fissile content of the pellets. Broken pellets are recycled.

The dry-blend process does not introduce any additional material into the product other than the DU. Isotopic dilution of 1 kg of ^{233}U by the dry-blend process will produce 9.5 kg of non-weapons-usable UO_2 (8.407 kg U) product having a pellet volume of 0.96 L. Blending 1 kg of ^{233}U with DU to eliminate long-term criticality will produce 214 kg of uranium oxide (189 kg U) product having a pellet volume of 21.7 L. A summary of the product volumes and mass per kilogram of ^{233}U processed is given in Table 4.8*a* (Forsberg et al. Sept. 30, 1998). However, the actual waste volume per kilogram ^{233}U will be higher because of the presence of other material (thorium, cadmium, and gadolinium oxides) in the ^{233}U material and any additional DU required to dilute ^{235}U contained in the ^{233}U material.

After sintering, the pellets are placed in the inner containment vessel (can), which is sealed by welding. The can is then enclosed in an outer container to provide double containment for storage and shipping. Off-site transportation is carried out in shielded overpacks that meet DOT requirements.

4.8.2.2 Dry-Melt Blending

In the dry-melt blending process (ORNL July 27, 1995), the ^{233}U oxide is mixed with DU oxide powder and solvent metal oxide powder [alkali oxide-silica, boron oxide (B_2O_3) or borax ($Na_2B_2O_7$)] and melted in an induction furnace. In the resulting material produced, the ^{233}U cannot be chemically or physically separated from the ^{238}U except by existing uranium isotopic separation technology. Ordinarily, an equal weight of solvent metal oxide and uranium oxide are used. The melt crucible also serves as the product container. A schematic flowsheet for the process is shown in Fig. 4.8*b*. The use of a silica-based solvent metal oxide produces an insoluble product. The use of B_2O_3 or $Na_2B_2O_7$ produces a product that allows easy recovery of the uranium at a future date.

The loading, unpackaging, and size reduction for the dry-melt blending is very similar to that for the dry-powder blending. The ^{233}U material to be processed is removed from the storage wells and transported in a shielded carrier to the processing hot cell. Material is processed in limited-sized batches for criticality control. Inside the hot cell, the material is inventoried for accountability control. After inventory, the containers are opened, and the contents are removed. Many of the containers, such as the CEUSP monoliths, require equipment to cut open the container and to drill or otherwise to extract the contents. After any large chunks are removed from the containers, the remaining chunks are crushed into granules before the material is sent to a ball mill to be powdered. Any of the oxide forms in which the uranium is stored (UO_2, U_3O_8) can be used. Metallic uranium and nonoxide uranium may require conversion to oxide (U_3O_8) before blending. If so, this is effected by heating the uranium in a furnace under an air or steam atmosphere. The nominal processing rate is 1.2 kg of fissile uranium per day, assuming a three-shift-per-day operation and a 4-h cycle per batch using one melt-blending furnace. However, the processing rate could be increased by installing parallel systems.

After the ^{233}U material is changed to powder form, it is blended with DU and a specified solvent oxide mix consisting largely of alkali-metal oxides and silica. Since the melt-product crucible (which is nominally 10 in. diam × 20 in. high) will not hold all of the material in powder form, several powder additions must be made. The initial charge does not contain the DU. With the onset of melting, DU oxide is periodically added while the mix is stirred. The final process temperature will be adjusted to achieve complete melting for the type of ^{233}U material being processed. The process is carried out under a vacuum. No significant chemical reactions occur during mixing and melting other than dissolution of the uranium oxide. The isotopic content of the mix is verified by sampling. After the contents are melted and mixed, the furnace is turned off, and the contents are allowed to solidify in the melt crucible.

To provide double containment for storage and shipment, the crucible containing the product is sealed inside an inner container by welding. The inner container is then placed inside a second container, which is also sealed by welding.

If processing alkali-metal oxide and silica glass is the final product, the isotopic dilution of 1 kg of ^{233}U to nonweapons-grade uranium by the dry-melt process will produce 19.1 kg of oxide product (containing 8.407 kg of U and 9.5 kg of alkali-metal oxide and silica) having a volume of 5 L. Blending 1 kg of ^{233}U to eliminate long-term criticality will produce 429 kg of oxide (189 kg U as UO_2 and 214.4 kg of alkali-metal oxide and silica) with a volume of 112.9 L. The actual waste volume per kilogram of ^{233}U will be higher than that of processing pure ^{233}U because of the presence of the other material in some of the ^{233}U material (thorium oxide, cadmium, and gadolinium oxides) and the additional DU required to dilute ^{235}U contained in the feed ^{233}U material.

4.8.2.3 Aqueous Nitrate Blending

In the aqueous nitrate blending process (ORNL July 13, 1995), solid ^{233}U material is dissolved in nitric acid to produce an aqueous uranyl nitrate solution which is mixed with a uranyl nitrate solution of DU. The ^{233}U cannot be separated from the ^{238}U without isotopic enrichment. After mixing, the solution is then denitrated (by heating) to form an oxide powder. The powder may be either pressed into pellets or incorporated into grout to provide an acceptable form for transport and disposal. The solution may also be denitrated to produce an oxide monolith similar to those monoliths made in CEUSP. A schematic flowsheet for the process is shown in Fig. 4.8*c*.

Uranium-233 material is lifted from the storage well into a shielded cask, which is then transported to the loading port at the manipulator hot cell. Processing the material is carried out on a batch basis to control criticality and inventory. After inspection and inventory, the containment vessels are opened, and the contents are removed. Equipment is provided for cutting the cans and mechanical removal of the contents when required. Caked or lumped material is crushed into granule-size pieces.

Granular or powdered material containing ^{233}U is converted to a uranyl nitrate solution by reaction of 3 L of 4 *M* nitric acid per kilogram of U (as oxide) to produce approximately 330 g U/L of solution. A uranyl nitrate solution of DU of the same concentration is prepared by the reaction of DU oxide (U_3O_8) with nitric acid outside the hot cell area. Dissolution of the thorium oxide–^{233}U oxide fuel currently stored at INEEL will require the addition of hydrofluoric acid and aluminum nitrate to the nitric acid to aid in dissolution.

Blending is done by mixing measured amounts of ^{233}U nitrate solution and depleted uranyl nitrate solution to produce controlled isotopic concentrations of uranium. To produce a free-flowing powder during denitration, 2 mol of ammonium nitrate per mole of uranium is mixed with the uranyl nitrate solution during the blending step (the modified direct denitration process).

A one-step conversion of the blended uranyl nitrate solution to uranium trioxide (UO_3) is accomplished by thermal denitration. The process produces a free-flowing fluffy powder. The powder has a low density (about 1 g/cm^3) and is in a form that might be easily dispersed. Two options were considered for further immobilizing the powder: (1) compaction by pressing and (2) compaction by incorporating the oxide powder into grout. Compaction of the powder to 4.3 g/cm^3 (about 60% of the theoretical density of UO_3) is considered sufficient such as to produce a nondusty, monolithic form. In the grouting option, the oxide is incorporated into grout at a 50 wt % loading.

A third option for producing an immobilized oxide is the denitration of the blended uranyl nitrate solution in the product can (similar to that done for the CEUSP material). Using this method, ammonium nitrate would not be added to the nitrate solution, and denitration would occur about 800°C to produce a U_3O_8 monolith product. The products from any of the immobilization methods are packaged in doubly contained vessels with welded seals for transport and disposal.

The production of uranium oxide by the aqueous nitrate blending process does not introduce additional material other than DU into the final product. Incorporation of the uranium oxide product into grout introduces an equal amount of grout into the final product. Isotopic dilution of 1 kg of UO_3 to nonweapons-grade uranium by the aqueous nitrate blending will produce 10.1 kg of UO_3 (8.407 kg U) as pellets having a volume of 2.3 L. Grouting the oxide will produce 20.2 kg of material having a volume of 4.8 L. In-can denitration will produce 9.9 kg of U_3O_8 product having a volume of 3.1 L. Blending 1 kg of ^{233}U to eliminate long-term criticality will produce 227 kg of UO_3 pellets (189 kg U) having a volume of 52.8 L. Incorporation of the oxide into grout will produce 454 kg of grout with a volume of 108.2 L/kg of ^{233}U. Denitration of the blended nitrate solution diluted in the product can will produce 223 kg of U_3O_8 having a volume of 67.4 L. The actual waste volume per kilogram of ^{233}U will be higher because other material present in some of the ^{233}U feed (thorium oxide, cadmium, and gadolinium oxides), the additional DU required to dilute ^{235}U contained in the ^{233}U material.

4.8.3 U-233 Storage Standards

DOE, in response to the Defense Nuclear Facility Safety Board (DNFSB Mar. 3, 1997) Recommendation 97-1, has developed long-term storage standards for ^{233}U. These standards include requirements that define (1) allowed chemical forms of the uranium for storage, (2) characteristics of the containers, and (3) facility capabilities. While the standards are being developed, the general outlines of such an overall standard are known. The chemical requirement is for an unreactive material. Acceptable chemical storage forms for ^{233}U-bearing materials are stated as metals and oxides.

4.8.4 References for Sect. 4.8

Listed below are the references cited in Sect. 4.8 for the storage requirements of ^{233}U-bearing material. This is followed by a list of additional sources providing more detailed information on this topic. Appendix A gives a draft of the latest ^{233}U Storage Standard.

4.8.4.1 References Cited

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4.8.4.2 Supplemental Resources

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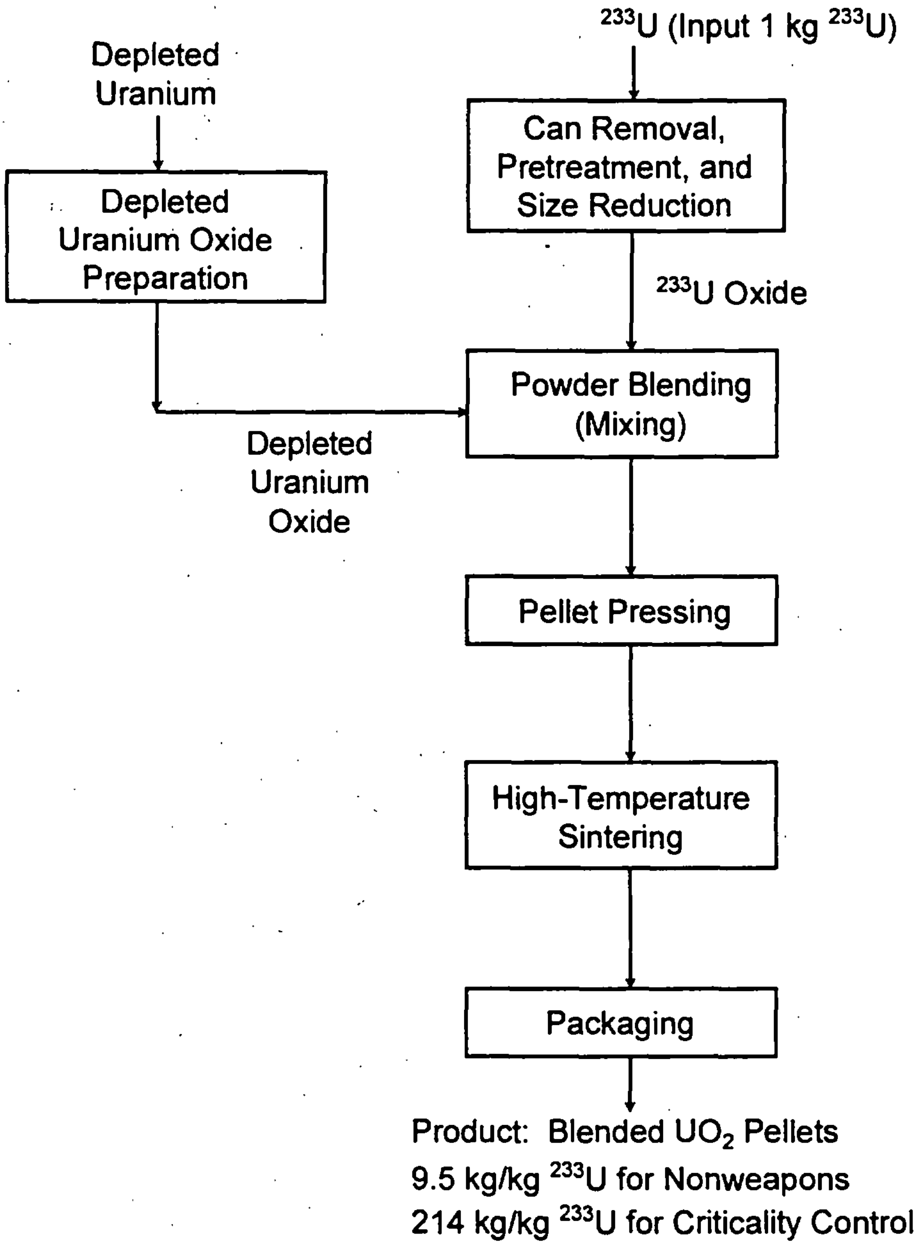

Fig. 4.8*a*. Isotopic dilution by the dry-powder blending process.

ORNL DWG 97A-35

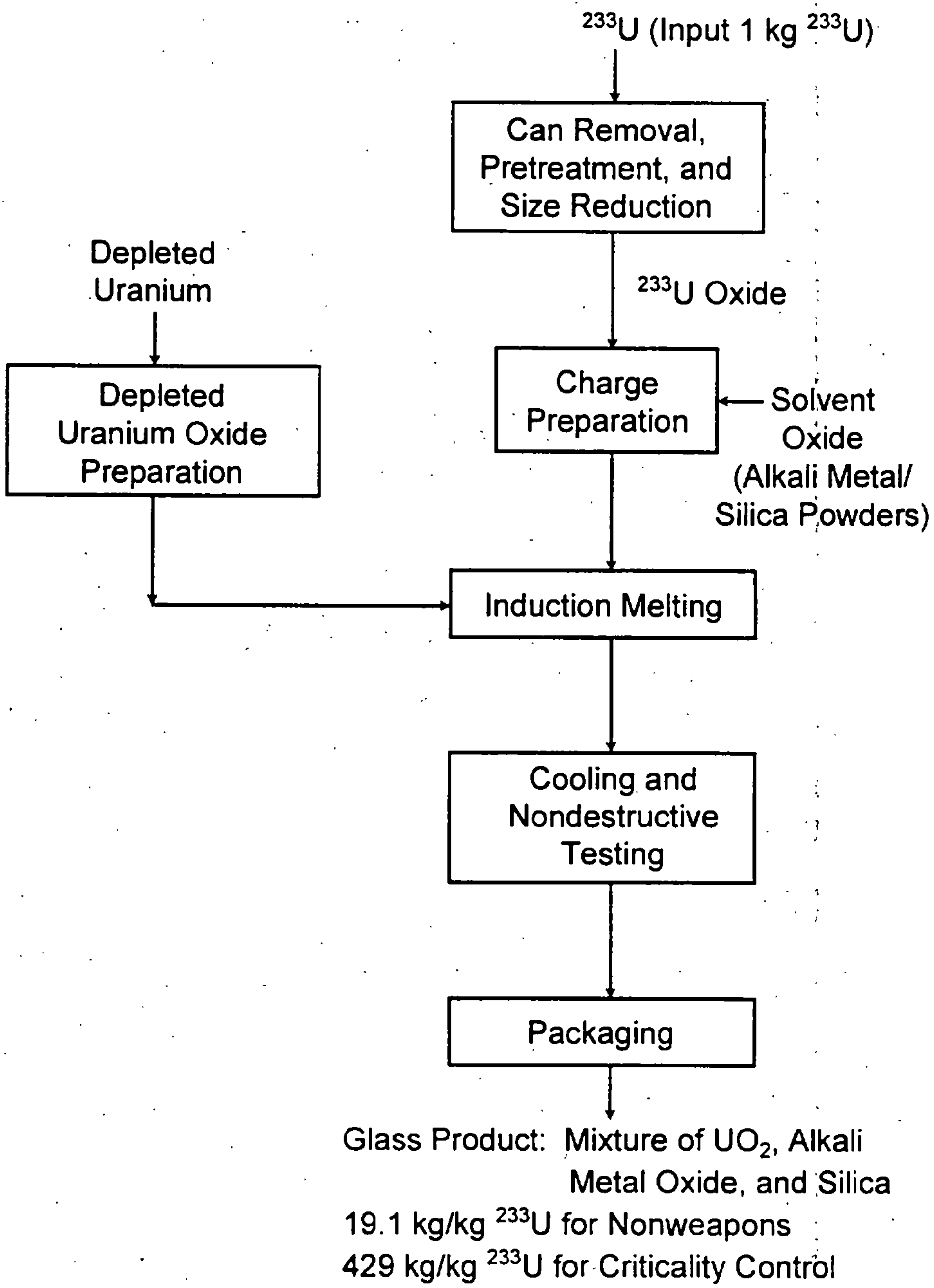

Fig. 4.8*b*. Isotopic blending by the dry-melt blending process.

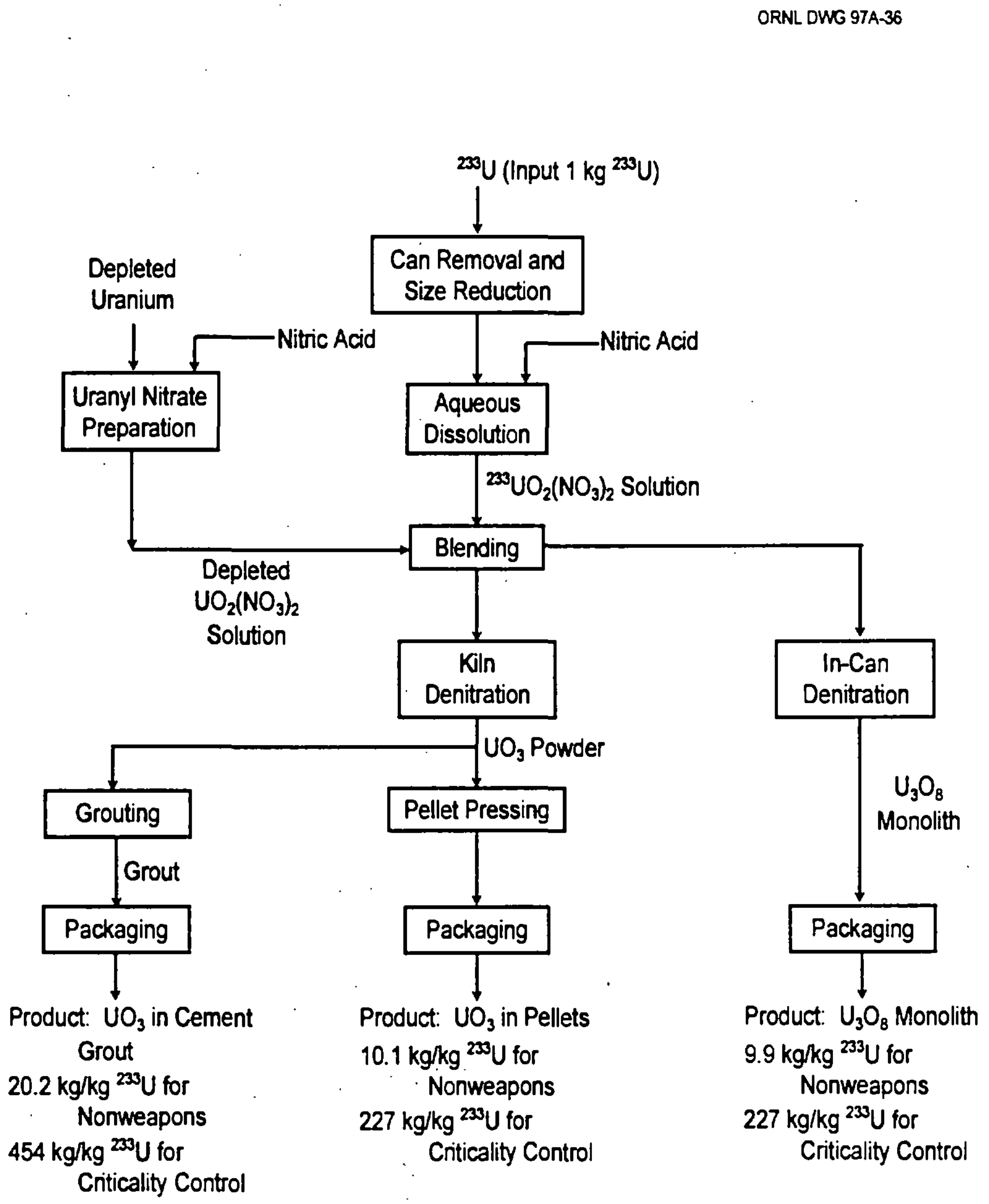

Fig. 4.8c. Isotopic dilution by the aqueous nitrate blending process.

Table 4.8a. Product volume and mass per kilogram of ^{233}U[a]

Processing option	Volume (L/kg ^{233}U)		Mass (kg/kg ^{233}U)	
	<12 wt % ^{233}U	<0.67[b] wt % ^{233}U	<12 wt % ^{233}U	<0.67[b] wt % ^{233}U
Dry-powder blending	0.96	21.7	9.5	214
Dry-melt blending	5.0	112.9	19.1	429
Aqueous nitrate blending				
Pellets (UO_3)	2.3	52.8	10.1	227
Grout	4.8	108.2	20.2	454
In-can denitration (U_3O_8)	3.1	67.5	9.9	223

[a] Based on Forsberg et al. Sept. 30, 1998, *Strategy for the Future Use and Disposition of Uranium-233: Disposition Options*, ORNL/TM-13553, Oak Ridge National Laboratory, Oak Ridge, Tenn.

[b] The required isotopic dilution for criticality control is 0.67 wt % ^{233}U in pure ^{238}U. If DU with 0.2 wt % ^{235}U is used, the final concentration of ^{233}U is 0.53 wt %. Some of the ^{238}U must be used for criticality control of the ^{235}U in the DU.

4.9 SAFEGUARDS, SECURITY, AND NUCLEAR MATERIALS ACCOUNTABILITY

Uranium-233 is included in the category of SNMs, which includes plutonium or fissile uranium (i.e., ^{233}U, ^{235}U) enriched to a higher than natural assay. Such materials require special programs for safeguards, security, and accountability. Requirements for the safeguards, security, and accountability of ^{233}U-bearing materials are discussed in this section. First, a discussion of the safeguards and security (S&S) requirements and the methods for managing these materials is provided. These requirements include those needed for domestic physical security facilities and systems and for international safeguards. A separate discussion is then provided of the requirements and methods for maintaining proper materials control and accountability of ^{233}U-bearing materials.

4.9.1 Safeguards and Security

A domestic (on-site) S&S program is designed to ensure that surplus fissile materials like ^{233}U-bearing materials meet security-related objectives. The vulnerabilities, designs, technologies, and operations associated with an S&S program are interrelated in the areas of physical protection, international safeguards containment and surveillance (C&S), and nuclear materials control and accountability.

As indicated in DOE Order 470.1, "Safeguards and Security Program" (U.S. DOE September 1995) the area of safeguards involves an integrated system of physical protection, material accounting, and material control measures designed to deter, prevent, detect, and respond to unauthorized possession, use, or sabotage of nuclear materials such as ^{233}U.

DOE Order 470.1 (U.S. DOE September 1995) describes the area of security as an integrated system of activities, other systems, programs, facilities, and policies needed for the protection of classified information, DOE contractor facilities, property, and equipment; nuclear weapons and weapons components; and other special nuclear materials such as ^{233}U. The security of ^{233}U-bearing materials includes surveillance and protective actions taken to prevent danger or risk of theft, diversion, or sabotage of these materials from facilities.

An S&S program for ^{233}U-bearing materials protects the environment and public from a wide range of threats:

- unauthorized access,
- material theft or diversion,
- sabotage (industrial, radiological, or toxicological),

- espionage,
- loss or theft of classified information or property, and
- other acts that may adversely impact national security, the environment, or the health and safety of employees or the public.

Protection of ^{233}U-bearing materials during all phases of handling and operation requires appropriate protection measures to deter, detect, assess, delay access to material, and respond to adversary attacks.

An S&S program helps ensure that ^{233}U-bearing materials are not diverted, that the amount of these materials transferred from one location to another is accountably disposed and are within acceptable physical measurement parameters, and that controls and standards of verifiability are satisfied. A vulnerability assessment (VA) is used to identify additional S&S needs and requirements at a site containing ^{233}U materials (U.S. DOE December 1996). Site VAs identify appropriate levels of protection for each potential type of adversary and threat (e.g., theft or sabotage). Uranium-233 materials are protected while undergoing all modes of handling (i.e., processing, storage, transit, and final disposition).

Because of its fissile nature, ^{233}U may be used to produce nuclear weapons. Therefore, safeguards to prevent theft are applied. Currently, DOE requirements are used exclusively for the nation's ^{233}U inventory (U.S. DOE Sept. 7, 1994). However, the United States is under international treaty obligations which could place the ^{233}U under International Atomic Energy Agency (IAEA) safeguards as well (U.S. DOE 1992). The requirements of these two organizations are similar. Both organizations use a graded approach to safeguards in which material that is most effective in making nuclear weapons is placed under the greatest control. However, the DOE-graded approach (attractiveness levels) is more extensive and provides more flexibility than the IAEA approach. Table 4.9*a* (Bereolos et al. April 1998) summarizes the different levels of the DOE requirements. IAEA requirements, which correspond roughly with DOE Attractiveness Level B, are also given for comparison. The specifics will be discussed in further detail in the following sections.

4.9.1.1 DOE Requirements

Under DOE Orders, ^{233}U is separated into four categories according to the amount of material present and its attractiveness level. The attractiveness levels correspond to the ease in which the material can be used to create nuclear weapons. The most attractive materials (Level A) are assembled weapons and test devices. All quantities of Level A fall into Category I. Pure products (e.g., pits, major components, buttons, ingots, recastable metal, and directly convertible materials) form Level B. These fall into Categories I–IV according to the amount of material. High-grade material [e.g., carbides, oxides, solutions (≥25 g/L), nitrates, fuel elements and assemblies, alloys, and mixtures] fall into Level C, which is also further separated into four categories according to the amount of material. Level D consists of low-grade materials (e.g., solutions with 1–25 g/L or process residues that require extensive reprocessing). These materials are classified as only Category II, III, or IV. The lowest level of attractiveness (Level E) materials (e.g., highly irradiated forms, very low SNM content by weight) is classified only as Category IV.

It should be noted that these categories make no distinction as to the isotopic concentration of ^{233}U. This is in sharp contrast to ^{235}U, whose safeguards requirements are based on different levels of concentration. Because ^{233}U was not originally deployed in nuclear weapons or commercial nuclear power plants, safeguards requirements for this nuclide as a function of isotopic levels have not been developed.

There are three functions of material control: access controls, material surveillance, and material containment. Each of these functions also takes a graded approach based on the category. Access controls are concerned with preventing unauthorized personnel access to materials, data, and equipment. The graded approach ranges from simple administrative controls for Category IV material to extensive, complex procedures for Category I material. Access controls are also designed to prevent Category III and IV materials of Levels B or C from accumulating into Category I or II amounts. Finally, there is a performance requirement that tests to detect unauthorized access to Category I or II material be at least 95% effective.

Material surveillance has as its goal the deterrence and detection of diversion, theft, and unauthorized flows of materials out of the material containment areas. This goal is accomplished using sensors, patrols, logs, tamper indication devices (TIDs), portal monitoring, waste monitoring, and other administrative checks. As with material access, the performance requirement for Category I and II materials is that unauthorized actions must be detected in at least 95% of tests. Surveillance ensures that Categories I and II materials are used only in the authorized locations described below. Category III materials that are outside of locked storage areas are also required to be kept under surveillance within authorized areas. The requirements for Category IV materials are site-specific.

Material containment applies to the security areas and physical storage facilities for the material. The Material Balance Area (MBA) is the geographical area in which nuclear material is used, processed, or stored. In accordance with the graded approach, the Protected Area (PA), which is used for Category II materials, has stricter access controls and increased surveillance. Finally, within the PA is the Material Access Area (MAA), in which Category I material is used, processed, or stored.

4.9.1.2 Physical Security Facilities and Systems

For ^{233}U-bearing materials, most safeguards and security requirements are handled by the facility that has custody of these materials. Material-handling activities for specific programs are to be conducted within the following designated security areas or zones depending on the category quantity of the material:

- property protected area (PPA),
- limited area (LA),
- PA, and
- MAA.

A sample site plan noting these areas for a Category I quantity of materials is provided in Fig. 4.9*a*. The following description describes a feature that could be used for the highest level of protection required. Processing of a Category I quantity of materials requires the highest level of protection. The site (shown in Fig. 4.9*a*) has several structures and protection measures which act as security barriers and provide appropriate levels of adversary delay. Barriers provide concentric layers of graded protection and defense measures and may be passive or active. Passive barriers include fencing, geologic formations, hardened walls, locking systems, and vault doors. Active barriers include smoke and dispersed foam. Information garnered from the use of various barriers, along with conduct of VA performance testing, provides the basis for determining appropriate delay times. Detection and assessment are determined through the most cost-effective use of intrusion detection systems, closed-circuit television, lighting, personnel and material sensors, and protective force personnel. For a facility with a significant ^{233}U inventory, such detection and assessment will accommodate concentric layers of graded protection and defense measures, which include permanent or temporary Perimeter Intrusion Detection and Assessment Systems (PIDAS) with dedicated uninterruptible power sources, explosive and metal detectors, interior alarms, multiple complementary sensors, primary and secondary station alarm monitoring and communication consoles, protective patrols, and SNM monitors.

Typical features provided for physical protection of a site which processes significant inventories of ^{233}U include closed-circuit, remote-viewing systems, communication systems, fencing, intrusion detection systems, lighting, personal access–exit control systems, and vehicle control stations (rail, truck, and passenger vehicles). PIDAS need to be lighted at night and be protected by intruder-alarm systems and remote surveillance capabilities 24 h/d. Staffed entry portals provide access to the site. Operations involving Category I SNM handling and access are performed within a MAA. Each PA normally is secured with a double fence and intruder-detection systems. The LA may sometimes surround the PA and include a buffer zone.

4.9.1.3 International Safeguards

Facilities storing SNMs like ^{233}U-bearing materials will also satisfy requirements for international safeguards if the facility has been selected for IAEA safeguards. The IAEA is responsible for independently verifying that significant quantities of SNM like ^{233}U material have not been diverted by the government for unauthorized uses. The objective of IAEA safeguards is the timely detection of the diversion of significant quantities of SNMs to activities that have military applications. Material accountancy (see Sect. 4.9.2) is used together with containment and surveillance as complementary safeguards techniques. A specific and primary goal of the IAEA is the detection of theft or diversion of one "significant quantity" (SQ) of SNM within a specified period of time. The IAEA (1987) defines a SQ as "the approximate quantity of nuclear material in respect of which, taking into account any conversion process involved, the possibility of manufacturing a nuclear explosive device cannot be excluded." One SQ of SNM as ^{233}U is defined to be a mass of 8 kg (IAEA 1987).

All facilities with SNM storage and processing activities are designed to accommodate international and domestic safeguards, security protection, and transparency requirements. Such facilities must have an International Inspection Area (IIA) for international inspectors to use for inspection and verification of any surplus SNM. The IIA also needs to provide equipment to conduct authorized surveillance without allowing access to classified information. International inspections may include the review of documentation and recorded information from installed instrumentation and closed-circuit television cameras. International agreements may require special systems like uninterruptible power supplies. Other international requirements are found in periodic

IAEA Information Circulars and in the latest documentation of IAEA safeguards criteria (IAEA November 1990).

To satisfy IAEA safeguard verification requirements, a facility with ^{233}U materials has acceptable procedures for identifying, reviewing, and evaluating differences in material accountability measurements at different points in processing and handling, for taking acceptable physical measurements of inventories, and for the evaluation of accumulations of unmeasured inventory and unmeasured losses. In addition, an acceptable record system shows receipts for changes involving material transfers into and out of certain areas known as MBAs (MBAs are discussed in Sect. 4.9.2). Provisions are made to ensure that material accounting procedures are being operated correctly.

The first IAEA activity is verification of storage design. For this phase, a storage facility would complete IAEA's Design Information Questionnaire (DIQ). Typically, there is a two-month period after selection before the DIQ is due.

The second stage of the process is verification of the stored quantity of nuclear material. Verification is accomplished by measuring items via sampling by destructive assay on a small selection of random items and nondestructive assay of a larger fraction of the items. IAEA then places the items under containment/surveillance (C/S) using cameras and TIDs.

Future inspection and inventory activities depend on the designation of the storage area and the safeguards approach applied by IAEA. At the worst extreme, future inspections (twice a month) would verify a random sampling of TIDs and perform gamma spectrometry verification of a random sampling of items. During an annual physical inventory, a random sampling of items would be removed for nondestructive measurements. The option of opening containers and removing samples for destructive measurements is reserved by IAEA. Because of the extreme gamma radiation hazard of ^{233}U (because of the presence of ^{232}U), significant handling precautions and expenses would be incurred.

Currently, no ^{233}U is under IAEA safeguards. However, IAEA does make recommendations on the physical protection ^{233}U (IAEA 1980 and IAEA 1989). These recommendations depend on the following categorizations according to mass: 2 kg or more of unirradiated ^{233}U is Category I, between 500 g and 2 kg is Category II, and 500 g or less is Category III. Radiologically insignificant quantities and irradiated ^{233}U are exempted from these classifications. (In contrast, as with DOE Orders, ^{235}U is categorized not only by mass but also according to three levels of enrichment: greater than 20%, 10–20%, and up to 10%.) Similar to DOE Orders, IAEA safeguards do not account for different isotopic levels of ^{233}U. The limited use of ^{233}U to date has not warranted development of such safeguards regulations.

The recommendations of IAEA for protecting materials have certain concepts which are generic to all three categories. Materials are stored in areas to which access is controlled. All personnel working in the facility are trained (a) about the importance of physical protection and (b) in the appropriate responses in cases of emergency. Alarms and guards detect and respond to sabotage or unauthorized removals of material. Finally, a security survey is made whenever a significant change in a facility or its function takes place. This survey is a critical examination to evaluate, approve, and specify physical protection measures.

As in DOE requirements, storage of Category I and II nuclear materials requires a PA that is under constant surveillance, either by guards or electronically, and that is surrounded by a physical barrier. Access to this area is kept to the minimum necessary and controlled through a limited number of entry points.

Category I materials are isolated further in an inner area within the protected area. (This corresponds to the MAA of DOE requirements.) This inner area is arranged with a minimum number of alarmed entrances and exists (ideally, only one). The storage area itself should be alarmed and locked. Authority as to who has these keys should be tightly controlled. Electronic surveillance is effected using at least two independent transmissions.

4.9.1.4 Elimination of Weapons Potential

The surest way to safeguard ^{233}U from theft or misuse is to reduce its ability to be used for weapons. Studies indicate that ^{233}U can be made unsuitable for military use by diluting it with DU to a fissile concentration of 12 wt % (Forsberg et al. March 1998, Dubrin Jan. 23, 1995, and Benedict et al. 1981). This level of dilution is equivalent to diluting weapons-grade HEU with ^{238}U to 20 wt % ^{235}U.

Earlier studies on demilitarization of the large quantities of weapons-grade HEU indicate that isotopic dilution of ^{235}U with ^{238}U is the preferred demilitarization option (U.S. DOE 1996*a*). The U.S. government has issued a Record of Decision (ROD) (U.S. DOE 1996*b*) making isotopic dilution the official policy for demilitarization of HEU. Given the relatively low cost, assured technical feasibility, and acceptance for demilitarization of HEU, the same approach may be used for demilitarization of ^{233}U. It is noted that any ^{233}U inventory that contains sufficient ^{235}U (>20 wt % ^{235}U) is classified as HEU; therefore, isotopic dilution is the stated policy for demilitarization of this material. As with safeguards categories, the required levels of isotopic dilution to eliminate weapons potential for ^{233}U have not been implemented in DOE Orders or IAEA regulations.

4.9.2 Nuclear Materials Control and Accountability

As described in DOE Order 470.1 (U.S. DOE September 1995), (nuclear) MC&A is that part of the safeguards area that detects or deters theft or diversion of nuclear materials, including SNMs like ^{233}U, and provides assurance that such materials are accounted for appropriately.

The MC&A program for ^{233}U-bearing materials includes a system of checks and balances sufficient such as to detect and deter unauthorized diversion or removal of any SNM (including ^{233}U) from its authorized location and provide assurance that such material is in its proper location and is being used for authorized purposes. A facility's MC&A program is consistent with a graded materials S&S program and encompass the systems and measurements necessary to track ^{233}U material inventories, control access, provide detection capability for material loss and diversion, and assure the integrity of the detection and measurement systems that are in place.

The storage and custody of ^{233}U-bearing material comply with existing requirements for MC&A, as specified in DOE Order 5633.3B (U.S. DOE April 1998). The MC&A requirements include periodic auditing and routine assaying of such stored materials for accountability and inventory controls.

DOE Order 5633.3B (U.S. DOE April 1998) has established guidelines for determining various groupings or categories of ^{233}U-bearing materials based on their suitability for use as weapon materials. Guidelines have been developed to identify and group ^{233}U materials by an "Attractiveness Level" (A–E, with A being the most Attractive) which correspond to the ease in which the material can be used to create a nuclear weapon. Each attractiveness level is subdivided into categories based on quantities. The level of physical protection and the requirement to implement and the rigor of the different MC&A element is determined by the category of the quantity of material in an item, process, or designated area. There are four safeguards categories for SNM, Categories I through IV. A Category I quantity requires the highest level of protection and implementation of the most MC&A elements. The quantity of material designated a certain category is different for each attractiveness. For example, the amount of Attractiveness Level B ^{233}U must be equal to or greater than 2 kg to be designated a Category I quantity. In comparison, the amount of Attractiveness Level C ^{233}U must be equal to or greater than 6 kg to be designated a

Category I quantity. Also, the value used for safeguards category determination of ^{233}U is the element weight of the total uranium, not just the ^{233}U isotope weight. This system of attractiveness levels and safeguards categories is how DOE implements its graded approach to safeguards and security for SNM. For more detail on category determination, see Chapter I of the *Guide for Implementation of DOE Order 5633.3A*, "Control and Accountability of Nuclear Materials" (U.S. DOE August 1994).

There are currently some difficulties in the proper attractiveness level for immobilized ^{233}U material forms. For example, it is not clear whether high-grade ^{233}U materials, which are immobilized and diluted in an inert matrix, can be identified with a lower level of attractiveness. In principle, such a reassignment would significantly lower the ^{233}U material category and, thereby, reduce the necessary level of protection.

An MC&A system for ^{233}U-bearing materials includes nondestructive assay systems and inventory tracking systems for material inventory control and accountability. The MC&A system could include bar-code readers, computers, nondestructive assay equipment, scales, and TIDs. MC&A systems in a facility should be applied to every process transfer point that involves ^{233}U-bearing material. An SNM physical inventory of ^{233}U-bearing materials at a facility must be periodically performed.

In practice, taking physical measurements of ^{233}U is difficult because of intense radiation from the associated ^{232}U isotope and its daughter products. The specific radiological characteristics of ^{233}U and ^{232}U are discussed in Sect. 2.1.

At a ^{233}U material facility, an integrated site material balance system is established to ensure SNM balance is accomplished and verifiable. As an integral part of the material accounting activity, measurement systems is provided to determine all SNMs received, diverted through waste streams, or otherwise disposed. To support domestic and international safeguards programs, a system of accounting for the control of all SNMs is established based on a structure of what are called MBAs. A facility handling SNM like ^{233}U-bearing material is subdivided into MBAs for inventory control and accounting. The amount of SNM entering a given MBA at a facility is recorded by shipping or transfer records and may be validated by direct measurement. An acceptable record system is established to show, for each MBA, receipts for changes involving material transfers into and out of such areas.

Other activities associated with the custody of ^{233}U materials, such as packaging, should not interfere with MC&A requirements. Identification markings are required by DOE Order 5633.3B

(U.S. DOE Sept. 7, 1994) and other MC&A directives for maintaining a material inventory database and to facilitate proper accountability and management of stored ^{233}U-bearing materials.

4.9.3 References for Sect. 4.9

A list of references cited in the previous discussion on the safeguards, security, and accountability for ^{233}U-bearing materials is provided below. This is followed by a list of other sources that provide additional information on this topic.

4.9.3.1 References Cited

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4.9.3.2 Supplemental Resources

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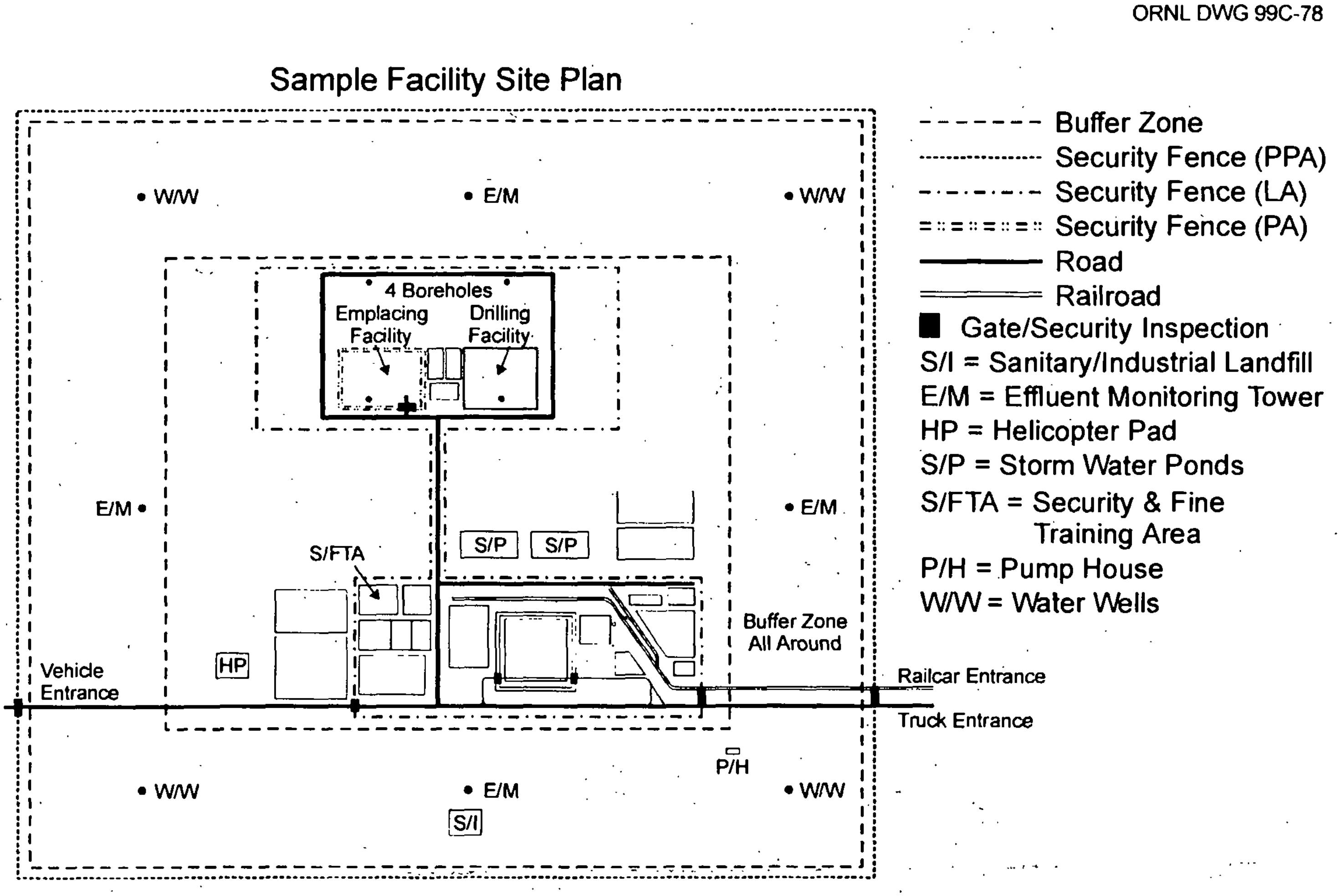

Fig. 4.9*a*. Sample layout of security systems for a site containing ^{233}U SNM. *Courtesy of Lawrence Livermore National Laboratory, as reported in Wijesinghe et al August 23, 1996.*

Table 4.9a. DOE nuclear material safeguards categories[a]

Attractiveness level	Category (quantities in kg of ^{233}U)			
	I (Highest safeguards)	II	III	IV (Lowest safeguards)
A (most attractive)	All quantities	NA[b]	NA	NA
B (IAEA)[c]	≥2 (≥2)	≥0.4 to <2 (>0.5 to <2)	≥0.2 to <0.4 (≤0.5)	<0.2 (NA)
C	≥6	≥2 to <6	≥0.4 to <2	<0.4
D	NA	≥16	≥3 to <16	<3
E (least attractive)	NA	NA	NA	Reportable quantities

[a] From Bereolos et al. April 1998.
[b] NA = not applicable.
[c] IAEA values are included for comparison.

4.10 TRANSPORTATION

This section is a discussion of the transportation requirements for ^{233}U-bearing materials. Separate discussions are provided on the regulations and standards that govern the transport of such materials. These are followed by a discussion of the pertinent transport packaging requirements.

4.10.1 Regulatory Background

As discussed in many sources (including Stewart 1988), the conventional transportation of radioactive materials, including that of ^{233}U-bearing materials, must account for a wide variation of several major factors. These include:

- radioactivity concentration,
- intrinsic hazardous toxicities,
- physical form,
- fissionable nuclide concentration (and, thus, nuclear criticality considerations),
- different available modes of transport (road, rail, air, and water),
- agreements for material transfer (domestic and international), and
- protection of humans (both workers and the public), the environment, and of sensitive cargoes in transit (e.g., camera film).

Regulations have evolved which address these factors on both the domestic and international level. The IAEA has worked for decades with competent authorities from countries throughout the world and representatives from other international organizations to develop regulatory standards. These standards serve as models for the domestic regulations used by individual countries and by international organizations such as the United Nations Committee of Experts, which promulgates standards for hazardous materials, and modal organizations such as the International Civil Aviation Organization (ICAO) and the International Air Transport Association (IATA) for air transport, and the International Maritime Organization (IMO) for sea transport. Domestically within the United States, the DOT serves as the competent authority, and promulgates regulations controlling the packaging and transport of all hazardous materials, including radioactive material; and for the more hazardous quantities of radioactive materials, the NRC issues regulations controlling the packaging of these materials. The U.S. requirements, as they apply to ^{233}U, are covered in Sects. 4.10.2 and 4.10.3, and the international requirements are addressed further in Sect. 4.10.4.

The Atomic Energy Act of 1954 gave the U.S. AEC (later NRC and DOE) safety responsibility for the use of SNM, like ^{233}U, by its licensees, including the transport of those materials. The DOT and NRC have a "memorandum of understanding" (U.S. DOT and U.S. NRC July 2, 1979) to avert duplication of effort and conflict. For regulation of intrastate shipments, the NRC, in turn, has passed some of its authority to Agreement States, which have written their own rules to be consistent with DOT regulations. The same regulations for shippers (packaging, marking, and labeling) and carriers (placarding of vehicles, loading, stowage, storage in transit, and monitoring) apply. NRC has authority for approving shipping containers (Type B) for ^{233}U materials, while DOT is responsible for investigating and documenting unusual events that may occur during transit (e.g., accidents and leakages). NRC investigates unusual events that occur during other times.

4.10.2 Standards for the Transport of ^{233}U-Bearing Materials

Issues concerning the transportation of radioactive nuclear materials, including ^{233}U materials, tend to focus on the DOT and NRC regulations promulgated in the *Code of Federal Regulations* (CFR). A list of the major coded regulations that govern the transportation of ^{233}U materials is provided in Table 4.10*a* (Doman 1988, Shappert 1998, and Stewart 1988). Federal regulations promulgated in 10 CFR Part 71.4 (NRC) and 49 CFR Part 173.403 (DOT) define ^{233}U as a fissile material for the purpose of transport regulations.

Of the federal regulations listed in Table 4.10*a*, the most significant include those of the NRC in 10 CFR Part 71 ("Packaging and Transport of Radioactive Material") and those of DOT in 49 CFR Part 173 ("Shippers—General Requirements for Shipments and Packagings") and 49 CFR Part 178 ("Specifications for Packagings"). A list of the sections of these coded regulations that significantly impact ^{233}U-bearing materials is provided in Tables 4.10*b*, 4.10*c*, and 4.10*d* for 10 CFR Part 71, 49 CFR Part 173, and 49 CFR Part 178, respectively.

Special definitions are associated with many of these regulations. Some of these include:

- Radioactive materials are defined in the regulations (10 CFR Part 71.4 and 49 CFR Part 173.403), for the purposes of transport, as those materials having specific activities (concentrations) greater than 70 Bq/g (0.002 μCi/g).
- The regulations provide a graded approach to packaging requirements depending upon the hazard posed by its contents; the greater the hazard, the more stringent are the packaging requirements. From the least hazardous contents to the most hazardous contents, and therefore

from the least robust to the most robust package design requirements, the packages are denoted as:

— excepted package,

— industrial packages (three types, and also, within the U.S. regulations, strong-tight packages are allowed for certain contents),

— Type A, and

— Type B.

The requirements for each of these package types and the contents limits allowed therein may be found in 10 CFR Part 71 and 49 CFR Part 173.

- The contents limits for Type A packages are specified in terms of radionuclide-specific values for A_1 ("special form"), and A_2 (other than special form, sometimes denoted as "normal form"). Special form, depending upon the radionuclide(s) involved, may allow a greater quantity of radioactive material to be carried in a Type A package. Special-form materials must either be a solid piece, or contained in a sealed capsule, where the piece or capsule design is shown to be capable of withstanding specific mechanical, thermal, leaktightness or dispersibility, and leaching tests (see 10 CFR Part 71.75 and 49 CFR Part 173.469). For ^{233}U, the Type A package contents limits are (see 10 CFR Part 71 Appendix A and 49 CFR Part 173.433):

  $A_1 = 10$ TBq (270 Ci)

  $A_2 = 1 \times 10^{-3}$ TBq (2.7×10^{-2} Ci)

  Should there be other nuclides mixed in with the ^{233}U, then an effective A_1 or A_2 value will need to be determined according to the equations and tables given in 10 CFR Part 71 Appendix A and 49 CFR Part 173.433.

- Contents or material limits for other packages are specified in terms of:

  — fractions of the A_1 or A_2 values in excepted packages (see 49 CFR Part 173.425),

  — specific activity limits (if the material qualifies as a low specific activity (LSA) material), where the limits are denoted in terms of fractional values of A_2/g (see 10 CFR Part 71.4 and 49 CFR Part 174.403), and

  — activity limits per unit surface area [if a nonradioactive object is contaminated and can satisfy all of the requirements for a surface-contaminated object (SCO)], where the limits are denoted in terms Bq/cm^2 (microcuries/cm^2) (see 10 CFR Part 71.4 and 49 CFR Part 174.403).

Contents limits are not specified in the regulations for Type B packages [see 49 CFR Part 173.431(b)]; rather, the contents limits are established by the package design which must be approved by the NRC (or the DOE for a DOE-owned package not certified by the NRC) during the regulatory bodies review of the package Safety Analysis Report for Packaging (SARP) and documented in the Certificate of Compliance (CoC) issued by the NRC or the DOE for that package design. It is unlikely that the ^{233}U currently stored by DOE facilities will satisfy the regulatory requirements for transport as either LSA material or SCO. Thus, the focus from this point onward is on transport of the material in Type B packages.

- For packages containing radioactive material, a "transport index" (TI) is assigned. The method for defining the TI is provided in 49 CFR Part 173.403. This TI serves two functions. It is used to provide controls on the radiation levels in any location during transport and storage incident to transport (see 49 CFR Part 173.447). It is also used to ensure criticality control for fissile materials. The TI is listed on shipping papers and is used to determine the label to be used on a packaging (i.e., I–White, II–Yellow, or III–Yellow). The labeling requirements are found in 49 CFR Part 172.403.
- The radiation levels on the outside of packages are controlled by 49 CFR Part 173.441. Specifically, if a package is carried in nonexclusive use, the radiation levels are limited to 2 mSv/h (200 mrem/h) at the package surface, and to 0.1 mSv/h (10 mrem/h) at 1 m from the package surface. If either of these levels are exceeded, then the package must be transported by surface mode (road, rail, or water), under exclusive use and, subject to other controls, for example:
  - — the surface radiation level limit is increased to 10 mSv/h (1000 mrem/h),
  - — the radiation level at any point on the outer surfaces of the vehicle is limited to 2 mSv/h (200 mrem/h),
  - — the radiation level 2 m from the outer lateral surfaces of the vehicle is limited to 0.1 mSv/h (10 mrem/h), and
  - — the radiation level in any normally occupied space is generally limited to 0.02 mSv/h (2 mrem/h).

This last limit may be avoided if the carrier is a private carrier and any exposed personnel under the control of that carrier wears radiation dosimetry devices as part of a radiation protection program.

There are different requirements for the transportation of nuclear materials like ^{233}U, depending upon whether the movement of materials is considered on-site (intrasite) or off-site (intersite). Currently, no federal regulations govern the on-site transport of hazardous substances like ^{233}U-bearing materials. For DOE facilities, on- and off-site transport requirements are defined in DOE Order 460.1A, "*Packaging and Transportation Safety*" (U.S. DOE Sept. 27, 1995). As defined in the Order, *on-site* is any area within the boundaries of a DOE site or facility that is fenced or otherwise access-controlled, and *off-site* is any area within or outside a DOE site to which the public has free uncontrolled access.

For this report, *intrasite transportation* means the transport of ^{233}U-bearing material between different areas on a particular site. In most facilities, SNM processing, use, and handling are performed in, and confined to, areas adjacent to each other. Consequently, intrasite transport of ^{233}U-bearing materials between buildings is usually not required.

Intersite transportation, as defined in this report, refers to the transport of ^{233}U-bearing material to a facility located outside the boundary of a given site. Off-site transportation of ^{233}U-bearing materials is subject to federal regulations from two government agencies: (NRC and DOT), and to compliance with DOE Orders. Different regulations may apply to different parts of the material-handling phase, depending upon which agency has authoritative control.

4.10.3 Packaging Requirements for Transport

The NRC transportation regulation documented in 10 CFR Part 71, "*Packaging and Transportation of Radioactive Material*" (U.S. NRC Jan. 1, 1999), establishes the requirements for packaging, preparing for shipment, and transportation of radioactive material, including ^{233}U-bearing material.

This regulation also defines the procedures and standards for obtaining NRC approval of shipping packages and shipping procedures for fissile material such as ^{233}U and Type B quantities of other radioactive materials. By reference, the 10 CFR Part 71 regulation incorporates the requirements of DOT regulation 49 CFR Parts 171–180, "*Hazardous Materials Regulations*" (U.S. DOE Oct. 1, 1998). Whenever possible, the DOE transports radioactive materials under DOT and NRC regulations.

Many ^{233}U materials are currently stored in DOT-6M and DOT- 2R packaging, whose specifications are provided in the sections of 49 CFR Part 178 (see Table 4.7*d*). DOT-6M packaging is authorized by the DOT regulations of 49 CFR Part 173 for the shipment of Type B quantities of radioactive materials, which includes most ^{233}U-bearing materials.

General construction requirements for the DOT-6M packaging may be found in 49 CFR Part 178.354, "*Specification 6M; Metal Packaging,*" and for the DOT-2R inner vessel in 49 CFR Part 178.360, "*Specification 2R; Inside Containment Vessel.*" Examples of a typical DOT-6M and DOT-2R inner containment vessel are provided in Figs. 4.10*a* and 4.10*b*, respectively (Kelly September 1994).

4.10.4 International Transportation Regulations

Regulations governing the design, testing, certification, and use of Type B and fissile radioactive material packages originated from the international regulatory structure, which is now maintained by the IAEA of the United Nations. Further discussion of the background for international regulation is provided in *The Radioactive Materials Packaging Handbook* (Shappert 1998). The IAEA has responsibility for the safety of the international transport of ^{233}U materials. A documentation of IAEA transportation standards for all radioactive materials is provided in the Agency's Safety Series No. 6 Report, *Regulations for the Safe Transport of Radioactive Material* (IAEA 1996). Documentation of IAEA transportation standards for all radioactive materials is provided in the IAEA Safety Standards Series No. ST-1, *Regulations for the Safe Transport of Radioactive Material, 1996 Edition, Requirements*. This document provides the current set of requirements which are expected to be adopted into U.S. regulations, by the NRC and the DOT, in the year 2000 or 2001. Currently, the U.S. regulations are based upon the IAEA *Regulations for the Safe Transport of Radioactive Material, 1985 edition, as amended 1990* (IAEA 1990).

4.10.5 References for Sect. 4.10

A list of cited references documenting the requirements for transporting ^{233}U-bearing materials is provided below. This is followed by a list of sources that provide additional information on this topic.

4.10.5.1 References Cited

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U.S. Nuclear Regulatory Commission. Jan. 1, 1999. "Packaging and Transportation of Radioactive Material," *Code of Federal Regulations*, 10 CFR Part 71, U.S. Government Printing Office, Washington, D.C.

4.10.5.2 Supplemental Resources

Martin Marietta Energy Systems, Inc. Nov. 7, 1994. *Design Guide for Packaging and Offsite Transportation of Nuclear Components, Special Assemblies, and Radioactive Materials Associated with the Nuclear Explosives and Weapons Safety Program*, Safety Guide 100, Rev. 1, Oak Ridge, Tenn.

Miller, K. L., ed. 1992. *CRC Handbook of Management of Radiation Protection Programs*, 2d ed., CRC Press, Ann Arbor, Mich.

Wijesinghe, A. M., et al. Aug. 23, 1996. *Alternative Technical Summary Report for Immobilized Disposition in Deep Boreholes*, UCRL-LR-121736, Lawrence Livermore National Laboratory, Livermore, Calif.

Wolff, Theodore A. December 1984. *The Transportation of Nuclear Materials*, SAND84-0062, TTC-0471, Sandia National Laboratories, Albuquerque, N. Mex.

ORNL DWG 98-4472

DOT Specification 6M Package
(Per 49 CFR 178.354)

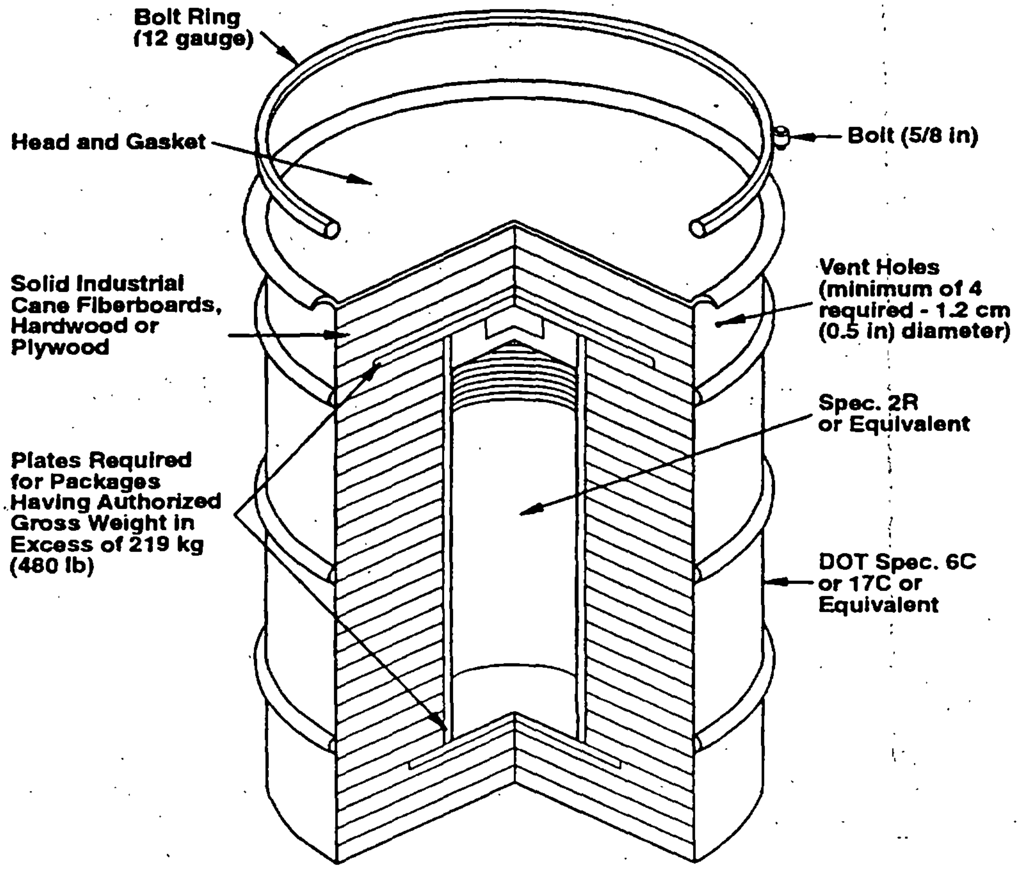


Fig. 4.10*a*. Typical DOT Specification 6M: a 6M overpack containing a 2R container. *Courtesy of U.S. Department of Energy, Richland Operations Office, as reported in Kelly Sept. 1994.*

ORNL DWG 98-4771

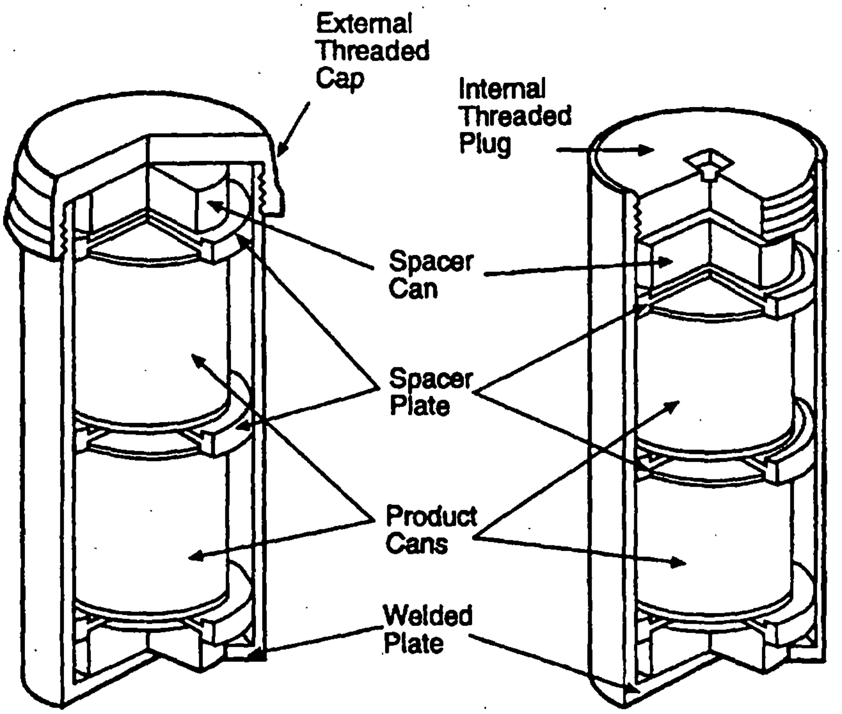


Fig. 4.10*b*. Typical DOT Specification 2R. *Courtesy of U.S. Department of Energy, Richland Operations Office, as reported in Kelly September 1994.*

Table 4.10*a*. Federal transportation regulations affecting ^{233}U-bearing materials[a]

Government agency	Code	Part No.	Title
NRC	10 CFR	20	Standards for Protection Against Radiation
NRC	10 CFR	70	Domestic Licensing of Special Nuclear Material
NRC	10 CFR	71	Packaging and Transportation of Radioactive Material
NRC	10 CFR	73	Physical Protection of Plants and Materials
DOT	49 CFR	171	General Information, Regulations, and Definitions
DOT	49 CFR	172	Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, and Training Requirements
DOT	49 CFR	173	Shippers–General Requirements for Shipments and Packagings
DOT	49 CFR	174	Carriage by Rail
DOT	49 CFR	175	Carriage by Aircraft
DOT	49 CFR	176	Carriage by Vessel
DOT	49 CFR	177	Carriage by Public Highway
DOT	49 CFR	178	Specifications for Packagings
DOT	49 CFR	179	Specifications for Tank Cars
DOT	49 CFR	180	Continuing Qualification and Maintenance of Packagings

[a] Adapted from Doman 1988, Shappert 1998, and Stewart 1988.

Table 4.10*b*. Major sections of 10 CFR Part 71 (*Packaging and Transport of Radioactive Material*) that affect ^{233}U-bearing materials

Subpart	Section	Title
A–General Provisions	71.4	Definitions
C–General Licenses	71.18 71.22 71.24	General License: Fissile Material, Limited Quantity Per Package General License: Fissile Material, Limited Moderator Per Package General License: Fissile Material, Limited Moderator, Controlled Shipment
E–Package Approval Standards	71.53 71.55 71.59	Fissile Material Exemptions General Requirements for Fissile Material Packages Standards for Arrays of Fissile Material Packages
F–Package, Special Form, and LSA-III Tests	71.71 71.73	Normal Conditions of Transport Hypothetical Accident Conditions
H–Quality Assurance	71.101–71.137	All sections, as appropriate

Table 4.10c. Major sections of 49 CFR Part 173 (*Shipper's—General Requirements for Shipments and Packaging*) that affect ^{233}U-bearing materials

Subpart	Section	Title
I–Class 7 (Radioactive Materials)	173.403	Definitions
	173.413	Requirements for Type B Packages
	173.431	Activity Limits for Type A and Type B Packages
	173.433	Requirements for Determining A_1 and A_2 Values
	173.435	Table of A_1 and A_2 Values for Radionuclides
	173.441	Radiation Level Limits
	173.457	Transportation of Fissile Material, Controlled Shipments

Table 4.10d. Major sections of 49 CFR Part 178 (*Specifications for Packaging*) that affect ^{233}U-bearing materials

Subpart	Section	Title
K–Specifications for packagings for Class 7 (Radioactive Material)	178.350	Specification 7A; General Packaging, Type A
	178.352	Specification 6L; Metal Packaging
	178.354	Specification 6M; Metal Packaging
	178.360	Specification 2R; Inside Containment Vessel

4.11 SAFE PLANT OPERATIONS

This section discusses the requirements for the safe operations of plants and facilities that process, handle, and store ^{233}U-bearing materials. Separate discussions are provided on general plant operational requirements, databases essential for supporting plant operations, and operational requirements for ensuring nuclear criticality safety.

4.11.1 Operational Requirements

For proper processing, storage, and handling of ^{233}U-bearing materials, facility operations should be conducted 1 to 3 shifts/d, 5 d/week. Typically, most facilities can be expected to fully function 5 d/week, 8 h/d, and 250 d/year. Allowing time for routine maintenance and required S&S and MC&A activities, normal facility availability would be considered to be about 200 d/year. Because of the rapid grow-in of gamma activity, an operation such as fuel fabrication, with ^{233}U fuel materials that have been processed to remove the daughter products would be more appropriately carried out on a 24-h work day, 7-d/week operation to get as much done as possible before the activity levels get too high for safe operation. For operations that involve working with aged material that has already reached secular equilibrium where it is not practical to remove the daughter products, a 5-d, 8-h/d schedule is probably appropriate.

4.11.1.1 Operating Staff Organization and Functions

The responsibility for the safe operation of a facility containing ^{233}U-bearing materials rests with the facility operations group, which also operates any hot cells, glove boxes, and other related processing equipment. The facility operations staff also operates and routinely checks building service equipment, including all ventilation systems. It is their responsibility to ensure that the required services are operating normally and efficiently for the supporting groups in the laboratories and other areas of the building (Horton et al. March 1972).

A typical staff organization of a ^{233}U material-processing and handling facility is schematically illustrated in Fig. 4.11*a*. This chart shows the overall organization of the facility relationships among the various groups that are involved. The core facility staff consists of a team of engineers and technicians. A typical facility operation occurs on a 5-d work week, 8-h work day schedule with a shift organization (as appropriate). Each work-shift organization is typically composed of a foreman-technician and several technicians, who are supported by technical and engineering groups, including a facility safety officer. Other facility organizations provide support for maintenance craft and repair, health physics, and safety (Horton et al. March 1972).

Major responsibilities of the individuals who comprise the organization, as shown in Fig. 4.11*a*, include:

- *Building supervisor*. This person is responsible for the operation of the entire facility.
- *Facility safety officer*. This person is responsible for all facility safety matters, including zoning regulations, emergency manuals and procedures, and safety training. This individual also reviews and approves all nonroutine maintenance requests and procedures and radioactive material transfer procedures.
- *Chief of operations*. In addition to supervising the facility work-shift groups, the chief of operations has primary responsibility for administrative control and supervision, with the assistance of a maintenance engineer, of all facility maintenance activities.
- *Shift supervisor*. The shift supervisor on duty is responsible for all operations in the processing area, including the determination that any required maintenance can be done safely and will not interfere with any process operation in progress. This person must be aware of all equipment and service operations that are in progress, and he or she has the authority and responsibility to stop or change any of these operations.
- *Technical and engineering groups*. These people review and analyze all data generated in the process operations and determine process conditions for all runs.
- *Health physics group*. These people are knowledgeable of the facility's radiological risks and the impacts of these risks on process operations and facility staff.

4.11.1.2 Equipment Requirements

To ensure the proper operations of plants and facilities that process, handle, and store ^{233}U-bearing materials, requirements in several areas must be met. A detailed set of documented procedures are used, and sample checklists that are based on these procedures are provided for each of the operational areas discussed in Sects. 4.11.1.2.1 through 4.11.1.2.3.

4.11.1.2.1 Preoperational System Testing

Preoperational system testing includes functional tests performed on a component, or system of components, to ensure the achievement of designed performance.

4.11.1.2.2 Equipment Calibration Methods

Equipment calibration involves establishing a quantitative verification of the accuracy of a sensing system.

4.11.1.2.3 Run-Sheet and Check-Sheet Use

Operations at ORNL involved with the processing of ^{233}U-bearing materials have been conducted with a minimum of two operators per 8-h shift and followed detailed operating sheets. Those operations involving significant quantities (>500 g) of ^{233}U were supervised by technical personnel.

In addition to standard operating procedures, operating check lists for ^{233}U-bearing facilities incorporate process limits for nuclear criticality safety as well as general facility safety. Examples of operating check lists are provided in Haws et al. August 1965.

4.11.1.3 Other Requirements

Other requirements for ensuring safe operations of a facility containing ^{233}U-bearing materials include those for lock out and facility sampling procedures and packaging. Lock-out requirements are described in DOE Order 5480.19, *Conduct of Operations Requirements for DOE Facilities* (U.S. DOE July 9, 1990). Examples of sampling procedures are described in various documents that reference the LWBR fuel fabrication experience (see Sect. 3.7.2). The sampling of ^{233}U material is difficult because of the need to consider both the alpha-containing material and the beta- and gamma-shielding issue. However, this kind of sampling is no more difficult than taking a sample of irradiated plutonium. It requires that the material be homogenized as much as possible to ensure that a representative sample of ^{233}U is obtained. The quality of the analysis is only as good as the sample. The actual operation of taking the sample will be done inside a hot cell or shielded glove box to minimize radiation exposure. The liquid samplers could be the recirculating type where a stream of the desired process stream is recycled through a sample bottle until the solution flowing through the bottle is representative. Other samplers are the evacuated-bottle or single-needle sampler where the vacuum in the bottle pulls a sample through the needle from the sample line. Sampling solids is much more difficult because of complications in ensuring that a homogeneous sample has been obtained and because of the difficulty of safely handling powders or particulate material. In addition, there are high contamination risks, and special precautions must be taken. Analytical techniques must also be carefully chosen to minimize contamination risks and waste disposal problems. The procedures that would be used in these operations are those that have been used in the DOE complex SNF reprocessing facilities at the Hanford Site, the ICPP, and the SRS canyons.

4.11.2 Databases Supporting Plant Operations

For proper control and maintenance of plant operations, databases should be developed and maintained to establish critical process parameters in the flowsheets for various ^{233}U separation methods. Such process parameters include the distribution and extraction coefficients for critical process materials, including uranium, organic extractants, and ion exchange resins.

4.11.3 Operational Requirements for Criticality Safety

The operational requirements for nuclear criticality safety in a facility containing ^{233}U-bearing materials are based on two sets of standards developed by the ANS and accredited by ANSI. One of the standards, ANSI/ANS-8.1-1998 (ANSI/ANS 1998), provides a set of general guidelines for nuclear criticality safety in operations with fissionable materials outside reactors. The other standard, ANSI/ANS-8.19-1996 (ANSI/ANS 1996), establishes administrative guidelines for an effective nuclear criticality safety program. The specific requirements of each of these standards are discussed below.

4.11.3.1 General Guidelines

General guidelines for good criticality practices at facilities that process and store ^{233}U-bearing materials are provided in the standard ANSI/ANS-8.1-1998 (ANSI/ANS 1998). Such criteria have been developed to ensure the implementation of safe operating practices for protection against the consequences (harmful releases of radiation) of an inadvertent nuclear chain reaction (criticality accident), preferably by prevention of such a reaction. To meet this objective, the standard ANSI/ANS-8.1-1998 (ANSI/ANS 1998) provides both administrative and technical practices for achieving and ensuring nuclear criticality safety.

Required administrative practices for criticality safety are covered in the following areas:

- *Management responsibilities*. These include:
  - — Establishing a level of supervision responsible for nuclear criticality safety. This supervision must ensure criticality safety training and periodic retraining of all facility

operations and maintenance personnel to the extent that each worker is aware that nuclear criticality safety in his or her work area is ultimately his or her own responsibility.

- — Providing a staff knowledgeable about nuclear criticality data, criticality safety, and facility operations who can serve as advisors to process supervision.
- — Establishing criteria to be satisfied by nuclear criticality safety controls.
- — Preparing and approving emergency procedures (see below).

- *Process analysis*. Before an operation with fissionable ^{233}U materials is either initiated or changed, it must be established that the entire process will be subcritical under normal or credible abnormal conditions. Facility conditions for the maximum effective multiplication factor (k_{eff}) must be carefully determined.
- *Documented procedures*. Procedures governing nuclear criticality safety operations must be written, must specify all controlling parameters, be understood by all individuals participating in these operations, and apply in such a way that no one inadvertent departure from a procedure could result in a criticality accident.
- *Materials control*. Movement of fissionable materials must be controlled and properly identified with appropriate labeling and area posting. Material limits must specify limits on parameters that are subject to procedural control.
- *Operational control*. Procedure deviations and unforeseen process alterations that affect nuclear criticality safety must be reported to management and promptly investigated. Measures must be taken to prevent recurrence.
- *Operational reviews*. Facility operations must be annually reviewed to verify that nuclear criticality safety has not been compromised by either unfollowed operational procedures or altered process conditions. Persons knowledgeable in nuclear criticality safety and not responsible for facility operations must perform this review.
- *Emergency procedures*. Facility organizations that are expected to respond to nuclear criticality emergencies must be aware of conditions that might be encountered and should be assisted in preparing suitable procedures that govern their responses.

Required technical practices for nuclear criticality safety are included in the following areas:

- *Controlling factors*. The major controlling factor for achieving nuclear criticality safety of a system containing fissionable material (like ^{233}U) is the effective multiplication factor (k_{eff}), which depends on:

— the mass and distribution of all fissionable materials, and

— the mass, distribution, and nuclear characteristics of all other materials associated with the fissionable materials.

Nuclear criticality safety is achieved by controlling one or more parameters of a system within subcritical limits (for which $k_{eff} < 1$). All controlled parameters and their limits for ensuring subcriticality must be specified. Nuclear criticality control for maintaining subcritical conditions may be established by:

— administrative procedures (e.g., established posted limits),

— physical constraints (e.g., subcritical dimensional limits),

— measurement instrumentation,

— chemical means (e.g., preventing conditions that allow precipitation), and

— relying on natural processes.

- *Double-contingency principle*. Facility process designs should incorporate sufficient safety factors that require at least two unlikely, independent and concurrent changes in process conditions before a nuclear criticality accident is possible.
- *Geometry control*. Process equipment designed with limited dimensions should be used where practicable. All dimensions and nuclear properties on which reliance is placed must be verified before the initiation of operations.
- *Neutron absorbers*. Neutron-absorbing materials (e.g., boron and cadmium) may be used for criticality control in process materials, equipment, or both.
- *Subcritical limits*. As applicable, subcritical limits based on experimental data must be established with adequate allowance for uncertainties in the data. In the absence of experimental data, limits may be derived from calculations made by comparisons with experimental data made in accordance with Sect. 4.3 of standard ANSI/ANS-8.1-1998 (ANSI/ANS 1998).

4.11.3.2 Additional Administrative Practices

The standard ANSI/ANS-8.19-1996 (ANSI/ANS 1996) provides additional criteria for administrating a nuclear criticality safety program for facilities containing fissile (including ^{233}U-bearing) materials. These additional criteria include:

- *Management responsibilities* (in addition to those covered in ANSI/ANS-8.1-1998) (ANSI/ANS 1998). These include:

  - — Formulating nuclear criticality policy and making it known to all facility employees involved in operations with fissile (in particular ^{233}U) material.
  - — Monitoring, auditing, and assessing the facility's nuclear criticality safety program and its effectiveness.
- *Supervisory responsibilities* (in addition to those covered in ANSI/ANS-8.1-1998) (ANSI/ANS 1998). Each supervisor in the facility must be responsible for:
  - — The safety of operations under his or her control.
  - — Knowing those aspects of nuclear criticality safety that are relevant to the operations under his or her control.
  - — Maintaining records of criticality safety training and of verification of personnel understanding.
  - — Development and appropriate upgrades of written procedures applicable to the operations under his or her control.
  - — Verifying compliance with nuclear criticality safety specifications for new or modified equipment before its use.
  - — Requiring conformance with good safety practices, including good housekeeping and clear identification of ^{233}U- and other fissile-bearing materials.
- *Nuclear criticality safety staff responsibilities*. This staff is responsible for:
  - — Providing technical guidance for the design of equipment and processes and for the development of operating procedures.
  - — Maintaining familiarity with current developments in nuclear criticality safety standards, guides, and codes.
  - — Maintaining familiarity with all facility operations requiring nuclear criticality safety controls.
  - — Assisting supervision, on request, in training personnel.
  - — Participating in audits of criticality safety practices and compliance with procedures as directed by management.
  - — Examining reports of procedural violations and other deficiencies in order to recommend improved safety practices and procedural requirements to management.
- *Operating procedures.* Facility operations must be reviewed annually to verify that standard procedures are being followed and that process conditions have not been altered so as to affect nuclear criticality safety. Nuclear criticality safety staff, not immediately responsible for

facility operations, will perform these reviews in consultation with operations personnel. Deviations from operating procedures and unforseen alterations in process conditions that affect nuclear criticality safety must be reported to facility management, promptly investigated, appropriately corrected, and documented. Documented operating procedures for ensuring criticality safety in a facility containing ^{233}U-bearing materials should have the following features:

— Facilitate safe and efficient conduct of operations.

— Be organized for convenient and efficient use by operations staff.

— Include significant controls and limits for the nuclear criticality safety of the operation and have a characteristic that no single, inadvertent departure from any procedure can cause a criticality accident.

— Be reviewed periodically by supervision and be reviewed by nuclear criticality safety staff if new or revised.

— Be supplemented by flowsheets, process limits incorporated in operational check lists, or automated inventory systems.

— Include deviations from operating procedures and unforeseen alterations in process conditions that affect nuclear criticality safety.

- *Process evaluation.* Nuclear criticality safety evaluations of facility processes must:

— Establish and document that an entire process will remain subcritical after new or modified operations with fissile materials (e.g., ^{233}U) have been implemented.

— Determine and identify the controlled parameters and their associated limits upon which nuclear criticality safety depends.

— Be verified by independent assessment before the start of operation.

- *Materials control* (in addition to those covered in ANSI/ANS-8.1-1998) (ANSI/ANS 1998). The control of fissile materials must include the following requirements:

— Access to areas where fissile material is handled, processed, or stored must be controlled.

— Documented procedures must specify the control of the movements of fissile materials.

— Material labeling and area posting must specify material identification and limits on parameters subject to procedural criticality control.

— Procedural criticality control must be imposed and maintained on any neutron-absorbing materials that are incorporated into the process material or equipment.

— To assure subcritical conditions, control of spacing, mass, density, and geometry of fissile material must be maintained.

4.11.4 References for Sect. 4.11

A list of cited references on safe plant operations is provided below. This is followed by a list of additional sources that provide information on this topic.

4.11.4.1 References Cited

American National Standards Institute/American Nuclear Society. 1998. *American National Standard for Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors*, ANSI/ANS-8.1-1998, American Nuclear Society, La Grange Park, Ill.

American National Standards Institute/American Nuclear Society. 1996. *American National Standard Administrative Practices for Nuclear Criticality Safety*, ANSI/ANS-8.19-1996, American Nuclear Society, La Grange Park, Ill.

Haws, C. C. August 1965. *Summary of the Kilorod Project—A Semiremote 10-kg/day Demonstration of* $^{233}UO_2$*–*ThO_2 *Fuel-Element Fabrication by the ORNL Sol-Gel Vibratory-Compaction Method*, ORNL-3681, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Horton, R. W., et al. March 1972. *Safety Analysis: LWBR Support Program in Building 3019 Pilot Plant*, ORNL/TM-3567, Oak Ridge National Laboratory, Oak Ridge, Tenn.

U.S. Department of Energy. July 9, 1990. *Conduct of Operations Requirements for DOE Facilities*, DOE Order 5480.19, Washington, D.C.

4.11.4.2 Supplemental Resources

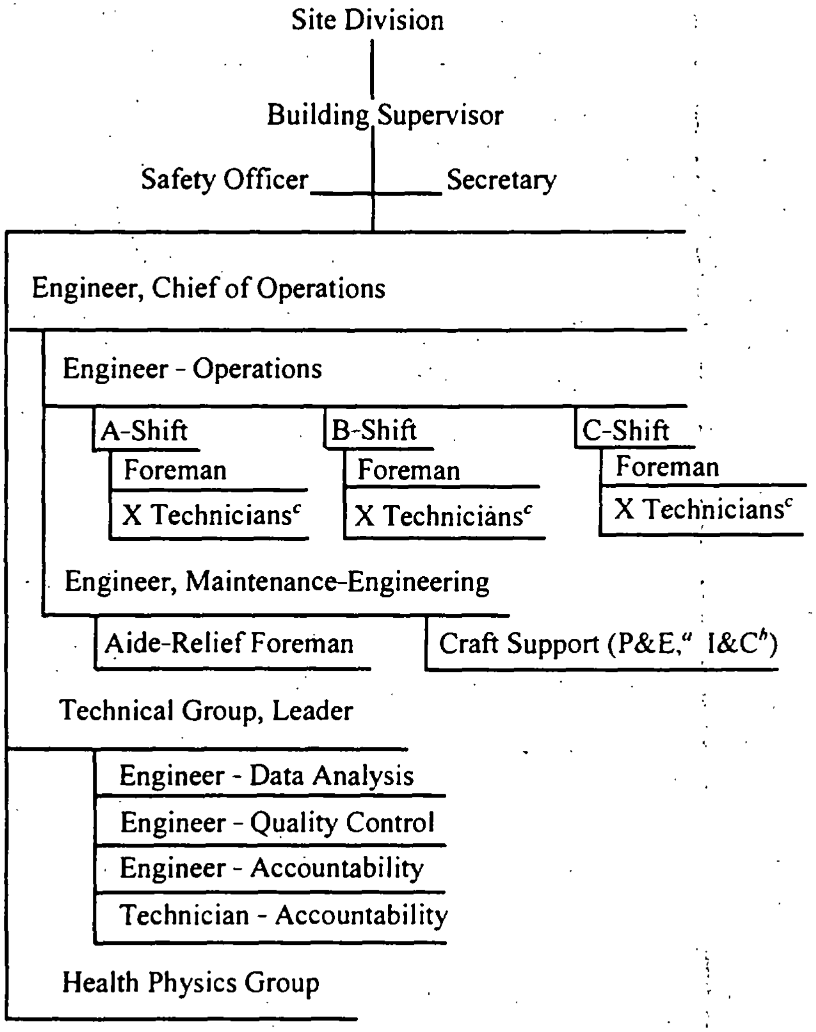
Chemical Technology Division. Aug. 24, 1984. *Final Operational Safety Requirements for the Radiochemical Processing Plant (RFP)*, ORNL/CF-81/37, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Chemical Technology Division. Sept. 14, 1984. *Final Safety Analysis Report for the Consolidated Edison Uranium Solidification Program (CEUSP) Facility*, ORNL/ENG/INF-83/2, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Horton, R. W., D. W. Magnuson, and W. T. McDuffee. March 1972. *Criticality Analysis: LWBR Assistance Program in Building 3019*, ORNL-TM-3469, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Immer, J. R. 1953. *Materials Handling*, McGraw-Hill Book Company, Inc., New York.

ORNL DWG 98-8105



[a] P&E = site plant and equipment organization.

[b] I&C = site instrumentation and controls organization.

[c] X = number of facility technicians, which is determined by the amount of material processed and handled.

Fig. 4.11*a*. Typical organization of a ^{233}U material processing and handling facility.

4.12 WORKER TRAINING AND CERTIFICATION

This section describes typical ^{233}U worker training program and certification requirements. The basis for most of the information presented is the *Radiochemical Technology Section Training and Qualification Program Plan, Rev. 3* (October 1996), prepared by the Radiochemical Technology Section (RTS) of the ORNL CTD. Hereafter, this document is referred to as the RTS Training and Qualification Program Plan (TQPP), or simply TQPP. The TQPP was prepared (a) to provide a detailed plan for developing, implementing, and maintaining RTS training programs and (b) to comply with the requirements of DOE Order 5480.2A, *Personnel Selection, Qualification, and Training Requirements for DOE Nuclear Facilities* (U.S. DOE Nov. 15, 1994). An outline of a typical ^{233}U worker training program is provided below followed by a discussion of worker certification requirements.

4.12.1 Typical Training Program

Requirements and methods of programs for training workers handling ^{233}U materials are outlined and described below. Specific details are given in the TQPP. Worker training, as covered in this section, pertains to the instruction that is required and designed to develop or improve job performance regarding the safe and proper handling and maintenance of ^{233}U-bearing materials.

The TQPP addresses the following requirements for ^{233}U worker training:

4. Qualification, organization, and responsibilities of training supervision and staff, including:
    a. facility manager,
    b. assistant facility manager,
    c. facility operations supervisor,
    d. training coordinator,
    e. training staff, and
    f. oral board leader;
2. Analysis and design of training program;
3. Development of training materials;
4. Implementation of training (including methods and procedures);
5. Evaluation of training program;
6. Administration of training program; and

7. Miscellaneous record forms and checklists, including:
    a. task-to-training matrix form (this references the training required for each task),
    b. oral board evaluation form,
    c. training materials instructional review checklist,
    d. training monitor sheet,
    e. surveillance form,
    f. student evaluation form,
    g. record of remediation, and
    h. experience verification sheet.

Specific details of each of the previous topics are provided in the TQPP.

Special topics that are covered in ^{233}U worker training include:

- general employee training (GET);
- material accountability, safeguards, and security;
- material handling;
- packaging;
- radiological safety, including nuclear criticality safety;
- safe plant operations;
- storage standard; and
- transportation.

4.12.2 Certification Requirements

Worker certification, as discussed in this section, pertains to the process by which authorized management provides written endorsement of the satisfactory achievement of the qualification of a worker for a position involved with the handling and maintenance of ^{233}U-bearing materials. The TQPP addresses the certification and recertification requirements for both training staff and workers handling ^{233}U-bearing materials. A certification proficiency verification list is also provided in the TQPP to identify personnel who have demonstrated proficiency in a designated facility. Specific details are provided in the TQPP.

4.12.3 References for Sect. 4.12

Listed below are the references cited in Sect. 4.12. This is followed by a list of additional resources that provide more detailed information on worker training and certification requirements for handling ^{233}U-bearing materials.

4.12.3.1 References Cited

Radiochemical Technology Section Training and Qualification Program Plan, Rev. 3. October 1996. Radiochemical Technology Section, Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

U.S. Department of Energy. Nov. 15, 1994. DOE Order 5480.2A, *Personnel Selection, Qualification, and Training Requirements for DOE Nuclear Facilities*, Washington, D.C.

4.12.3.2 Supplemental Resources

U.S. Department of Energy. August 1994. *DOE Handbook—Training Program Handbook: A Systematic Approach to Training*, DOE-HDBK-1078-94, Washington, D.C.

5. CURRENT AND POTENTIAL ^{233}U MATERIAL APPLICATIONS

5.1 INTRODUCTION

5.1.1 Discussion

Most of the current DOE inventory of ^{233}U is considered surplus. As discussed in Bereolos et al. (June 1998), some of this material will be disposed of as waste, but some may be kept for future use. Several potential uses of ^{233}U are described in this section. The decision as to which portions of the inventory should be retained for use depends on two considerations: (1) future needs and (2) existing inventory. Specific needs have specific requirements, depending upon the quality of the ^{233}U-bearing material. Not all ^{233}U is suitable for all uses. This may result in excess ^{233}U with specific characteristics, although the potential future uses of ^{233}U exceed the current inventory. From the standpoint of future use, the important characteristics of the inventory are:

- *^{232}U content*. Materials with high concentrations of ^{232}U are characterized by high radiation levels which impose restrictions on possible future uses and high processing costs to accommodate the radiation fields accompanying such materials.
- *^{235}U and ^{238}U content*. Materials with high concentrations of uranium isotopes other than ^{233}U indicate high volumes of uranium per unit of ^{233}U. If the other uranium isotope is ^{235}U, additional complications exist in terms of safeguards and nuclear criticality. If the other uranium isotope is ^{238}U, the material mass is increased, but weapons safeguards issues can be avoided and nuclear criticality issues can be reduced if the fissile concentrations are kept sufficiently low.
- *Chemical and packaging characteristics*. The ^{233}U inventory is in multiple chemical and physical forms and packaging systems. Large fractions of material are cast-in-place oxide monoliths in welded stainless steel containers, Zircaloy-clad rods of dioxide fuel pellets made with large amounts of natural thorium, or oxide powders packaged in stainless-steel screw-top containers, welded aluminum cans, or welded stainless steel plates. A variety of other chemical forms exist in other, diverse packaging configurations in the inventory. The diversity of chemical and physical material characteristics and packaging systems influences ^{233}U usefulness and complicates the approach to its use or disposition.

Major applications that have been identified thus far for ^{233}U-bearing materials are described in Sects. 5.2 through 5.6. Additional information on the uses and potential needs for ^{233}U is provided in ORNL-6952 (Forsberg and Lewis March 1999).

5.1.2 References Cited for Section 5.1

Bereolos, P. J. et al. June 1998. *Strategy for Future Use and Disposition of Uranium-233: History, Inventories, Storage Facilities, and Potential Future Uses*, ORNL/TM-13551, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Forsberg, C. W. and L. C. Lewis. March 1999. *Uses and Potential Needs for Uranium-233*, ORNL-6952, Oak Ridge National Laboratory, Oak Ridge, Tenn.

5.2 MEDICAL USES

5.2.1 Discussion

One potential large-scale use for ^{233}U involves one of its decay products, ^{213}Bi. During the past decade, considerable research has been conducted in the area of radioimmunotherapy using alpha receptors. Specifically of interest is that of antitumor antibodies radiolabled with an alpha emitter (Knapp and Mirzadeh 1994; Geerlings 1993). In this method, the isotopes are attached to antibodies which specifically target the cancer cell, where the resulting alpha emissions kill these cells with high efficiency.

Previous work in this area focused on using ^{212}Bi, produced by the decay chain of ^{232}U (or ^{228}Th). However, the undesirable side effect of ^{212}Bi is the 2.6-MeV gamma radiation emitted during the decay of ^{208}Tl. The radiation level from this decay could prove to be a debilitating hazard to the patient and an unacceptable risk to the patient's family members and the medical staff involved in the treatment. Also particular concerns exist about long-term dose levels to medical personnel who treat multiple patients.

A potential solution to this dilemma is to use ^{213}Bi produced from the decay chain of ^{233}U (Pippin et al. 1995). Bismuth-213 has the unique properties of being primarily an alpha emitter (by way of ^{213}Po) and having only a 2% probability of decaying to ^{209}Tl, which emits a 1.5-MeV gamma ray. This compares to a 36% probability for ^{212}Bi to decay to ^{208}Tl, which emits a 2.6-MeV gamma. Still, ^{213}Bi is chemically identical to ^{212}Bi with a similar short half-life (about 1 h).

After the first recovery step, the remaining uranium in solution is resolidified and stored in standardized packages for future use or disposal. The entire process may be repeated after several years to allow for ingrowth of ^{229}Th and other decay products.

Currently, ^{229}Th produced from the decay of ^{233}U is the only source of ^{213}Bi. Further, ^{229}Th could be produced by irradiation of ^{226}Ra in a nuclear reactor. However, the levels of the contaminant, ^{228}Th, produced by irradiation of radium, are much higher than those from decay of ^{233}U–^{232}U in the inventory. The existing capacity for such production is about 100 g/year (Feinendegen and McClure 1996).

It is likely that isotopic dilution of the ^{233}U to remove weapons usability would have little effect on this application. The decay chain of ^{238}U, which would be used as the blend-down material, does not contain actinium. Therefore, the third separation step in the recovery of ^{213}Bi would still isolate the desired part of the ^{233}U decay chain.

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5.3 NUCLEAR REACTOR FUEL

Direct use of ^{233}U to fabricate reactor fuel is possible for both DOE's research reactors and as part of a larger program to develop a mixed oxide (MOX) fuel of plutonium and uranium. Because of the limited inventory of ^{233}U, the latter option would not be an economic option for using ^{233}U by itself, but it could be viable as a part of the plutonium program (Bereolos et al. June 1998).

5.3.1 Deep-Space Missions

Since ^{233}U has a lower minimum critical mass than ^{235}U or ^{239}Pu (for neutron flux in the thermal regime), it may be desirable to use ^{233}U as a nuclear reactor fuel for deep-space missions for which a premium is placed on minimizing mass. For this application, high-grade ^{233}U would be required to minimize spacecraft launch weight. A space reactor is launched into earth orbit before the reactor is started. This procedure avoids the need for massive shielding of the reactor before and during launch operations. High-purity ^{233}U would be required to avoid the need to shield the reactor before launch.

Uranium-233 may have unique advantages for certain types of deep-space reactors (Howe et al. 1991). There are two potential applications: (1) electric power and (2) propulsion. For missions to Mars and beyond, nuclear energy sources are the only available sources of electric power for spacecraft because of the reduction of solar radiation with distance from the sun. Second, the cost of deep-space missions is directly dependent upon the total mass of the spacecraft. While the cost to put satellites in earth orbit is measured in thousands of dollars per kilogram in orbit, the cost to put a spacecraft beyond Mars may be measured in millions of dollars per kilogram. Thus, mass (or weight) controls cost.

The preferred type of nuclear power source to provide electricity for a deep-space mission depends upon the power requirements. For power production levels up to several kilowatts, the minimum-mass nuclear power source is a radioisotope generator. The currently preferred radioisotope is ^{238}Pu. Nuclear reactors provide minimum-mass, steady-state power generation at higher power levels. For steady-state power levels of a few kilowatts to several megawatts, nuclear power reactors fueled with ^{233}U may provide the minimum mass (MacFarlane 1963; Lantz and Mayo 1972). For each fissile material, a minimum mass of that fissile material is required for a nuclear reactor to operate. This minimum mass is substantially smaller for ^{233}U than for ^{235}U. Uranium-233 and plutonium have similar nuclear characteristics; however, the physical properties of uranium in high-temperature space reactors are substantially better than those of plutonium and there may be fewer launch safety issues (see the following). This difference may make ^{233}U the preferred material for such applications.

At steady-state power generation levels of several megawatts and above, ^{233}U HEU or plutonium can each be used with little difference in spacecraft mass. There are two reasons for this:

- At high power levels, the reactor must have large, internal, heat-transfer surfaces to transfer heat from the reactor to the electric generator. To obtain the heat transfer, the reactor fuel assemblies require a significant amount of fissile material. In a large nuclear system, the choice of fissile material does not significantly impact weight because the amount of fissile material needed for heat transfer far exceeds the minimum critical mass needed for a reactor.
- At high power levels, there must be significant quantities of fissile materials to provide the energy for a long-term mission.

Uranium-233 may also be used for small nuclear propulsion units to boost spacecraft from earth orbit to deep space (Ludewig et al. 1989; Hyland 1970). These units have moderate power levels for short times (<1 h). The interest in using ^{233}U is that it minimizes fuel mass in the spacecraft.

It currently appears unlikely that ^{233}U would be used for near-earth missions because of the interactions between safety concerns and economics. The primary safety issue associated with space reactors is a launch failure with loss of the spacecraft. Space reactors are not operated until they are in earth orbit or beyond to minimize launch risks. For reactors fueled with HEU, launch safety concerns are minimized because a failure of the rocket would result in (a) only HEU dust over the launch pad or (b) burnup in the atmosphere. The toxicity of HEU is relatively low and less than other components of conventional rockets. Plutonium-238, ^{233}U, and ^{239}Pu are alpha emitters that are much more hazardous than is HEU. Uranium-233 is hazardous, but it is the least hazardous of these materials. For more hazardous radionuclides, the standard procedure is to encase the fissile material in a special container or containers to withstand launch accidents. This adds costs and complexities to the reactor. For a near-earth spacecraft, the relatively low-launch cost for earth orbit makes HEU the preferred reactor material—it is not worth the complexity of using ^{233}U or plutonium. For deep-space missions with very high costs to deliver a kilogram of spacecraft into deep space, more complex systems are required to (1) make the mission possible and (2) limit costs.

The potential demand for ^{233}U in this application is probably a fraction of the total inventory. The unique advantages of ^{233}U are only for small reactors with small quantities of ^{233}U per reactor. Any ^{233}U for space missions must be of high purity. Uranium-233 with significant quantities of other uranium isotopes has no value for this application.

5.3.2 Reactor Fuel Cycle Research

The major historical application for ^{233}U has been for research into new nuclear power reactors and associated fuel cycles. This is also a potential future application.

There are four incentives for considering a ^{233}U-thorium fuel cycle.

- The global resources of thorium are about four times greater than for uranium. If uranium becomes scarce (perhaps hundreds or thousands of years in the future), thorium is a more abundant fertile material to use in reactors to breed nuclear fuels.
- In thermal reactors, such as LWRs or MSRs, thorium fuel cycles breed more fissile material (^{233}U) than reactors fueled with LEU.
- SNF and other wastes from the thorium–^{233}U fuel cycle, as compared to uranium–plutonium fuel cycles, contain smaller quantities of long-lived actinides that are a concern in disposal of wastes in geological repositories.
- Some ^{233}U–thorium fuel cycles may have lower risks of diversion of weapons-usable material than do conventional uranium–plutonium fuel cycles. In power reactors, the impurity of ^{232}U and its daughter products build up to very high levels with correspondingly high radiation levels associated with the separated ^{233}U.

For this application, only relatively pure ^{233}U would be used. For research, high-purity material with low radiation levels is desired to (1) allow low-cost fabrication of test nuclear fuel assemblies and other equipment and (2) make possible more nearly accurate measurements of equipment and material performance.

The U.S. inventory of ^{233}U partly reflects the use of ^{233}U for power reactor R&D. The largest batch of ^{233}U in the inventory, the CEUSP material at ORNL, is from a power reactor and has the high concentrations of ^{232}U. The ZPR ^{233}U is from reactor criticality experiments. The Idaho LWBR fuel is a test core of ^{233}U, and finally, ^{233}U is currently being recovered from the MSRE.

A recent proposal that would involve the use of ^{233}U as nuclear fuel is the Energy Amplifier concept of Rubbia (Aldhous Nov. 26, 1992; Carminati et al. 1993; Rubbia 1995). The idea is to use a particle accelerator to supply neutrons to drive a thorium-fueled reactor. This setup has the advantage from the safety perspective that fission can be sustained only while the accelerator is running. It is also noted that Japan is currently acquiring limited quantities of ^{233}U for tests for their advanced reactor concepts.

The total domestic inventory of ^{233}U (<2 t) is small when compared to inventories of other fissile materials (HEU inventories are measured in hundreds of metric tons) and small when compared to the fissile requirements to fuel the nation's nuclear power reactors. As such, the total ^{233}U inventory is not a significant energy resource from a national perspective nor a significant energy resource for startup of a ^{233}U fuel cycle. Decisions on keeping such materials for this application depend upon whether the United States wants to maintain the capability to restart research on fuel cycles using thorium–^{233}U fuel.

5.3.3 Commercial Reactors

The inventory of ^{233}U is not significant as an energy source. In the United States, current commercial reactor fuel is based solely on ^{235}U, so all licensing and specifications are set up for this situation. Furthermore, there is currently an excess of ^{235}U. The CEUSP material, which has large quantities of ^{235}U, would still have to undergo additional processing to remove the soluble neutron poisons cadmium and gadolinium.

By contrast, in countries like India, ^{233}U offers a promising future as a fuel in power reactors whose fuel cycle is based on thorium. The utilization of both ^{233}U and thorium in commercial power reactors on the international scale is discussed and described in many references (notably, IAEA 1966, U.S. DOE/EIA April 1997, and Bhagwat et al. August 1993).

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5.4 RADIOACTIVE TRACERS

5.4.1 Discussion

In general, tracers are foreign materials that are either mixed with or attached to a given substance and used to determine the location or path of that substance. Radioactive tracers are often used to follow a series of processes or events commonly found in industrial process streams or in the metabolic systems of living organisms. As a radioactive tracer, ^{233}U has been used in small amounts (~20 ng) to:

- track radionuclide migration in groundwater and other aquifer systems (Laul et al. June 1985; Meier et al. 1992; Meier et al. 1994; and Zeh, Klotz, and Lazik March 1995) as well as in geologic media (Shihomatsu 1987; Shihomatsu December 1988),
- determine the concentration and distribution of uranium in minerals (Shihomatsu and Iyer 1988) and measure the diffusion of radionuclides in sediment rocks (Meier et al. 1987), and
- calibrate other radionuclide tracers, such as ^{243}Am. In such calibrations, ^{233}U enables the evaporation rate of the test solution to be monitored (Eliot, Louis, and Lucas Sept. 13, 1987).

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5.5 SPIKE MATERIALS

5.5.1 Discussion

Uranium-233 is used as a spike isotope in the determination of uranium concentrations and isotopic compositions in materials containing natural uranium or uranium enriched in ^{235}U. In these materials, ^{233}U is generally not present or can be found only in very small amounts. A spike is a measured quantity of an isotope that is added to an aliquot of a sample. The isotope used for spiking must either not be present or present only at trace levels in the original sample. This is the case when ^{233}U is used with natural or enriched uranium samples. After chemical and isotopic equilibration, the quantities of the isotopes in the sample are measured relative to the added isotope. From the change in the isotopic ratios of the sample caused by the spike, measured by mass spectrometry, the elemental content of the sample may be determined. As a spike, ^{233}U has been used to:

- accurately measure the half-lives of other radioactive actinides, most notably ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu (Chitambar et al. Dec. 13, 1986; Abernathey and Marsh October 1981; Jaffey August 1978);
- determine the concentration and isotopic composition of uranium in environmental air filters (Russ and Bazan Aug. 26, 1997); and
- determine the concentrations of uranium, plutonium, and their relative isotopic abundances by an analytical technique known as isotope dilution mass spectrometry (IDMS).

IDMS is an effective method for accurately measuring element or isotopic assays and concentrations. It is especially useful when only small samples of an element or isotope of interest are available. IDMS is frequently used to accurately measure concentrations of uranium and plutonium in dissolved, irradiated nuclear materials such as those resulting from nuclear fuel reprocessing. As part of the IDMS analysis procedure, a known quantity of a unique element or isotope to be measured (referred to as the "spike") is added to a solution containing the analyte. The resulting solution is then chemically purified and afterwards analyzed by mass spectrometry. By measuring the magnitude of the response for each isotope (including that for the unique spike) and then relating these results to the known quantity of the spike, the isotopic composition of the nuclear material under investigation can be accurately determined (Bayne July 1991; Maxwell and Clark July 1990).

For safeguards and accountability purposes, concentrations of uranium and plutonium in highly radioactive solutions from dissolved spent reactor fuel elements are determined by IDMS using ^{233}U along with other radionuclides as spikes. Such an analysis is also useful for determining the burnup level of reactor fuel (IAEA May 1989).

Currently, ^{233}U is used as a baseline spike material to calibrate the samples used for uranium accountability analyses that are performed in the ICPP at INEEL. A precisely measured aliquot (on the order of 1 mg) of an isotopically pure ^{233}U compound is added to samples to determine the concentration of uranium and of the accountable uranium isotopes present (mainly for the isotope ^{235}U) by IDMS. The analyzed sample size that is spiked with ^{233}U typically has on the order of 1 mg of uranium. Discussions with INEEL/ICPP personnel involved with such analyses indicate that only about 20 g of ^{233}U have been used as a spike in IDMS analyses performed at the ICPP during the past 20 years (Hand Mar. 5, 1997; Lewis Mar. 7, 1997).

At the SRS, an automated spike preparation system for IDMS was developed. To prepare ^{233}U spikes for this system, 200 μL containing approximately 140 μg of ^{233}U is dispensed (Maxwell and Clark 1990).

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5.6 MISCELLANEOUS USES

5.6.1 Discussion

Two less common uses for ^{233}U materials have been identified. One involves use as a sensing material in fission counters for reactor startup applications (Prasad and Balagi June 1996). In this application, about 75 mg of ^{233}U are required in a fission counter providing a sensitivity of 0.02 counts per second per nanovolt (cps/nv). Another less common application involves ^{233}U use as one of several selected reference radionuclides for measuring the effects and limits of radiation exposure on embryo and fetal tissue (Matsusaka March 1993). Such analyses have included investigations made of the deposition, distribution, retention, and toxicity of several radionuclides in prenatal and juvenile mammals (Sikov and Park 1987).

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APPENDIX A. ^{233}U STORAGE STANDARD

This appendix provides a reprint of the report, *DOE Standard—Criteria for Preparing and Packaging Uranium-233-Bearing Materials for Safe Long-Term Storage* (SAFT-0067). This draft report is an officially published interim standard for the storage of ^{233}U-bearing materials. The document is printed in full from its current web site location, which is

http://www.doe.gov/techstds/tsdrafts/saft0067.pdf

This draft, December 1998, prepared by DP-45, has not been approved and is subject to modification. Project No. SAFT-0067. Issued for Comment and Interim Use

TS

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PROPOSED

DOE STANDARD

CRITERIA FOR PACKAGING AND STORING URANIUM-233-BEARING MATERIALS

U.S. Department of Energy
Washington, D.C. 20585

AREA SAFT

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FOREWORD

This standard establishes the criteria for the safe packaging and storage of Uranium-233(^{233}U)-bearing materials and aims to obviate subsequent repackaging during their storage or from their existing storage facilities until their respective dispositions are identified. Materials conforming to these criteria should be contained and stored safely for a nominal 50 years (pending disposition). Periodic inspections of ^{233}U packages shall be conducted in order to confirm the storage lifetime objectives covered by this standard. The justifications and bases for the criteria are given in Appendix A. This Department of Energy (DOE) standard is approved for use by all DOE components and their contractors.

The Department of Energy (DOE) was producing special nuclear materials (SNM) in their purest forms for weapons production and reactor fuel fabrication during the Cold War period. Typically the SNM, which includes plutonium (Pu), enriched uranium-235 (^{235}U) or ^{233}U, were either in the forms of metals or relatively pure oxides. These SNM materials were also the most "attractive" from a safeguards perspective because they could most readily be used to fabricate nuclear weapons.

The DOE mission has been refocused in the past few years to emphasize weapons dismantlement, safe fissile materials storage and disposition of excess SNM to Departmental needs, while preserving a reduced stockpile. Aside from weapons dismantlement and production activities, significant quantities of Departmental fissile materials also exist in a variety of chemical forms from fuel cycle programs and from other nuclear research and development (R&D) projects. These materials shall be safely stored in the interim until their ultimate dispositions are identified. Coincidentally, safeguards and nonproliferation concerns should be integrated into these storage criteria. Safe storage of these reactive materials is the current end-point for the SNM inventories prior to disposition.

Existing Departmental storage facilities at Oak Ridge National Laboratory (ORNL) and Idaho National Enginnering and Environmental Laboratory (INEEL) will be used for near-term storage of the ^{233}U materials until such time as new or upgraded storage systems become available, the material is dispositioned, or transferred for reuse. Building 3019 at ORNL has been the National Repository for separated ^{233}U materials since 1962. It has most of the existing separated inventory in a variety of packages and diverse chemical and physical forms. The Idaho Chemical Processing Plant (ICPP) at INEEL has held the major ^{233}U inventory in fabricated forms of unirradiated nuclear fuel assemblies, rods, and sintered pellets since the early 1980s.

The major elements for the safe storage of separated ^{233}U are preventing criticality, containing radioactive materials, protecting personnel from penetrating radiation, and safeguarding this special nuclear material. The storage facility plays a primary role in addressing all of these safety elements except containment. The facility plays a principal backup role (i.e., defense in depth) in confining radioactive contaminants during upset conditions. Material stabilization, consolidation, access limitation, low maintenance storage and reliability in verification of the inventory are the Department's present goals for the ^{233}U-bearing materials.

The existing materials should not be repackaged if the existing container(s) pose no safety hazards. However, if repackaging is required, a standardized package, which considers the disposition mode, is the preferred option, while ensuring overall safety. An integrated approach that considers the packaging in combination with specified control measures is also acceptable.

DOE technical standards do not by themselves establish mandatory requirements. However, all or part of the provisions in a technical standard can become requirements under the following circumstances:

(a) they are explicitly stated to be requirements in a DOE requirements document; or

(b) the organization makes a commitment to meet a standard in a contract or in a plan or program required by a DOE requirements document.

Throughout this standard, the word "shall" is used to denote actions that must be performed if this standard is to be met. If the provisions in this technical standard are made mandatory through one of the two ways discussed above, then the "shall" statements become requirements.

TABLE OF CONTENTS
CRITERIA FOR PACKAGING AND STORING URANIUM-233-BEARING MATERIALS

1. INTRODUCTION

1.1 Purpose and Scope

This standard provides criteria for safely packaging and storing ^{233}U-bearing solid materials for a nominal 50 years without subsequent repackaging. Periodic inspections of ^{233}U packages shall be conducted to confirm the storage lifetime objectives covered by this standard. This standard does **not** apply to packaging for liquids, wastes, spent fuels, irradiated targets, in-process materials, or small quantities involved in research and development studies. Furthermore, this standard does **not** apply to packaging for uranium with isotopic content less than 1 wt % ^{233}U or to packaging for uranium-bearing materials contaminated with plutonium in amounts greater than 2 % (on a weight basis relative to ^{233}U content).

A majority of the ^{233}U in inventory consists of mixtures of ^{233}U and ^{232}U or mixtures whose properties are dominated by the ^{233}U and ^{232}U content. These materials have substantially different radioactive and nuclear characteristics than the other two special nuclear materials (SNMs), ^{235}U and Pu (note that ^{232}U is not an SNM). For example, the ^{232}U decay chain produces ^{208}Tl, which emits a 2.6 MeV gamma-ray. This highly energetic gamma-ray and the high alpha activity associated with ^{232}U necessitate facility safety characteristics such as shielding in addition to material and packaging considerations for safe storage. Therefore, guidance for facility features addressing the unique properties of ^{233}U and ^{232}U is provided in this standard.

Bases for the criteria in this standard are provided in Appendix A and are organized to correspond, section-by-section, with the standard. Users of this standard are advised to consult and ensure adherence with other applicable directives while implementing these criteria. It is the responsibility of the organization in custody of the material to provide safe conditions for handling and storing the material.

1.2 Equivalency

This standard allows using systems, methods, material forms, or devices that are functionally equivalent or superior in the place of those prescribed herein if demonstrated by technical documentation.

2. DEFINITIONS

Terms and acronyms applicable to this standard and to the criteria bases are listed and defined in Appendix B.

3. REFERENCES

Specific DOE and other Federal agency regulations and other documents used in developing this standard and the bases for the standard are listed in Appendix C.

4. MATERIAL AND PACKAGING CRITERIA

The following criteria are established to control potential hazards to workers, the public and the environment for packaging and safely storing separated ^{233}U-bearing materials. Technical bases for the criteria are provided in Appendix A. Besides conforming with these safe storage criteria, the reader should review other specific DOE directives which address SNM issues, e.g., Orders on materials control and accountability (MC&A), radiation protection controls, criticality and transportation.

Some of the following sections are specific to the material form. The table below provides a mapping of material form to the applicable sections.

Table 1. Roadmap of Sections 4 and 5.

Material Form	Material Specific Sections
Metals	4.1.1, 4.2.1, 4.2.2, 4.2.3
Oxide Powders	4.1.2, 4.2.1, 4.2.2, 4.2.3, 4.3.2b
Monoliths	4.1.3, 4.2.1, 4.2.3, 4.2.5, 4.3.2b, 5.2
Ceramics	4.1.4, 4.2.6, 4.3.2b
All	4.2.4, 4.3.1, 4.3.2a, 4.4, 4.5, 4.6, 5.1, 5.3, 5.4

4.1 Material Criteria

Storable ^{233}U-bearing solid forms include metals, alloys, oxide powders, oxide monoliths, and ceramic oxide pellets.

4.1.1 Metals and Alloys. Metal and alloy pieces shall have a specific surface area of less than 50 cm^2/g. Particles and metal pieces larger than 8 mesh (2.38 mm) meet this criterion. Metal pieces with a specific surface area greater than 50 cm^2/g, thin foils, and turnings shall be thermally stabilized to oxides for storage. Thermal stabilization shall be at a temperature of at least 650 °C (1200°F) for at least 6 hours in air. Loose oxide on outer surfaces of metal pieces shall be removed prior to packaging metals for storage.

4.1.2 Separated Oxide Powders. Stored materials may include oxide powders of ^{233}U and mixed uranium isotopes. These materials shall be thermally stabilized by heating to a nominal 650 °C (1200 °F) or hotter for a nominal 6 hours or longer to remove moisture and to convert residual salts to oxides.

4.1.3 Oxide Monoliths. Oxide monoliths are large, brick-like pieces of oxide, typically U_3O_8, which have been calcined in a denitration process and baked at a nominal 800 °C (1470°F) or hotter for a nominal three hours or longer to remove moisture and convert residual salts to oxides.

4.1.4 Ceramic Oxides. Ceramic oxide pellets are high-fired ceramic matrices formed by sintering at greater than 1750 °C (3180°F) in air for at least 12 hours.

4.2 Packaging for Storage Criteria

Packaging provides a principal barrier for isolating stored material from the environment. As such, it should be designed to maintain mechanical integrity, including closure, during anticipated handling and storage operations. General issues surrounding the package relate to material of construction, internal package atmosphere, identification and closure. The storage package for metals and powders shall consist of a minimum of two nested, leaktight containers to isolate the stored materials from the environment and to prevent the release of contamination. This two-container system is also acceptable for monoliths and ceramic oxides. However, the storage system for monoliths may consist of a minimum of one container combined with facility features described in Section 5.2.1.

The storage system for ceramics may consist of containers described in Section 4.2.6. Sections 4.2.1, 4.2.2, 4.2.3, and 4.2.5 do not apply to ceramic material. Sections 4.2.2 and 4.2.6 do not apply to oxide monoliths.

4.2.1 <u>General Requirements</u>. Required containers used in packaging:

a. Shall be fabricated of materials that are resistant to corrosion due to contact with the material and the anticipated storage environment. It is recognized that stainless steel, aluminum, zirconium alloys, and nickel-based alloys are considered resistant to corrosion in most applications. No plastics are allowed in direct contact with the material.

b. Shall have permanent (e.g., etched, engraved, or stamped) identification markings.

c. Shall be leaktight as defined by ANSI N14.5-1997 at the time of closure for newly repackaged material or shall meet Section 4.2.3b for existing containers.

d. Shall be designed and constructed to facilitate non-destructive assay (NDA) requirements for MC&A.

e. Shall have structural properties meeting acceptance criteria that satisfy anticipated package storage conditions and handling accidents.

4.2.2 <u>Inner Container</u>. The inner container, if required:

a. Shall be sized to fit into an outer container (with clearance for optional welding, if applicable).

b. Shall conform to the limits specified in 10 CFR 835 (for transuranics) for removable contamination of the exterior surface at the time of repackaging.

4.2.3 <u>Outer Container</u>. The following apply to the outer container:

a. Shall be sized to fit into the storage configuration. A maximum container height may be specified but should be related to physical handling operations and compatibility with transport casks.

b. Shall conform to the limits specified in 10 CFR 835 (for transuranics) for removable contamination of the exterior surface.

4.2.4 <u>Optional Container(s)</u>. Additional optional containers, sometimes referred to as "material" or "convenience" containers, may be used. If the optional container is in direct contact with the material, the requirements of Sections 4.2.1a shall also be met. Sections 4.2.1b and 4.2.1d are considered as good practice for optional containers. Sections 4.2.1c and 4.2.1e are not required.

4.2.5 <u>Oxide Monoliths</u>. For oxide monolith materials, which are non-dispersible and of a non-respirable size, the primary barrier to confinement shall be provided by a container(s) that meets the provisions of Sections 4.2.1 and 4.2.3. The secondary confinement barrier shall be provided by a second container or by the facility as described in Section 5.2.

4.2.6 <u>Ceramic Fuel Materials</u>. For ceramic fuel materials, the primary level of containment is the robust, high-fired ceramic matrix of the fuel pellet. The secondary containment shall be provided by a container closed either by a screwed-on lid on a 2R container inside a 6M drum or a bolted-on lid stored in a storage vault. The following apply to the storage containers:

a. Shall be fabricated of, or coated with, materials that are resistant to corrosion in the anticipated storage environment.

b. Shall have permanent (e.g. etched, engraved, or stamped) identification markings.

c. Should be designed and constructed to facilitate NDA requirements for MC&A.

d. Should have structural properties meeting acceptance criteria that satisfy anticipated package storage conditions and handling accidents.

4.3 Contained Materials

4.3.1. Quantities

a. Criticality limits shall be addressed through nuclear criticality safety evaluations as specified by DOE O 420.1. (See Section 5.1)

b. The mass of fissile material per storage container shall not exceed (a) 5.4 kg (11.9 lb.) for metal and 9.1 kg (20 lb.) for oxides (including powders, monoliths, and ceramics), or (b) the limits specified in site-specific nuclear criticality safety programs, policies, and procedures. If Pu is present, this limit must be addressed on a case by case basis.

4.3.2. Internal Atmosphere

a. The package shall contain a non-corrosive atmosphere (e.g., nitrogen or inert gas for metals and oxides; oxides also may be packaged in ambient air).

b. The maximum anticipated internal pressure of any required container shall be less than the maximum allowable working pressure determined by proof tests as described in Section VIII-Division 1 Part UG-101 of the ASME Boiler & Pressure Vessel Code. The maximum anticipated internal pressure shall be determined by measurement, data from relevant experiments, or by use of Equation A-1 in Appendix A.

4.4 <u>Inspection and Surveillance for Safety</u>. Inspection and surveillance procedures shall be site-specific and shall identify:

a. Prerequisites;

b. Acceptance criteria;

c. Specific instructions to ensure that items not meeting acceptance criteria are addressed in accordance with approved procedures and DOE reporting requirements; and

d. Frequency for surveillance for safety.

4.4.1 Documentation of inspection and surveillance methods. Formal methods and responsibilities shall be documented and maintained for independent review and evaluation.

4.4.2 Surveillance Plan. The surveillance plan shall include all packages and should include provisions for:

a. Initial baseline package inspection after an appropriate initial delay interval after repackaging;

b. Surveillance frequency, sample population, and package selection should be established by a statistical approach;

c. Integrating safety (e.g., ALARA, evaluation of indications of container deformation) and MC&A requirements (DOE 5633.3B).

4.4.3 Surveillance Parameters. Each sampled package:

a. Shall be inspected for an indication of internal pressure build-up and evaluated per Section 4.3.2b.

b. Shall be inspected for transferable contamination on the outer container and evaluated per 10 CFR 835 Appendix D (for transuranics).

c. Shall be inspected (e.g., by radiography, by weight change of metals) for signs of changes in material form within the container and evaluated versus previous inspections.

d. Shall be inspected for signs of leakage and/or degradation of the container and evaluated versus previous inspections.

4.4.4 Evaluation of Surveillance Data

a. Parameters obtained during surveillance inspections shall be compared against previous measurements to detect changes.

b. If at any time a deleterious change in the material or the container is noted, a safety evaluation shall be performed. This evaluation shall include, as appropriate, 1) evaluation of the detected change(s), 2) assessment of the potential consequences, 3) options for repackaging or overpacking the container, and 4) consideration for inspecting other packages that are similar, based on factors such as contents, origin, and date of closure.

4.5 Documentation

4.5.1 Database. An electronic database shall be maintained to serve as a source of relevant information about the stored materials and packages. If database information is classified, the database shall be subject to the requirements of DOE M 5639.6A-1. To ensure consistency between databases, this database should be integrated with the MC&A database or electronically linked and coordinated with the MC&A database.

4.5.2 Database Requirements. The database should include:

a. Identification of the following material characteristics:
   1) Chemical composition;
   2) Physical form (e.g., ^{233}U metal, oxide powder, monolith, or ceramic);
   3) Elemental mass;
   4) Fissile isotope fraction (or mass) and ^{232}U fraction (in ppm);
   5) Source of stored material (facility that prepared the material in its current form);
   6) Specific processing condition(s);
   7) Moisture content;
   8) Production date; and
   9) Other information relevant to the contents (e.g., major impurities, radiation level).

b. Identification of the following package characteristics:
   1) Type of fill gas on closing;
   2) Package configuration - number of inner containers in package;
   3) Initial radiation field [gamma and neutron radiation levels at contact and 30 cm (12 in)];
   4) Date of packaging; and
   5) Baseline package weight and outer dimensions.

c. Record of the inspections performed, names of individuals performing inspections, and dates of inspections. Historical records on packages shall be maintained for the life of the packages.

d. Location(s) of stored materials.

4.6 Quality Assurance/Control Requirements

4.6.1 Personnel participating directly and with key responsibilities in essential processes and procedures shall be trained and qualified as appropriate to their assigned responsibilities.

4.6.2 Materials used in the fabrication and sealing of repackaging containers shall satisfy specifications necessary to comply with the requirements of this standard.

4.6.3 Procedures and processes that are essential for assuring compliance with these criteria shall be subject to Quality Assurance (QA) per 10 CFR 830.120 and DOE O 414.1, and controlled by Quality Control (QC) Procedures.

4.6.4 Essential procedures and processes covered by QA and QC requirements shall include (but will not be limited to):

a. Thermal stabilization procedure;

b. Sealing (e.g., welding) procedure used in container fabrication and closure;

c. Package surveillance procedure(s);

d. Database recording procedure and characterization parameters addressed in Section 4.5.2; and

e. Assaying of container contents for MC&A and criticality safety requirements.

5. STORAGE FACILITY FEATURES

A facility used for the storage of ^{233}U should address the unique characteristics of the material and include nuclear criticality safety, confinement of radioactive materials, radiation shielding, and safeguarding SNM.

5.1 Nuclear Criticality Safety

Storage and handling of ^{233}U-bearing materials shall conform to the criticality safety requirements of DOE O 420.1. Criticality safety evaluations shall document that storage and handling activities shall remain subcritical during all normal and credible abnormal events. Criticality safety evaluations shall be performed for operations (under normal conditions) within any facility containing ^{233}U in excess of the limits specified in DOE O 420.1 or as specified in site-specific nuclear criticality safety program policies and procedures.

Special care should be exercised in validating calculation methods supporting criticality safety evaluations because of the paucity of data in the intermediate energy regime that may be important for some ^{233}U-bearing matrices under specified operational conditions.

5.2 Confinement of Contamination

The material form, material containers, or containment vessels serve as the principal barrier for confinement of contamination. Depending on the material storage system, the facility itself may serve as another confinement barrier. The combination of the material storage system and the storage facility represents a defense-in-depth safety confinement system.

5.2.1 Facility Confinement. The facility where ^{233}U-bearing material is stored may provide a physical barrier to the release of contamination if the material is in a non-respirable form. The integrity of the storage facility shall be maintainable through normal operations, anticipated operational occurrences, and any design basis accidents (DBAs) the barrier is required to withstand. The particular DBAs the storage facility is required to withstand shall be determined on a case-by-case basis. The DBAs to be considered include external events, including severe natural phenomena and man-made events, and internal events (e.g., container overpressurization). The adequacy of these confinement systems to effectively perform their required functions shall be demonstrated by the safety analysis. Requirements governing the safety analysis process include the applicable portions of DOE Orders 420.1, 5480.21, 5480.22, and 5480.23. The need for ventilation systems for confinement purposes shall be based on the results of the safety analysis.

5.3 Radiation Shielding

Owing to the presence of ^{232}U in ^{233}U inventories, radiation shielding is required to attenuate the 2.6 MeV photon emitted by the ^{232}U daughter, ^{208}Tl. Depending on the material form and material storage system used, the facility itself may serve as a radiation shield. The regulations pertaining to occupational radiation protection as specified in 10 CFR 835, shall be met.

5.4 SNM Safeguards

Uranium-233 is a weapons-usable material due to its fissile properties and its ability to be produced in sufficient quantities for manufacturing nuclear weapons. This material shall be protected from unauthorized access and unauthorized use. Safeguards measures shall meet the requirements of DOE O 470.1, DOE O 471.2A, DOE O 472.1B, DOE 5632.7A, and DOE 5633.3B.

APPENDIX A
TECHINCAL BASES FOR URANIUM-233 PACKAGING AND STORAGE CRITERIA

This Appendix provides the bases for the criteria presented in this document. The section numbers in this Appendix correspond to the sections in the body of the standard.

1. INTRODUCTION

1.1 Purpose and Scope

This standard establishes the criteria for safely packaging and storing ^{233}U-bearing solid materials for a nominal 50 years. The bulk of this material is stored at ORNL and INEEL. Uranium-233-bearing solid forms include metals, alloys, oxide powders, cermets, ceramic oxide pellets, and oxide monoliths. This standard does not apply to ^{233}U-bearing liquids, residues, wastes, spent fuels, irradiated targets, in-process materials or small quantities involved in R&D studies since these materials are either addressed by other storage programs or are not germane to the intended storage activity.

Much of the material covered by this standard is nearly isotopically pure ^{233}U with small amounts of ^{232}U; isotopes of uranium that may be present (with their half-lives in parentheses), include ^{238}U(4.5 x 10^9 y), ^{236}U(2.4 x 10^7 y), ^{235}U(7.0 x 10^8 y), ^{234}U(2.4 x 10^5 y), ^{233}U(1.6 x 10^5 y), and ^{232}U(69 y). Uranium-233 and its associated isotope ^{232}U are man-made and present much more severe radiological hazards than any of the naturally occurring uranium isotopes. Therefore, an isotopic level of 1 wt % ^{233}U in total uranium represents the lower isotopic threshold since this is the ^{233}U isotopic concentration at which the inhalation hazard posed by ^{233}U (in terms of release limits from 10 CFR 20) exceeds that for uranium highly enriched in the ^{235}U isotope (Bereolos et al. 1998). Similarly, an upper plutonium contamination level was established at 2 wt % of the ^{233}U content because this is the concentration at which the inhalation hazard (from Radionuclide Concentration Guide in 10 CFR 20) posed by an isotopic blend for weapons-grade Pu exceeds that for currently stored ^{233}U with high levels of ^{232}U (~200 ppm).

1.2 Equivalency

The basis for equivalency shall be a technical justification for any departure from specific provisions of the standard. This technical justification will be subject to oversight by the authorizing official.

2. DEFINITIONS

The terms and acronyms applicable to this standard are adopted from relevant titles of the Code of Federal Regulations (CFR) and the Handbook of Acronyms, Abbreviations, Initialisms, Proper Names and Alphanumerics Encountered in Nuclear Safety Literature, March 1993.

3. REFERENCES

No Basis Required.

4. MATERIAL AND PACKAGING CRITERIA

4.1 Material Criteria

4.1.1 Metals and Alloys. Potentially pyrophoric metals are not acceptable storage forms because this could lead to fires and dispersal of the uranium. Metallic uranium in massive form presents little fire hazard, but it will burn if exposed to a severe, prolonged fire. By contrast, finely divided uranium metal powder is pyrophoric (L. Bretherick, *Hazards in the Chemical Laboratory*, 1986), and can ignite spontaneously, if confined in a container without liquid or without air movement. The presence of moisture in the gas phase over exposed chips increases this possibility (J. J. Burke, et al. *Physical Metallurgy of Uranium Alloys*, 1976). The flammability of uranium depends almost entirely on the specific surface area. Finely divided uranium metal ignites spontaneously upon exposure to air and burns rapidly to the oxide. For uranium foils and wires, the experimentally determined ignition temperatures are somewhat higher than for powders having the same specific surface area. The recommended upper limit of specific surface area is 50 cm^2/g, based on the analysis presented in Section 4.9 of the *Draft Hazard Analysis for Storage of* ^{233}U. This is considered a conservative value since the corresponding ignition temperature of about 255 °C is far above temperatures expected to be achieved during storage. Uranium metal pieces larger than sieve mesh size 8 (2.38 mm) are assured of having a specific surface of less than 50 cm^2/g and may be stored in tube vaults. Uranium metal of less than sieve mesh size 8, powders, thin foils, and turnings of uranium are more susceptible to ignition at temperatures below 255 °C. Therefore, these materials need to be converted to stabilized oxide prior to storage or stored in a sealed container with an inert atmosphere (ANL-6287).

Some loose removable oxides associated with metals may also be pyrophoric. An adherent oxide layer on stored metal is generally beneficial because it tends to retard further oxidation. However, as UO_2 (the first oxide produced), this coating may be pyrophoric. Therefore, prior to repackaging ^{233}U metal, readily removable loose oxide shall be removed from outer metal surfaces.

4.1.2 Separated Oxide Powders. Water and salts present in the oxide powders can cause corrosion of the container and reduce its integrity. Corrosion, or oxidation, of metal by water produces hydrogen gas, which could lead to pressurization of the container. Liquids are also subject to radiolysis that would result in increased pressure within the container. The complete radiolysis of one gram of water produces 1.87 liters of gas at standard temperature and pressure. Therefore, only uranium oxides that have been thermally stabilized to remove moisture and to convert residual salts are acceptable for storage without further stabilization. Processing of UO_2 at ORNL demonstrated that heating to 650 ± 25 °C hydrogen atmosphere zone for 6 ± 0.5 h is sufficient to bring the moisture content below 0.5 wt % (Parrott et al. 1979).

Materials that could lead to overpressurization of the inner container are not acceptable for storage and shall be thermally stabilized. Uranium oxide powders can have a high surface area depending on preparation conditions. All three predominant uranium oxide forms are acceptable for storage. The most desirable form is U_3O_8 because it can potentially adsorb less moisture per U atom than other oxides (UO_2, UO_3). The potential storage hazard concern associated with adsorbed moisture is the ultimate pressurization of a sealed oxide container over a prolonged period through any of several radiolytic and chemical processes. The adsorbed moisture also could be a potential problem for criticality if the associated moderation is not considered.

4.1.3 Oxide Monoliths. Oxide monoliths are more stable and physically more resistant to dispersion than oxide powders. Oxide monoliths have been formed at ORNL by a denitration technique (McGinnis, et al. 1986) that excludes enhanced fluidization, which would promote powder formation. These materials were calcined to an oxide and baked out at ~800 °C (1472°F) for ~3 hours. Formation of the oxide monoliths under these conditions assures that there are essentially no fine particles available for dispersion and respiration upon a hypothetical container breach and that there are only minimal amounts of moisture or nitrates present. Elimination of moisture and undecomposed salts mitigates the formation of gases by radiolysis.

4.1.4 Ceramic Oxides. Ceramic mixed oxide pellets are very stable since the temperature reached during their formation is high enough (> 1750°C) to ensure that there is no residual moisture or salt in the material. Prior processing operations and chemical compositions of ceramic ^{233}U mixed oxide pellets and sintered fuel result in more stable physical forms that provide inherent self-shielding, criticality constraints, and contamination controls.

The lack of fine materials in these products precludes them from being dispersible. The ceramic oxides are highly resistant to oxidation and require no further stabilization to be acceptable for storage [WAPD-TM-1244(L)].

The ^{233}U inventory at INEEL includes ceramic mixed oxide pellets, and unirradiated fuel rods composed of Zircaloy-clad ^{233}U-bearing ceramic pellets from a former fuel cycle program. The mixed oxide ceramics consist of an average 97 wt % thorium and 3 wt % ^{233}U oxides with less than 10 ppm ^{232}U.

Pellets were fabricated by high pressure compaction of finely ground ^{233}U oxide with finely ground thorium oxide powders into cylindrical pellets. These pellets were sintered at temperatures in excess of 1750 °C (3182°F) for at least 12 hours to form pellets that resist chemical and physical degradation. The densities of these pellets are approximately 98% of theoretical (>10.6 g/cm^3), effectively self-shielding emitted alpha and gamma radiation, inhibiting particulate dispersal, and serving as a containment for the incorporated ^{233}U oxide.

Finished, unirradiated fuel elements (Zircaloy-clad pellets) further enhances the safety and safeguards character of the ^{233}U-bearing processed material.

4.2 Packaging for Storage Criteria

4.2.1 General Requirements

a. Materials of construction shall be selected so that their resistance to corrosion ensures structural integrity for prolonged periods of storage. Corrosion of the container during storage is a potential problem for two primary reasons: (1) if the corrosion is significant, it could result in loss of strength of the container or permit loss of containment of the packaged material; and (2) the resulting hydrogen evolution (as a by-product of corrosion) could cause container pressurization and pose a fire or explosion hazard. The facility is responsible for ensuring that the selected material of construction is appropriate to the environment.

b. Permanent markings ensure the integrity of identification for material control. (DOE 5633.3B)

c. For new packages: the definition of leaktight is 1×10^{-7} ref·cm^3/s of air at an upstream pressure of 1 atm abs and a downstream pressure of 0.01 atm abs or less. This rate is equal to 4.09×10^{-12} gram-moles/s of dry air or helium and is equivalent to a helium volumetric leakage rate, under the same conditions, of approximately 2×10^{-7} cm^3/s (ANSI 1997).

For existing packages: Conforming to limits in 10 CFR 835 for removable contamination on the exterior surface is a sensitive and non-invasive means of ascertaining the current state of leaktightness for containers that have been in storage beyond some initial period (i.e., to detect infant mortalities). Other techniques include undesirable conditions (e.g., helium leakcheck pressurizes the container) or are inconclusive (e.g., radiography provides insufficient detail to detect features that would more readily appear as a contamination leak). Limits for ^{233}U are not specified in 10 CFR 835. The limits for transuranics are used because they are the most restrictive and have the most similar characteristics to ^{233}U.

d. Ease of performing NDA is desirable from an operational point of view. If material is repackaged, facilitating MC&A requirements shall be considered. Repackaging the material solely for purposes of enhancing MC&A is not mandatory because of ALARA considerations and prior MC&A survey history. ORNL has been granted a waiver to the accounting requirements of DOE O 5633.3B because of the hazards involved in handling of ^{233}U packages (DOE ORO 1998).

e. The storage container should be designed to maintain its physical integrity, including its seal, during anticipated handling and storage conditions.

4.2.2 Inner Container

a. Two containers are needed to provide a defense-in-depth for ^{233}U metals and powders in prolonged storage. The inner container serves as the primary barrier isolating the stored dispersible material from the environment. Dimensional limits, based on the outer container design, are such that positive closure of the inner container is facilitated. The facility operator is responsible for ensuring compatibility with the outer container. At ORNL, the inner container should be no greater than 8.6 cm (3.375 in.) I.D. (Primm 1993) and sized to fit into the outer container.

b. External surfaces of the inner container shall be as free from removable contamination as practical at the time of repackaging. Exterior surface contamination may be evidence of potential leakage of radioactive materials (10 CFR 835). The inner container is only required to meet 10 CFR 835 removable contamination limits at the time of repackaging because confirmation of the inner container status requires destruction of the outer container after sealing. Limits for ^{233}U are not specified in 10 CFR 835. The limits for transuranics are used because they are the most restrictive and have the most similar characteristics to ^{233}U.

4.2.3 Outer Container

a. The outer container is sized to fit into tube vaults and current shipping containers. Consideration of compatibility with transport casks will minimize future prepackaging and avoid unnecessary additional personnel exposure, operational risk and waste generation.

At ORNL, the dimensional requirements for the outer cylindrical container should be as follows:

1. Maximum outside diameter <11.0 cm (4.4 in).
2. Minimum external height >10.1 cm (4.0 in).

The minimum height ensures that the container will not tumble when placed into the tube vault.

b. External surfaces of the outer container shall be as free from removable contamination as practical. Exterior surface contamination may be evidence of potential leakage of radioactive materials (10 CFR 835). Limits for ^{233}U are not specified in 10 CFR 835. The limits for transuranics are used because they are the most restrictive and have the most similar characteristics to ^{233}U.

4.2.4 Optional Container(s). To facilitate material handling, additional packaging layers may be used for convenience.

4.2.5 Oxide Monoliths. The resistance of these materials to dispersal of solid particulates and release of radon is considered sufficient.

4.2.6 Ceramic Fuel Materials. The ceramic fuel pellets provide the primary level of containment for the ^{233}U-ThO$_2$ oxide, ceramic-based light water breeder reactor (LWBR) fuel materials stored at the INEEL. Additional levels of containment are provided by the physical packaging. The packaging at the RWMC consists of Zircaloy-clad fuel rods, stainless steel rods closed with an O-ring sealed plug, PVC bags of pellets, or polyethylene bottles of pellets. These units are placed inside a steel 2R container that has been coated with a rust resistant paint and closed with a lightly oiled pipe cap. The 2R containers are put into an epoxy-coated galvanized steel 6M drum closed with an epoxy-coated steel lid sealed with an elastomer seal ring. The 2R container is located in the center of the drum by layers of fiberboard packing. The drums are then packed inside a lead/steel shielded overpack which is then stored inside a steel building on a concrete pad. This combination of physical barriers presents an effective level of containment and radiation shielding for the ceramic pellets.

The LWBR fuel materials stored at the CPP-749 facility are in the form of Zircaloy clad fuel rods and O-ring sealed, stainless steel rods. These rods are stored inside a larger stainless steel pipe container that is also sealed with an O-ring. These shipping containers are then placed inside a steel-lined, below-grade storage vault, which has an elastomeric gasket-sealed lid. This system also provides an effective level of containment.

Thus, the INEEL material utilizes the robust ceramic pellet as its primary level of containment and the various layers of physical barriers as the secondary and further levels of containment and radiation shielding.

4.3 Contained Materials

4.3.1 Quantities

a. Criticality safety evaluations shall be obtained for the specific ^{233}U-bearing storage configurations for quantities in excess of the limits listed in ANSI/ANS-8.1 or the requirements specified in site specific nuclear criticality safety programs as applicable. The evaluations shall consider the presence of other fissile isotopes and other materials, such as low-Z materials, plastics, moisture, and geometry as required by ANSI/ANS-8.1.

b. When the mass limits on ^{233}U as listed in ANSI/ANS-8.1 are used, it should be noted that these limits are the most restrictive limits for the prevalent fissile nuclides (i.e., ^{233}U, ^{235}U, ^{237}Np, and ^{241}Am) except for Pu. If Pu is present, further restrictions on the mass limit should be considered on a case by case basis.

4.3.2 Internal Atmosphere

a. Any non-corrosive atmosphere is acceptable for packaging solid materials. However, an inert or nitrogen atmosphere is needed for metals to ensure that metal surfaces are not oxidized—the form of which can be reactive. (J. J. Dawson, et al., 1956)

b. Sealed containers storing ^{233}U-bearing material must be able to withstand the anticipated buildup of pressure. The containers are exempt from the ASME Boiler and Pressure Code because of their diameter (ASME Section VIII-Division 2 Part AG-121). However, this standard is incorporating, as good practice, applicable elements of the Code. Section VIII-Division 1 Section UG-101 provides methods for proof tests to determine the maximum allowable working pressure. The maximum allowable working pressure must be greater than any pressure increases caused by temperature increases, evolved gases, helium from alpha decay, and radon.

There are many ways to determine the internal pressure (e.g., lid deflection on a CEUSP can). In the absence of any measured pressure, the following equation bounds the internal pressure of a container

$$P = \left(\frac{T}{T_0}\right) [P_0 + A + B + C + D + E] \qquad \text{(Eq. A-1)}$$

where P is the pressure, T_0 is the package temperature at the time of sealing, T is the storage temperature, and P_0 is the pressure at the time of sealing. The terms A, B, C, D, and E are terms that give the contributions from various sources of pressure described as follows:

A. Radiolysis of water. Research on the radiolysis of water indicates that hydrogen and oxygen form a steady state pressure between 1 and 2 atmospheres under intense radiation fluxes (Allen et al. 1952, Hochanadel 1952, Allen 1961, Firestone 1957). Lower levels of radiation from decaying radioisotopes such as ^{232}U and ^{233}U should produce only a fraction of an atmosphere at steady state conditions. However, for a conservative determination, 2 atmospheres should be used.

B. Reaction with water. Only unstabilized UO_2 powder undergoes this reaction. Furthermore, any water that undergoes reaction will be unavailable for radiolysis, thus the value of term A could be reduced, or eliminated for the case of complete reaction. The maximum pressure generated from hydrogen accumulation, assuming complete reaction of all oxygen dissociated from water, is given by

$$B = \left(\frac{RT}{V_c - \frac{m}{\rho}}\right)\left(\frac{mX_{H2O}}{MW_{H2O}}\right) \qquad \text{(Eq. A-2)}$$

where R is the gas constant, V_c is the volume of the container, m is the mass of UO_2, ρ is the density of the material, X_{H2O} is the moisture fraction, and MW_{H2O} is the molecular weight of water.

C. Radiolysis of plastic. There is evidence that only plastic in direct contact with bulk material undergoes radiolysis (Shaw and Freestone 1998). However, the conservative assumption is to assume all plastic decomposes. The maximum pressure generated is given by

$$C = \left(\frac{RT}{V_c - \frac{m}{\rho}}\right)\left(\frac{m_p X_{H2,P}}{MW_{H2}}\right) \qquad \text{(Eq. A-3)}$$

where m_P is the mass of any plastic present in the material, $X_{H2,P}$ is the mass fraction of hydrogen in the plastic and MW_{H2} is the molecular weight of H_2.

D. Helium from alpha decay. The pressure from helium generated by 50 years of alpha decay is given by

$$D = \left(\frac{RT}{V_c - \frac{m}{\rho}}\right)\left(\frac{m\Sigma b_i X_i}{MW_{He}}\right) \qquad \text{(Eq. A-4)}$$

where b_i is the fraction of the isotope i that is emitted as a helium ion through alpha decay over a fifty-year period, and X_i is the mass fraction of isotope *i*, and MW_{He} is the molecular weight of helium.

E. Radon. The longest-lived isotope of radon, ^{222}Rn, has a half-life of 3.8 days. Over a 50-year period, any Rn intermediate on a decay chain will reach a steady-state concentration that is insignificant when compared to the helium that is produced by alpha decay of other radionuclides in the same decay chain. Thus, the partial pressure contribution of all isotopes of Rn may be neglected.

4.4 Inspection and Surveillance for Safety. Inspection and surveillance are to be non-intrusive, maintaining intact containers.

4.4.1 Documentation of Inspection and Surveillance Methods. Inspection and surveillance methods must be documented to ensure consistency. Delineation of responsibilities is needed to ensure a consistent management approach and awareness of responsibilities.

4.4.2 Surveillance Plan. The function of the inspection and surveillance program is to identify errors and flaws in the initial packaging as well as to detect package degradation and contents changes that might affect package integrity during storage. Therefore, all packages (repackaged and previously existing) must be part of the surveillance program.

a. Inspection of every container after repackaging, but prior to emplacement in the storage configuration, is expected to detect flaws in the initial repackaging. This initial inspection should also provide baseline information on the leak rate, package mass, verification of contents through NDA measurements, and any other information deemed desirable and attainable through non-intrusive measurements such as radiography. This inspection may be part of the quality program for verifying package integrity.

b. After the package is placed into the storage configuration, mechanical failures are random. Uniform changes in the storage package population, such as a gradual pressure generation in oxide containers, are also expected to occur during this period. Surveillance during this period should consist of statistical sampling to monitor the behavior of the population. The ultimate storage life of the packages is unknown and must be established using surveillance data.

c. No additional basis required.

d. No additional basis required.

4.4.3 Surveillance Parameters. These parameters are indicators of the stability of the container and its contents.

4.4.4 Evaluation of Surveillance Data. No additional basis required.

4.5 Documentation

4.5.1 Database. An electronic database is specified because a manual database would be overly cumbersome. The architecture is not specified here so that maximum flexibility to interface with existing databases and files is maintained.

4.5.2 Database Requirements

a. These parameters allow as complete a characterization of the contents as is possible without undertaking additional characterization. It is recognized that some information may be redundant. The apparently redundant items permit better characterization when some of the data is missing.

b. Package data can meet a number of needs. For example, if a package exhibits unexpected behavior, these data can help identify other, similar packages than may require inspection. These data also facilitate disposition process planning.

c. No additional basis required.

4.6 Quality Assurance

The appropriate QA requirements are given in 10 CFR 830.120 and DOE O 414.1.

5. STORAGE FACILITY FEATURES

5.1 Nuclear Criticality Safety

A principal safety consideration for the safe storage of ^{233}U is eliminating the possibility of the material reaching a configuration that would result in criticality. Criticality avoidance is a prime priority in safety considerations in the design and operation of a ^{233}U storage facility. In addition to providing an array that is criticality safe, the packages and facility shall be engineered, constructed, controlled, and monitored to avoid the occurrence of accidental criticality for all credible natural phenomena events such as fires, flooding, earthquakes, and tornadoes. Because criticality safety is considered to be the dominant safety concern in the design and operation of a ^{233}U storage facility, the vault area should be designed with consideration of water sources such as fire sprinklers. Co-existing combustible materials should be minimized or eliminated from the facility in order to minimize the potential for fires and the need for fire suppression systems.

A majority of the ^{233}U in inventory consists of mixtures of ^{233}U and ^{232}U or mixtures whose properties are dominated by the ^{233}U and ^{232}U content. Uranium-233 has substantially different nuclear criticality properties than the other two SNMs, ^{235}U and Pu. Therefore, facilities designed for ^{235}U and Pu may not be acceptable for comparable activities involving ^{233}U from a nuclear criticality safety standpoint and shall be evaluated to meet the requirements for criticality safety specified in DOE O 420.1.

5.2 Confinement of Contamination

The matrix of the material and/or the inner container provide the first barrier against spread of contamination; the outer container and the tube vaults provide additional barriers. The packaging should be designed to maintain mechanical integrity, including its seal, during normal handling. However, this package is not expected to provide protection against all perils such as major fires and earthquakes; design of the facility and of the storage array are expected to address these considerations.

5.2.1 Facility Confinement. No additional basis required.

5.3 Radiation Shielding

Uranium-233 with its associated sister isotope ^{232}U present much more severe external radiation hazards than any of the naturally occurring uranium isotopes. Massive biological shielding is required, where high concentrations of ^{232}U occur, to protect personnel from the 2.6 MeV gamma emission of ^{232}U daughter product ^{208}Tl. The occupational radiation exposure should be kept as low as reasonably achievable (ALARA) and radiation protection be provided as specified in 10 CFR 835, "Occupational Radiation Protection." Dose rates are dependent on the source (e.g., activity, geometry, and matrix), shielding, and source-to-detector configuration, so expected dose rates for actual conditions should be determined on a case-by-case basis.

Except for spontaneous fission, neutrons are not directly produced during the radioactive decay of any of the uranium isotopes or the sequential decays. However, alpha-neutron reactions, in which alpha particles react with low-Z isotopes such as ^{6}Li, ^{7}Li, ^{9}Be, ^{10}B, and ^{19}F, (and to a lesser extent ^{27}Al and ^{28}Si), generate neutrons. Depending on the material storage system used, the facility itself may serve as a shield.

5.4 SNM Safeguards

DOE requirements for safeguards are given in DOE O 470.1, DOE O 471.2A, DOE O 472.1B, DOE 5632.7A, and DOE 5633.3B.

APPENDIX B
GLOSSARY AND ACRONYMS

1. GLOSSARY

Acceptable - Conforming with safety requirements, directives, or regulations.

Accountability - That part of Safeguards and Materials Management that encompasses the management system and records and reports to account for source and special nuclear material to minimize the possibility of diversion and to detect diversion promptly should it occur. Accountability does not include physical protection.

ALARA (as low as reasonably achievable) - The implementation of good radiation-protection programs and practices which traditionally have been effective in keeping the average and individual exposures for monitored workers well below allowable limits.

Alloy - A substance composed of two or more metals united by being fused together and dissolving in each other when molten.

Approved - Acceptable to the "authority having jurisdiction."

Authority Having Jurisdiction - The organization, office, or individual responsible for approving equipment, installation, or procedure.

Barrier - A restraint that provides containment of stored material and protection from the environment.

Calcine, Calcining - The process of heating materials to remove combustible or volatile materials such as organic matter, salts, and moisture.

Ceramic - A class of inorganic, nonmetallic solids formed at high temperature (>1000 °C) in manufacture or use.

Cladding - An outer metal jacket or can that surrounds and protects fuel pellets containing source and special nuclear material. Typical cladding materials are alloys of aluminum or zirconium and stainless steel.

Combustible - In the form used and under the conditions anticipated, will ignite, burn, support combustion, or release flammable vapors when subjected to fire or elevated temperature.

Container - A structurally closed barrier outside of which the concentration of hazardous materials is normally expected to be lower than allowable limits. A container is designed to remain closed and intact during all design basis accidents.

Contamination - The presence of residual radioactivity in excess of levels that are acceptable for release of a site, a facility, or a package.

Conversion - An operation for changing from one material form, use, or purpose to another.

Criterion - A quantitative or qualitative measure of what is acceptable or desirable for one or more factors (e.g., individual dose limit, subcritical mass limit, mechanical strength limit, etc.) for packaging and safe storage.

Criticality Safety Evaluation (CSE) - Documents the parameters, limits, and controls required to ensure that the analyzed conditions are subcritical for normal and credible abnormal conditions. Reviews of operations to ascertain that limits and controls are being followed and that process conditions have not been altered such that the applicability of the nuclear criticality safety evaluation has been compromised. It is acceptable to DOE to follow DOE-STD-3007-93, Guidelines for Preparing Criticality Safety Evaluations at Department of Energy non-Reactor Nuclear Facilities, when preparing Criticality Safety Evaluations (420.1).

Database - A large collection of data in a computer, organized so that it can be expanded, updated, and reviewed rapidly for various uses.

Dilution - In general the addition of inert material or solvent with the result that the concentration of the material of interest is reduced.

DOT-2R – Containers that meet the specifications of 49 CFR 178.360.

DOT-6M – Drums that hold DOT-2R containers and meet the specifications of 49 CFR 178.354.

Effective Neutron Multiplication Factor (k_{eff}) - The ratio of the total number of neutrons produced during a time interval (excluding neutrons produced by sources whose strengths are not a function of fission rate) to the total number of neutrons lost by absorption and leakage.

Enclosure - A physical structure that provides a barrier between the internally contaminated package and the worker, facility, and environment.

Engineered Safety Feature - Systems, components, or structures that prevent and/or mitigate the consequences of potential accidents including the bounding design basis accidents.

Handling Enclosure - A glove box line or similar equipment that isolates ^{233}U-bearing materials from the worker's environment while allowing the material to be handled or processed.

Hot Cell - A heavily shielded enclosure in which radioactive materials can be handled by persons using remote manipulators and for viewing the materials through shielded windows or periscopes.

Inert Gas - A non-reactive gas or combination of gases appropriate to the material being stored that will not support corrosion of the container or oxidation of its contents.

In-Line - Something located inside a material handling enclosure (e.g., glove box or "hot" storage vault). When material is stored "in-line," the enclosure provides one barrier for storage.

In-Process, In-Use Material - Material that is integral to the continuing manufacture or recycle operations of the nuclear weapons complex and may not be considered as excess material for storage.

Inventory - The total quantity of radioactive material at a site.

Irradiated Nuclear Material - Nuclear material that has been subject to nuclear irradiation in a reactor or accelerator and that consequently delivers an external radiation dose requiring special containment and handling.

Leaktight - A degree of package containment that in a practical sense precludes any significant release of radioactive materials. This degree of containment is achieved by demonstration of a leakage rate less than or equal to 1×10^{-7} ref·cm^3/s, of air at an upstream pressure of 1 atm abs and a downstream pressure of 0.01 atm abs or less.

Low-Z Material - Elements of atomic number 9 or less.

Material Container - The container that is in contact with the uranium material being stored. If structurally adequate and sealed, the material container provides one barrier for containment and environmental protection.

Nondestructive Assay (NDA) - A procedure (e.g., calorimetric or radiometric measurement) for determining the amount of fissionable uranium in a container without physically sampling the material.

Nondestructive Examination (NDE) - A procedure (e.g., radiography) for examining the contents of a container without opening the container.

Nonproliferation Treaty - A Treaty (to prevent the spread of nuclear weapons) presented to the Eighteen-Nation Disarmament Committee in Geneva by the U. S. and USSR in identical texts on January 18, 1968. The Treaty entered into force March 5, 1970.

Nuclear Criticality Safety - The prevention or termination of inadvertent nuclear criticality and protection against injury or damage due to an accidental nuclear criticality.

Oxide Monolith - A large, brick-like piece of oxide, typically U_3O_8, that has been calcined in a denitration process and baked at greater than 800 °C (1472 °F) for at least three hours to remove moisture and convert residual salts to oxides.

Packaging - The assembly of materials and components in compliance with storage/shipment requirements.

Process - To extract, separate, purify, or fabricate a material by physical, chemical, or mechanical means.

Pyrophoric - Capable of igniting spontaneously when exposed to air.

Quality Assurance (QA) - All planned and systematic actions necessary to provide adequate confidence that a structure, system, or component will perform satisfactorily in service.

Quality Control (QC) - The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by DOE. QC includes operational techniques and activities that are used to fulfill requirements for quality.

Removable Activity - Surface activity that can be readily removed and collected for measurement by wiping the surface with moderate pressure.

Residue - Process-generated uranium-bearing materials not classified as storable metal or stabilized oxide that contains a non-discardable quantity of uranium.

Safeguards - An integrated system of physical protection, material accounting, and material control measures designed to deter, prevent, detect, and respond to unauthorized possession, use, or sabotage of nuclear materials.

Sealed - A container has been closed (e.g., welded) and does not exceed the maximum permissible limits defined in ANSI N 14.5-1997.

Sealed Source - Any SNM that is encased in a capsule designed to prevent leakage or escape of the SNM.

Shall, Should and May - "Shall" denotes that something is required. "Should" denotes that something is recommended but is not required. "May" denotes that something is permitted but is neither a requirement nor a recommendation.

Significant Quantity of Fissionable Material - The minimum quantity of fissionable material for which control is required to maintain subcriticality under all normal and credible abnormal conditions.

Sinter - To form a homogeneous mass by heating compacted material without melting.

Site Safeguards and Security Plan - A plan developed at the site level under direction of the cognizant field element manager that provides a description of site-wide protection programs and evaluations of risk associated with DOE design basis threat policy and identified facility targets.

Specific Surface Area - The ratio of the geometric surface area of a material to its mass in units of cm^2/g.

Standard Cubic Centimeter of Gas - The quantity (moles) of gas in one cubic centimeter of volume at 1 atmosphere pressure and 25°C (298 K).

Storage - Any method for safely maintaining items in a retrievable form for subsequent use or disposition.

Storage Facility - The building structure and other confinement systems that house storage packages.

Storage Package - A configuration of nested containers including package content.

Survey - A systematic evaluation and documentation of radiological measurements with a correctly calibrated instrument(s) that meets the sensitivity required by the objective of the evaluation.

Thermal Stabilization - A process that exposes a uranium-bearing material in air to an elevated temperature for the duration required to convert reactive constituents present to a stable oxide form and to remove adsorbed moisture and other volatile species.

Tube Vaults - Tubular storage devices (steel lined and encased in concrete) used for the storage of packages containing ^{233}U.

Unirradiated Material - Material that has not been subjected to the high-neutron-flux environment existing near the core of a nuclear reactor, or material irradiated in a reactor but with a radiation level equal to or less than 100 rad/h at 1 m unshielded or material that has been irradiated in a reactor but has been separated from fission products to permit reuse.

Waste - Uranium-233 containing material that meets three requirements: (1) there is no existing, planned, or proposed use; (2) the ^{233}U (a) has a concentration of <200 g ^{233}U/55-gal drum or (b) the enrichment level is <0.66 wt % ^{233}U in ^{238}U; and (3) the ^{233}U (a) has an approximately homogeneous concentration of <1 kg ^{233}U/m^3 (equivalent to <200 g/55-gal drum) or (b) the enrichment level is <12 wt % ^{233}U in ^{238}U.

2. Acronyms

ALARA	As low as reasonably achievable
ANSI	American National Standards Institute
CFR	Code of Federal Regulations
DOE	U. S. Department of Energy
DOT	Department of Transportation
ICPP	Idaho Chemical Processing Plant
INEEL	Idaho National Engineering and Environmental Laboratory
MC&A	Material Control and Accountability
NDA	Nondestructive Assay
NDE	Nondestructive Examination
ORNL	Oak Ridge National Laboratory
ppm	Parts per million, or grams of designated material per megagram (metric ton) of net representative sample

psi	Pounds per square inch
Pu	Plutonium
Rn	Radon
SNM	Special nuclear materials
Th	Thorium
Tl	Thallium
U	Uranium
UO_2	Uranium Dioxide
UO_3	Uranium Trioxide
U_3O_8	Triuranium Octoxide

APPENDIX C
REFERENCES

Specific DOE and other Federal agency regulations and other documents used in developing this standard and the bases for the standard are listed below.

1. **Federal Regulations.** The following Federal Regulations are referenced in this standard:

10 CFR 20, Standards for Protection Against Radiation;

10 CFR 830.120, Nuclear Safety Management, Quality Assurance Requirements;

10 CFR 835, Occupational Radiation Protection, Surface Radioactivity Values;

29 CFR 1910, Occupational Safety and Health Standards;

40 CFR 61 Subpart H, National Emission Standards for Emissions of Radionuclides other than Radon from Department of Energy Facilities;

49 CFR 173, Shippers – General Requirements for Shipments and Packagings;

49 CFR 178.354, Specification 6M; metal packaging;

49 CFR 178.360, Specification 2R; inside containment vessel.

Copies of Federal Regulations are available from the Government Printing Office (GPO), Superintendent of Documents, Mail Stop: SSOP Washington, DC 20402-9329

2. **Department of Energy Orders, Manuals, Reports, and Letters.** The following DOE Orders, Manuals and Reports are referenced in this standard:

DOE O 231.1, Environment, Safety, and Health Reporting, November 7, 1996;

DOE M 231.1, Environment, Safety, and Health Reporting Manual, September 30, 1995;

DOE G 414.1-1, Assessment Guide for QA, August 1996;

DOE O 420.1, Facility Safety, October 13, 1995;

DOE O 425.1, Startup and Restart of Nuclear Facilities, October 26, 1995;

DOE O 430.1, Life Cycle Asset Management, October 26, 1995;

DOE O 470.1, Safeguards and Security Program, June 21, 1996;

DOE O 471.2A, Information Security Program, March 27, 1997;

DOE O 472.1B, Personnel Security Activities, March 24, 1997;

DOE 5400.1, General Environmental Protection Program, June 29, 1990;

DOE 5480.21, Unreviewed Safety Questions, December 1991;

DOE 5480.22, Technical Safety Requirements, January 23, 1996;

DOE 5480.23, Nuclear Safety Analysis Reports, March 1994;

DOE 5632.7A, Protective Force Program, February 13, 1995;

DOE 5633.3B, Control and Accountability of Nuclear Materials, September 1994;

DOE M 5639.6A-1, Manual of Security Requirements for the Classified Automated Information System Security Program, July 1994;

Department of Energy, Oak Ridge Operations Office, January 21, 1998. Approval of Extension of Waiver of DOE Order 5633.3B Requirements for Physical Inventory in Material Balance Area (MBA) 070 (Deviation Request No. OSS-OR-95-009), letter to Dr. J.H. Swanks, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Copies of DOE Orders and reports are available from:
U.S. Department of Energy, AD-631/FORS, Washington, DC 20585, (202)586-9642

3. **Non-Federal References.** The following non-government documents are referenced in this standard.

Allen, A. O. 1961. *The Radiation Chemistry of Water and Aqueous Solutions*, Van Nostrand Co., Inc., Princeton, N. J.

Allen, A. O. et al. 1952. *Decomposition of Water and Aqueous Solutions under Mixed Fast Neutron and Gamma Radiation*, J. Phys. Chem., 56, 575.

American National Standards Institute/American Nuclear Society, 1983. *Nuclear Criticality Safety in Operations with Fissionable Materials Outside of Reactors*, ANSI/ANS-8.1-1983, La Grange Park, Illinois.

American National Standards Institute, 1997. *Leakage Tests on Packages for Shipment*, ANSI N14.5-1997, New York, New York.

ANL-6287, Chemical Engineering Division, Argonne National Laboratory, Summary Report, March 1961.

Bereolos, P.J., C.W. Forsberg, D.C. Kocher, and A.M. Krichinsky, *Strategy for the Future Use and Disposition of Uranium-233: Technical Information*, ORNL/TM-13552, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1998.

Bereolos, P.J. et al. 1998. *Assessment of Uranium-233 Storage Safety Issues at Department of Energy Facilities.* ORNL/TM-13685, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1998.

Bretherick, L. *Hazards in the Chemical Laboratory*, Royal Society of Chemistry, London, 1986.

Burke, J. et al. *Physical Metallurgy of Uranium Alloys*, 1976.

Dawson, J.J. et al., 1956. *Some Aspects of the System Uranium Trioxide - Water,* J. Chem. Soc., 3531-3540.

Firestone, R. F. 1957. *The Radiation Chemistry of Water Vapor. "The Indirect Effect on Deuterium and the Exchange of D-Atoms with Water Molecules,"* J. Phys. Chem., 79, 5593.

Hochanadel, C. J. 1952. *Effects of Cobalt Gamma-Radiation on Water and Aqueous Solutions*, J. Phys. Chem., **56**, 587.

Parrot, Sr., J.R., McDuffee, W.T., Nicol, R.G., Whitson, W.R., and Krichinsky, A.M. 1979. *The Preparation of Kilogram Quantities of* $^{233}UO_2$ *for the Light Water Breeder Reactor Demonstration Program.* ORNL/CF-79/279, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Primm, III, R.T., *Criticality Safety Studies of Building 3019 Cell 4 and In-Line Storage Wells*, ORNL/TM-12374 November 1993;

Shaw, S.J. and V. Freestone, V. 1998. *Interim Storage of Plutonium Bearing Materials in Food Product Containers*, NMD01/17/05/SJS/16/98, United Kingdom.

WAPD-TM-1244(L), ThO_2 and ThO_2-$^{233}UO_2$ High Density Fuel Pellet Manufacturer for the Light Water Breeder Reactor (LWBR Development Program), January 1976; **(Reference has limited distribution)**

APPENDIX B. INTERNET SITES THAT CONTAIN ^{233}U INFORMATION

This appendix provides a listing in Table B.1 of Internet sites that contain information on ^{233}U-bearing materials. In general, such sites have posted documents and other information sources on ^{233}U materials and ^{233}U-Th fuel cycle activities and facilities. These resources are accessible through various World Wide Web (WWW) servers. For each Internet site identified in Table B.1, the Uniform Resource Locator (URL) is provided.

Table B.1. Internet sites containing information on ^{233}U-bearing materials

Site/description	URL[a]
ANS (Technical Reports)	http://www.ans.org/pubs/catalog
DNFSB (Technical Reports)	http://www.dnfsb.gov/techrpts/techxx.html (*xx* = report number)
DOE-EIA Documents	http://www.eia.doe.gov/cneaf/nuclear/uia/feature.html
DOE Technical Standards[b]	http://www.doe.gov/techstds/standard/standfrm.html
DOE Information Bridge Home Page	http://www.doe.gov/bridge/home.html
IAEA (Technical Reports)	http://www.iaea.org/worldatom/publications
Indira Gandhi Centre for Atomic Research	http://www.igcar.ernet.in/igcabout.html
Radkowsky Thorium Power Corporation (RTPC) Home Page	http://www.rtpc.com/home.shtml

[a] In some cases, the URL listed accesses a particular document of the type listed in the left-hand column.

[b] Includes the DOE ^{233}U Storage Standard (see Appendix A).

APPENDIX C. ^{233}U INVENTORY CHARACTERISTICS

C.1 DISCUSSION

This appendix summarizes the characteristics of current ^{233}U-bearing material inventories at various domestic sites. The information and data reported are based on reports (Bereolos et al. June 1998, Lewis and Wilkinson March 1998, and U.S. DOE-ID and INEEL December 1998).

A list of domestic sites that have accountable quantities of ^{233}U materials is provided in Table C.1. Table C.2 summarizes the current inventories of ^{233}U at each domestic site. The information and data reported in certain columns of this table are based on specific code definitions defined in Tables C.3, C.4, and C.5. Table C.2 lists the following ^{233}U information and data:

- material form description (based on the material type and form listed in Table C.3),
- packaging types (based on the packaging types and codes listed in Table C.4),
- number of packages,
- material type code (based on the codes listed for ^{233}U and ^{235}U in Table C.5); and
- accountable mass (by total U, ^{233}U, and ^{235}U).

ORNL currently has the largest site mass inventory of ^{233}U-bearing materials. This inventory resides in the storage vaults of Building 3019. Major characteristics of this inventory are given in Table C.6.

C.2 REFERENCES

Bereolos, P. J. et al. June 1998. *Strategy for the Future Use and Disposition of Uranium-233: History, Inventories, Storage Facilities, and Potential Future Uses*, ORNL/TM-13551, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Lewis, L. C., and D. R. Wilkinson. March 1998. *INEEL Initial Site Assessment Report on the Storage of U-233*, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.

U.S. Department of Energy–Idaho and Idaho National Engineering and Environmental Laboratory. December 1998. *Program Execution Plan for the ^{233}U Safe Storage Program*, Idaho Falls, Idaho.

Table C.1. Domestic sites that have accountable quantities of ^{233}U materials

Site	Acronym
DOE sites	
Argonne National Laboratory–East	ANL–E
Argonne National Laboratory–West	ANL–W
Bettis Atomic Power Laboratory	BAPL
Brookhaven National Laboratory	BNL
Hanford Site	Hanford
Idaho National Engineering and Environmental Laboratory–	
Idaho Chemical Processing Plant	INEEL–ICPP
Radioactive Waste Management Complex	INEEL–RWMC
Knolls Atomic Power Laboratory	KAPL
Lawrence Berkeley National Laboratory	LBNL
Lawrence Livermore National Laboratory	LLNL
Los Alamos National Laboratory	LANL
Mound Plant	Mound
New Brunswick Laboratory	NBL
Oak Ridge National Laboratory	ORNL
Pacific Northwest National Laboratory	PNNL
Rocky Flats Environmental Technology Site	RFETS
Savannah River Site	SRS
Y-12 Plant	Y-12
NRC-licensed sites	
Commonwealth Edison: Dresden Reactor–Unit 3	COMED3
Fort St. Vrain Reactor	FSVR
General Atomics Laboratory, San Diego	GA

Table C.2. Summary of domestic ^{233}U material characteristics and inventories[a]

Site	Material form description[b]	Packaging types[c]	No. of packages	Material-type code[d,e]		Total U (kg)	^{233}U[e] (kg)	^{235}U[e] (kg)
				^{233}U	^{235}U			
ANL–E	MP, MI, SN, RS, RU	B1, B2, C2, G3, P0, V5, X2	5	71, 72, 74		0.028	0.028	0
ANL–W	MA, MP, PI, PO, SN, SS, SZ	B1, C0, C2, D1, G0, G1 P0, P1, P3, V1, V5, V7	63	71, 72		0.155	0.154	0
BAPL	RO, HO, SR	C4, D1, *f*	13	71, 72, 74	38	0.427	0.405	0.014
BNL	*g*	*g*	4	*g*	*g*	*g*	0.002	*g*
COMED3			0			0	0	0
FSVR[h]			0			0	0	0
GA	SS, SO	C2, C4	2	72	38	0.172	0.031	<0.001
Hanford	PO, PI, SN	B1, C0, W1	3	71		0.597	0.079	0
INEEL/ICPP	PO, RO, RU, SN	X2	213	72, 73		358.6	351.6	0
KAPL	*g*	*g*	26	*g*	*g*	*g*	<0.010	*g*
LANL	PO, PI, MP, MI, MA, UO, SO, SS, CP, NM, RO, SN, OO	B1, B2, C0, C1, C2, C3, C4, F2, G1, P0, P1, U0, U1, U2, V1, V5, V7, W4, and X2	109	72		7.243	7.105	0
LBNL	*g*	*g*	*g*	*g*	*g*	0.031	*g*	*g*
LLNL	MP, MA, PO, PI, RO	C0, C2	50	72		3.321	3.253	0
Mound[i]	*g*	*g*	1	*g*	*g*	*g*	<0.005	*g*
NBL	*g*	*g*	3	*g*	*g*	*g*	0.005	*g*

Table C.2 (continued)

Site	Material form description[b]	Packaging types[c]	No. of packages	Material-type code[d,e]		Total U (kg)	^{233}U[e] (kg)	^{235}U[e] (kg)
				^{233}U	^{235}U			
ORNL	MA, UO, OO, MP, PO	C3, C4, V1, X1	1,054	71–74	36	1,387.709	427.341	796.334
PNNL	MA, PO, PI, SN, SZ	C0, C1, C2, G2, P0	15	71, 72		0.048	0.047	0
RFETS	CP, NO	D1	5	72		0.008	0.008	0
SRS			0			0	0	0
Y-12	MP, PI	X1	5	[g]	37	42.6	0.8	38.7
Total			1,571			1,800.9	790.8	835.0

[a] Excludes contributions from irradiated SNF.
[b] Material-type and form codes listed in Table C.3 of Appendix C.
[c] Packaging types and codes listed in Table C.4 of Appendix C.
[d] Nuclear material-type codes listed for ^{233}U and ^{235}U in Table C.5 of Appendix C.
[e] Accountable amounts only. See nuclear material-type codes listed in Table C.5 of Appendix C.
[f] Entrained in equipment.
[g] Information not available.
[h] Excludes contributions from irradiated SNF owned by DOE.
[i] Most ^{233}U material was shipped to ORNL in 1996 and is now included in the ORNL inventory.

Table C.3. Material-form code definitions

Material type	Form	Code
Weapon component	Parts	PA
	Pits	PT
	Canned subassembly (CSA)[a]	CS
Metal	Pure	MP
	Impure	MI
	Alloys	MA
Oxides	Pure	PO
	Impure	PI
	Other (specify)	OO
Compounds	Uranium hexafluoride	UF
	Other (specify)	UO
Sources and samples	Sealed	SS
	Other (specify)	SO
Combustibles	Graphite	CG
	Paper, plastics, wood, mop heads, etc.	CP
	Other (specify)	CO
Noncombustibles	Glass	NG
	Nonuranium metal	NM
	Other (specify)	NO
Process residues	Reduction	RR
	Incinerator ash	IA
	Sludge	SR
	Filters	RF
	Other (specify)	RO
Solutions	Nitric acid	SN
	Basic	SC
	Organic	OS
	Other (specify)	SZ
Reactor fuel	Unirradiated	RU
	Targets	RT
	Slightly irradiated	RS
	Other (specify)	RO
Hold-up	Materials in pipes, tanks, ducts, equipment, etc.	HO

[a] When seal is broken, canned subassembly is called *parts*.

Table C.4. Packaging types and codes

General description	Packaging code	Subcode	Packaging details
Cans	C	0	Food-pack/rim seal (tinned)
		1	Food-pack/rim seal (stainless)
		2	Slip lid
		3	Screw lid
		4	Other (specify)
Plastic bagging	B	0	Unknown
		1	Polyethylene
		2	Polyvinylchloride (PVC)
		3	Other (specify)
Metal foil	F	0	Unknown
		1	Aluminum
		2	Lead
		3	Other (specify)
Vessels	V	0	Unknown
		1	Welded
		2	Knife-edge seal (i.e., Conflat®)
		3	Elastomeric seal (O-ring)
		4	Compression seal (Swagelock® etc.)
		5	Screw lid
		6	Gas cylinder (UF_6)
		7	Other (specify)
Glass	G	0	Other (specify)
		1	Screw lid
		2	Sealed vials/capsules
		3	Glass-metal seal
Plastic containers	P[a]	0	Polyethylene/polypropylene–sealed
		1	Polyethylene/polypropylene–unsealed
		2	Polyethylene/polypropylene–unknown
		3	Other (specify)
Unknown	U	0	Unknown
		1	Suspected to be metal
		2	Suspected to be plastic
		3	Other (specify)
Drums	D	1	55-gal
		2	30-gal
		3	<30-gal
		4	Unspecified (add V if vented)
Tanks	T	0	Unknown
		1	Raschig ring–filled
		2	Geometrically favorable
		3	Other (specify)

Table C.4 (continued)

General description	Packaging code	Subcode	Packaging details
Wooden crates or boxes	W	0	Metal burial box
		1	Cardboard
		2	Wooden
		3	Fiberglass
		4	Other (specify)
Shipping containers and overpacks	X	0	5A overpack
		1	6M 110-gal
		2	Other (specify)
		3	Birdcage (storage only)

[a] P = bottle.

Table C.5. Nuclear material-type codes

Type code	Type description	Reporting unit	Type code	Type description	Reporting unit
	Uranium—depleted in ^{235}U, wt %		44	^{241}Am	g
10	Total	kg	45	^{243}Am	g
11	<0.21	kg	46	Curium	g
12	0.21–<0.24	kg	47	Berkelium	µg
13	0.24–<0.26	kg	48	Californium	µg
14	0.26–<0.28	kg		Plutonium	
15	0.28–<0.31	kg	50	Total	g
16	0.31–<0.50	kg		^{240}Pu	
17	0.50–<0.60	kg	51	<4.00	g
18	0.60–<0.711	kg	52	4.00–<7.00	g
	Uranium—enriched in ^{235}U, wt %		53	7.00–<10.00	g
20	Total	g	54	10.00–<13.00	g
21	>0.711–<0.90	g	55	13.00–<16.00	g
22	0.90–<1.15	g	56	16.00–<19.00	g
23	1.15–<1.60	g	57	19.00 and above	g
24	1.60–<2.00	g		*Lithium—enriched in ^{6}Li*	kg
25	2.00–<2.60	g	60	Total	kg
26	2.60–<2.90	g	61	>Normal to <55.00	kg
27	2.90–<3.10	g	62	55.00–<80.00	kg
28	3.10–<3.40	g	63	80.00 and above	kg
29	3.40–<3.90	g		*Uranium—enriched in ^{233}U*	
30	3.90–<4.10	g	70	Total	g
31	4.10–<5.00	g	71	<5 ppm ^{232}U	g
32	5.00–<10.00	g	72	5–<10 ppm ^{232}U	g
33	10.00–<20.00	g	73	10–<50 ppm ^{232}U	g
34	20.00–<35.00	g	74	50 ppm and above ^{232}U	g
35	35.00–<45.00	g	81	Normal uranium (0.711 wt % ^{235}U)	kg
36	45.00–<80.00	g	82	^{237}Np	g
37	80.00–<92.00	g	83	^{238}Pu	g (1×10^{-1})
38	92.00–<94.00	g	86	D_2	kg (1×10^{-1})
39	94.00 and above	g	87	Tritium	g (1×10^{-2})
	^{242}Pu		88	Thorium	kg
40	Total	g	89	Uranium in cascades	g
41	20–60	g	90	This series available for local use	
42	>60	g			

Table C.6. Uranium-233 material currently in the storage vaults of ORNL Building 3019[a]

Material form	Package assembly[b]	Package configuration	No. of outer packages	^{233}U (kg)	^{232}U (ppm)
U metal	LANL	Unique SST[c]	2	5.89	40
U oxide powder	Savannah River SRO-9	Welded Al in welded Al	6	2.98	7
U oxide powder	Savannah River LZB	Welded Al in welded Al	6	2.94	4.5
U oxide powder	ORNL-RDF samples	Tin-plated steel over plastic-bagged sample vials	10	0.82	6–10
UF_4 × LiF	RCP-04	Welded Ni in Al	2	1.06	220
UF_4 × LiF	RCP-04	Screw-top Al in Al	1	1.55	220
UF_4 × LiF	RCP-04	SST in welded Al	1	0.31	220
U_3O_8 monolith	CEUSP	Tin-plated steel over welded SST	403	101.14	140
U_3O_8 monolith	RCP-06	Tin-plated steel over welded SST	27	60.27	20
U oxide powder	Savannah River aluminum (RCP-02)	Welded Al in welded Al	27	10.72	38
U oxide powder	Savannah River aluminum (RCP-03)	Welded Al in welded Al	140	61.57	220
U oxide powder	Short oxide-product can (PZA BPL)	Tin-plated steel over plastic-bagged SST	22	15.02	6
U oxide powder	Short oxide-product can	Tin-plated steel over plastic-bagged SST	68	54.64	6.5–10
U oxide powder	Tall oxide-product can	Tin-plated steel over plastic-bagged SST	71	33.51	5.6–8.3
U oxide powder	Mound	Glass within SST within SST	19	3.29	2–16
U_3O_8 powder	ANL-ZPR (5 packet)	Welded Ni-plated SST packets within tin-plated steel	2	0.27	7
U_3O_8 powder	ANL-ZPR (12 packet)	Welded Ni-plated SST packets within tin-plated steel	101	32.94	7
U_3O_8 powder	ANL-ZPR (16 packet)	Welded Ni-plated SST packets within tin-plated steel	27	11.83	7
U metal	ANL-ZPR (metal)	Welded Ni-plated SST packets within tin-plated steel	1	0.56	5
U oxide powder	Oxide	Tin-plated steel over plastic-bagged, tin-plated steel	6	1.48	7–10.8
U oxide powder	Oxide scrap	Tin-plated steel over plastic-bagged, tin-plated steel	7	3.80	6–42
U metal	RCP-20(#2 and #3)	Tin-plated steel over plastic-bagged, tin-plated steel	2	3.99	5–42

Table C.6 (continued)

Material form	Package assembly[a]	Package configuration	No. of outer packages	^{233}U (kg)	^{232}U (ppm)
U metal	Metal scrap	Tin-plated steel over plastic-bagged, tin-plated steel	3	0.53	5–42
Ammonium diuranate powder	ADU scrap	Tin-plated steel over plastic-bagged, tin-plated steel	1	0.00	7
U oxide powder	Hanford HUA-2	SST in welded SST	6	0.35	8–38
U metal	LANL AUA-84	Welded SST in welded SST	3	0.49	8
U oxide microspheres	ORNL-RDF misc. samples	Plastic-bagged glass in cardboard within tin-plated steel	3	0.39	7
Ammonium diuranate powder	ADU product	Tin-plated steel over plastic-bagged SST	1	0.09	7
UO_2 powder	KZA-8	Tin-plated steel over tin-plated steel	1	0.19	2.5
U oxide powder	ARF-32	Tin-plated steel over SST	1	0.07	7
U_3O_8 powder	FZA-88	Tin-plated steel over unknown	2	0.02	5
U foil	CZA-90	Tin-plated steel over welded SST	1	0.57	5
U metal	ARF-33 metal	Tin-plated steel over tin-plated steel	4	1.43	7
U oxides and U foil	CZD-G (CZ)	Tin-plated steel over glass	1	0.09	1
U foil	CZD-G (CX)	Tin-plated steel over plastic	1	0.01	6
U metal	SNM-4031	Tin-plated steel over glass	1	0.03	1
U metal button and plates	CZA-93(U-233-4)	Tin-plated steel over glass	1	1.25	5
Oxides and metal pieces and foil	CZA-93(U-233-5)	Welded SST over tin-plated steel	1	1.06	42
U metal	AUA-84 (jar)	Welded SST over unknown	2	0.46	8
U metal	CZA-91	Tin-plated steel over welded SST	1	0.86	42
U metal	KZA-G1B	Welded SST in welded SST	3	0.24	5
U metal	SNM-9514 and LAE-03	Tin-plated steel over unknown	2	0.02	50
U metal	LAW-40	Tin-plated steel over plastic	1	0.52	4
U oxide powder	PZA-126	SST in welded SST	1	0.28	1
U oxide powder	ARF-33 oxide	SST in SST	2	1.21	7
U oxide powder	ASA-94 (233-1,2,3-74)	Tin-plated steel over plastic	3	1.43	7

Table C.6 (continued)

Material form	**Package assembly**[b]	**Package configuration**	**No. of outer packages**	**^{233}U (kg)**	**^{232}U (ppm)**
U oxide powder	ASA-94 (233-4-74)	Tin-plated steel over tin-plated steel	1	0.24	7
UO_2 powder	CZA-92	Welded SST in welded SST	1	2.25	5
U oxide powder	LZB-18	Tin-plated steel over welded SST	3	1.04	7
U oxide microspheres	MM-4899	Tin-plated steel over glass	1	0.13	7
UF_4 powder	CZD-G (CY)	Tin-plated steel over glass	1	0.02	70
Total			1004	425.85	–

[a] As of May 8, 1998. Does not include material being recovered from MSRE.

[b] For some of these package assemblies, an identification or label number is also indicated.

[c] SST = stainless steel.

NOMENCLATURE AND NOTATION

LIST OF CHEMICAL ELEMENTS BY ATOMIC NUMBER (Z)

Z	Symbol	Name	Z	Symbol	Name
1	H	hydrogen	46	Pd	palladium
2	He	helium	47	Ag	silver
3	Li	lithium	48	Cd	cadmium
4	Be	beryllium	49	In	indium
5	B	boron	50	Sn	tin
6	C	carbon	51	Sb	antimony
7	N	nitrogen	52	Te	tellurium
8	O	oxygen	53	I	iodine
9	F	fluorine	54	Xe	xenon
10	Ne	neon	55	Cs	cesium
11	Na	sodium	56	Ba	barium
12	Mg	magnesium	57	La	lanthanum
13	Al	aluminum	58	Ce	cerium
14	Si	silicon	59	Pr	praseodymium
15	P	phosphorus	60	Nd	neodymium
16	S	sulfur	61	Pm	promethium
17	Cl	chlorine	62	Sm	samarium
18	Ar	argon	63	Eu	europium
19	K	potassium	64	Gd	gadolinium
20	Ca	calcium	65	Tb	terbium
21	Sc	scandium	66	Dy	dysprosium
22	Ti	titanium	67	Ho	holmium
23	V	vanadium	68	Er	erbium
24	Cr	chromium	69	Tm	thulium
25	Mn	manganese	70	Yb	ytterbium
26	Fe	iron	71	Lu	lutetium
27	Co	cobalt	72	Hf	hafnium
28	Ni	nickel	73	Ta	tantalum
29	Cu	copper	74	W	tungsten
30	Zn	zinc	75	Re	rhenium
31	Ga	gallium	76	Os	osmium
32	Ge	germanium	77	Ir	iridium
33	As	arsenic	78	Pt	platinum
34	Se	selenium	79	Au	gold
35	Br	bromine	80	Hg	mercury
36	Kr	krypton	81	Tl	thallium
37	Rb	rubidium	82	Pb	lead
38	Sr	strontium	83	Bi	bismuth
39	Y	yttrium	84	Po	polonium
40	Zr	zirconium	85	At	astatine
41	Nb	niobium	86	Rn	radon
42	Mo	molybdenum	87	Fr	francium
43	Tc	technetium	88	Ra	radium
44	Ru	ruthenium	89	Ac	actinium
45	Rh	rhodium	90	Th	thorium

LIST OF CHEMICAL ELEMENTS BY ATOMIC NUMBER (Z) (continued)

Z	Symbol	Name	Z	Symbol	Name
91	Pa	protactinium	101	Md	mendelevium
92	U	uranium	102	No	nobelium
93	Np	neptunium	103	Lr	lawrencium
94	Pu	plutonium	104	Rf	rutherfordium
95	Am	americium	105	Ha	hahnium
96	Cm	curium	106	Sg	seaborgium
97	Bk	berkelium	107	Ns	nielsbohrium
98	Cf	californium	108	Hs	hassium
99	Es	einsteinium	109	Mt	meitnerium
100	Fm	fermium			

RADIOLOGICAL SYMBOLS

α	Alpha particle (He nucleus)	ν	The average number of neutrons produced per nuclide undergoing fission
β	Beta particle (electron)	η	Regeneration factor (the average number of fission neutrons produced per neutron absorbed)
γ	Gamma ray		
n	Neutron		
$t_{½}$	Half-life		

UNITS OF MEASURE

Å	Angstrom	kg/m^3	Kilogram(s) per cubic meter
at. %	Atomic percent	m^2	Square meter(s)
amu	Atomic mass unit	m^3	Cubic meter(s)
b	Barns	mrem/h	Millirem(s) per hour
C	Coulomb	mrem/y	Millirem(s) per year
Ci	Curie(s)	nCi	Nano (10^{-9}) curie
Ci %	Curie (radioactivity) percent	ng	Nano (10^{-9}) gram
cm	Centimeter	nv	Nano (10^{-9}) volt
cm^2	Square centimeters	ppm	Part(s) per million
cm^3	Cubic centimeters	pCi/g	Picocuries(s) per gram
cps/nv	Counts per second per nanovolt	R	Roentgen
d	Day(s)	s	Second(s)
°C	Degree(s) centigrade	scfm	Standard cubic feet per minute
°F	Degree(s) Fahrenheit	t	Metric ton(s) (1000 kg)
°K	Degree(s) Kelvin	vol %	Volume percent
g	Gram(s)	wt %	Weight (or mass) percent
gU/L	Grams of uranium per liter	y	Year(s)
Gy	Gray	μm	Micron (10^{-6} meter)
h	hours	μs	Micro (10^{-6}) second (s)
kg	Kilogram(s)		

GLOSSARY OF TERMS

This glossary gives the definitions of terms commonly associated with ^{233}U material properties, processing, and handling.

Actinides: Elements with atomic numbers from 89 (actinium) or 90 (thorium) to 103 (lawrencium) inclusive.

Alloy: A condensed substance composed of two or more metallic elements formed by melting and intercomponent dissolution when molten.

Alpha decay: Radioactive decay in which an alpha particle (^4He nucleus) is emitted.

Alpha recoil: The backscattering of an atomic nucleus as a result of its emission of an alpha particle. The backscattering of the nucleus is the kinetic energy imparted to it as a consequence of the conservation of momentum.

Amsco™: A commercial high-grade kerosene.

Antibody: A protein produced by immune system cells that combines with a specific antigen and normally facilitates the destruction of that antigen.

Antigen: A complex molecule, normally a protein or polysaccharide, that stimulates production of a specific antibody.

Atomic mass unit: The ratio of a mass of a neutral atom to one-twelfth the mass of an atom of ^{12}C.

Barrier: A confinement that prevents the dispersion of stored material.

Beta decay: Radioactive decay in which a beta particle (negative or positive electron) is emitted.

Branching ratio: In branching radioactive decay, the fraction of nuclei that disintegrates in a specific way. (It is usually expressed as a percentage.)

By-product material: (1) Any radioactive material (except special nuclear material) yielded in, or made radioactive by, exposure to the radiation incident to the process of producing or utilizing special nuclear material. For purposes of determining the applicability of the Resource Conservation and Recovery Act of 1976 to any radioactive waste, the term "any radioactive material" refers only to the actual radionuclides dispersed or suspended in the waste substance. The nonradioactive hazardous waste component of the waste substance will be subject to regulation under the Resource Conservation and Recovery Act; (2) the tailing or waste produced by the extraction or concentration of uranium or thorium from any ore processed primarily for its source material content. Ore bodies depleted by uranium solution extraction operations and which remain underground do not constitute by-product material.

Cloning: The process of producing many identical copies of a gene; also, the production of many genetically identical copies of an organism.

Code of Federal Regulations: A documentation of the general rules by the executive departments of the federal government. The code is divided into 50 titles that represent broad areas subject to federal regulation. Each title is divided into chapters that usually bear the name of the issuing agency. Each chapter is further subdivided into parts covering specific regulatory areas.

Critical mass: The minimum quantity of fissile material capable of sustaining a nuclear fission reaction chain.

Critical organ: The human organ to which the greatest damage is done by the radiation dose delivered by an internal emitter.

Decay, radioactive: The transition of a nucleus from one energy state to a lower one, usually involving the emission of a photon, electron, neutron, or alpha particle.

Decay chain, radioacitve: A series of nuclides in which each member decays to the next member of the chain through radioactive decay until a stable nuclide has been formed.

Decay product: A nuclide formed by the radioactive decay of the parent radionuclide. Formerly called daughter product.

Decommissioning: Activities taken to reduce the potential health and safety impacts of commercial and DOE-contaminated facilities, including removing a unit from operation, decontamination, entombment, dismantlement, or conversion of the site to another use.

Decontamination: Activities taken to remove unwanted (typically radioactive) material from facilities, soils, or equipment by washing, chemical action, mechanical cleaning, or other (treatment) techniques.

Decontamination factor: The ratio of the amount of undesired radioactive material initially present to the amount remaining after a suitable processing step has been completed. Decontamination factors may refer to the reduction of some particular type of radiation, or to the gross measurable radioactivity.

Depleted uranium: Uranium having a weight (mass) percentage of ^{235}U that is lower than the 0.7 wt % found in natural uranium.

DOE Order: A documented set of internal requirements or directives issued by the U.S. Department of Energy (DOE) that establish DOE policy and procedures (including mandatory guidance) for compliance with applicable laws and regulations. DOE orders impose requirements upon DOE personnel and its contractors.

Electron capture: Radioactive decay in which an orbital electron is captured by the nucleus of the radionuclide.

Elute: To remove an adsorbed material from an adsorbent by means of a solvent.

Environmental Impact Statement: A report that documents the information required to evaluate the environmental impact of a project. Such a report informs decision-makers and the public of the reasonable alternatives which would avoid or minimize adverse impacts or enhance the quality of the environment.

Extractant: A substance added to a solvent in order to enhance the extraction process.

Fertile nuclide: A nuclide capable of being transformed into a fissile nuclide by neutron capture.

Fissile nuclide: A nuclide capable of undergoing nuclear fission with thermal neutrons.

Fission, nuclear: The division of a heavy atomic nucleus into two or more isotopes, usually accompanied by the emission of neutrons and gamma radiation.

Fission products: Nuclides produced either by fission or by the subsequent decay of the nuclides thus formed.

Fuel assembly: A grouping of nuclear fuel rods that remains integral during the charging and discharging of a reactor core.

Fuel cycle, nuclear: The complete series of steps involved in supplying fuel for nuclear reactors. It includes mining, refining, UF_6 conversion, enrichment, fabrication of fuel elements, use in a reactor, and management of radioactive waste. It may also involve chemical processing to recover the fissionable material remaining in the spent nuclear fuel, reenrichment of the fuel material, and/or refabrication of new fuel elements.

Half-life, radioactive or physical: For a single radioactive decay process, the time required for the activity to decrease to one-half of its initial value by that process.

Half-life, biological: The time required for the body to eliminate half of an administered dose of a radioactive substance by the regular (natural) processes of elimination. The biological half-life is different for different organs of the body.

Handling enclosure: A glovebox line or similar equipment that isolates uranium-233-bearing materials from the worker's environment while allowing the material to be handled or processed.

Highly-enriched uranium (HEU): Uranium with more than 20 wt% of the ^{235}U isotope, used for making nuclear weapons and also as fuel for some isotope production, research, and power reactors. Weapons-grade uranium is a subset of this group.

Hot cell: A heavily shielded enclosure in which radioactive materials can be handled by persons using remote manipulators and viewing the materials through shielded windows or periscopes.

Hybridoma: A cell produced by fusing an antibody-producing cell with a myeloma (cancerous tumor) cell; used to produce monoclonal antibodies.

Material container: The container that is in contact with the ^{233}U material being stored. This may be either the boundary container, or a container that resides inside of a boundary container. If structurally adequate and sealed, the material container provides one barrier.

Matrix: In waste management, a nonradioactive material used to immobilize radioactive waste in a monolithic structure. Examples of matrices include bitumen, cement, various polymers, etc.

Mixed-oxide fuel: A mixture of two or more actinide oxides serving as a nuclear reactor fuel. Examples include $(Pu, U)O_2$ and $(Th, U)O_2$.

Monoclonal antibody: An antibody produced by the cloning of hybridoma cells, each clone of cells produces a single antibody.

Multiplication factor (k): The ratio of neutron production rate from neutron-induced fission to neutron absorption rate in a base, critical finite system.

Nuclear criticality: A condition that occurs when the number of neutrons released by the fissioning of nuclear material is exactly balanced by the number of neutrons being absorbed by either the material itself or some absorbing medium. **(See also critical mass.)**

Packaging: The assembly of materials and components in compliance with storage/shipment requirements.

Parent: A radionuclide that upon decay yields a specified nuclide (the daughter) either directly or as a later member of a radioactive decay series.

Primary containment vessel: The outer-most sealed container intended for safe storage. When used as the outer-most container for storage, it would also be used for shipping.

Process: To extract, separate, purify, or fabricate a material by physical, chemical, or mechanical means.

Progeny: Radioactive decay products that comprise a particular decay chain.

Purex process: A solvent extraction process that may be used in the reprocessing of spent nuclear fuel for the separation of uranium and plutonium from fission products.

Pyrophoric: Capable of igniting spontaneously when exposed to air.

Quality Assurance (QA): All planned and systematic actions necessary to provide adequate confidence that a structure, system, or component will perform satisfactorily in service.

Quality Control (QC): Those quality assurance activities that provide a means to control and measure the characteristics of a structure, system, or component to established requirements.

Reactor, breeder: A reactor that produces more fissionable fuel than it consumes. The new fissionable material is created by a process (breeding) in which fission neutrons are captured in fertile materials.

Reactor, fast flux: A reactor in which fission is induced predominantly by fast neutrons.

Reactor, high-temperature, gas-cooled: A nuclear reactor that uses an inert gas (helium) as the primary coolant and graphite as the moderator.

Reactor, light-water: A nuclear reactor that uses light water (H_2O) as the primary coolant and moderator and slightly enriched uranium as the fuel. There are two types of commercial light-water reactors: boiling-water and pressurized-water.

Reactor, pressurized-water: A light-water reactor in which heat is transferred from the core to a heat exchanger via water kept under high pressure, so that high temperatures can be maintained in the primary coolant system without boiling the water. Steam is generated in a secondary circuit.

Reactor, production: A reactor whose primary purpose is to produce fissile or other materials or to perform irradiations on an industrial scale. Unless otherwise specified, the term usually refers to either a tritium- or plutonium-production facility used to produce materials for nuclear weapons.

Reactor, research: A reactor whose nuclear radiations are used primarily as a tool for basic or applied research. Typically, it has a thermal power of 10 MW(t) or less and may include facilities for testing reactor materials.

Reactor, test: A reactor associated with an engineering-scale test program conducted to develop basic design information or demonstrate safety characteristics of nuclear reactor systems.

Reprocessing, fuel: The chemical/mechanical processing of irradiated nuclear reactor fuel to remove fission products and recover fissile and fertile material.

Salting agent: A salt [e.g., $Al(NO_3)_3$] or an acid [e.g., $H(NO_3)$] the anion (–) of which is the same as that of solutes.

Sealed: Sealed means that a container has been closed (e.g., welded) and certified to be leak-tight in accordance with ANSI NI4.5-1987 standard.

Separation factor: A dimensionless quantity that measures the degree of physical separation of a material from other materials in an environment or medium.

Solvent extraction: The separation of materials of different chemical types by exploiting the relative chelating ability of different chemicals which preferentially dissolve in one of the two phases. In spent nuclear fuel reprocessing, liquid-liquid contact of two immiscible solvents (one aqueous, one organic) permits recovery and separation of uranium and plutonium in one phase and fission products in the other phase.

Source material: (1) Material containing any combination of uranium or thorium in any physical or chemical form, or (2) ores containing 0.05 wt% or more of uranium, thorium, or both. Source materials excludes special nuclear material (see below).

Sparge: To agitate a liquid by means of compressed air or gas.

Special nuclear material: Plutonium or fissile uranium (i.e., ^{233}U, ^{235}U) enriched to a higher-than-natural assay.

Spent nuclear fuel: Nuclear fuel that has been permanently discharged from a reactor after it has been irradiated. Typically, spent nuclear fuel is measured in terms of either the number of discharged fuel assemblies or the quantity of discharged fuel mass. The latter is measured either in metric tons of heavy metal (i.e., only the heavy-metal content of the spent nuclear fuel is considered) or in metric tons of initial heavy metal (essentially, the initial heavy-metal mass of the fuel before irradiation). The difference between these two quantities is the weight of the fission products produced during irradiation.

Storage: Any method for safely maintaining items in a retrievable form for subsequent use or disposition.

Storage facility: The building structure and other confinement systems that house the storage containers.

Storage package: A configuration of nested containers including package content.

TBP: Tributyl phosphate, also called tri-n-butyl phosphate or phosphoric acid tributyl ester [$(C_4H_9O)_3PO$]. This is an extractant used in liquid-liquid extraction processes to effectively separate Th from U and fission products.

Thermal power: A measure of the rate of heat-energy emission that results from the radioactive decay of a material. A unit of thermal power commonly used is the watt (W).

Thorex process: A solvent extraction process developed to reprocess thorium-based nuclear fuels in which uranium and thorium are separated from fission products.

Transuranic waste: As defined and used by the U.S. Department of Energy (DOE Order 5820.2A), radioactive waste that, at the time of assay, contains more than 100 nCi/g of alpha-emitting isotopes with atomic numbers greater than 92 and half-lives greater than 20 years.

Transuranic waste acceptance criteria: A set of requirements/criteria that must be satisfied prior to transport to and emplacement in the Waste Isolation Pilot Plant for disposal.

Transuranic waste certification: The process for verifying that waste meets the applicable requirements/criteria for transport to and emplacement in a repository for disposal.

Transuranic waste, contact-handled: Transuranic waste with a surface dose rate of less than 200 mrem/h.

Transuranic waste, remote-handled: Transuranic waste with a surface dose rate of greater than 200 mrem/h.

TRISO: A three-layer coating consisting of two layers of pyrolytic graphite separated by a mechanically strong, combustion-resistant layer of silicon carbide.

Ultrasene™: A refined kerosene product used to provide a solvent solution for tributyl phosphate (TBP) in the extraction of Th from U and fission products. Ultrasene is comprised of a mixture of normal, iso-, and cycloparaffins with a very low content of olefins and aromatics.

Waste Isolation Pilot Plant: A facility, located near Carlsbad, New Mexico, to be used for demonstrating the safe disposal of transuranic wastes from DOE defense-related activities.

Yellowcake: A uranium oxide concentrate that results from milling (concentrating) uranium ore. It typically contains 80 to 90 wt % UO_3.