NAS-NRC 2003
p.65
cite

IMPROVING THE SCIENTIFIC BASIS FOR MANAGING DOE'S EXCESS NUCLEAR MATERIALS AND SPENT NUCLEAR FUEL

Committee on Improving the Scientific Basis for Managing Nuclear Materials and Spent Nuclear Fuel through the Environmental Management Science Program

Board on Radioactive Waste Management

Division on Earth and Life Studies

NATIONAL RESEARCH COUNCIL
OF THE NATIONAL ACADEMIES

THE NATIONAL ACADEMIES PRESS
Washington, D.C.
www.nap.edu

Template=SECY-028

SECY-02

COMMITTEE ON IMPROVING THE SCIENTIFIC BASIS FOR MANAGING NUCLEAR MATERIALS AND SPENT NUCLEAR FUEL THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

WM. HOWARD ARNOLD, Chair, Westinghouse Electric Corporation (retired), Coronado, California
GREGORY B. COTTEN, U.S. Naval Academy, Annapolis, Maryland
KATHRYN A. HIGLEY, Oregon State University, Corvallis
LINN W. HOBBS, Massachusetts Institute of Technology, Cambridge
DONALD A. ORTH, E.I. du Pont de Nemours and Company (retired), Aiken, South Carolina
IRVIN OSBORNE-LEE, Prairie View A&M University, Texas
MARK T. PAFFETT, Los Alamos National Laboratory, New Mexico
DALE L. PERRY, Lawrence Berkeley National Laboratory, California
PER F. PETERSON, University of California, Berkeley
STEVEN M. THORNBERG, Sandia National Laboratories, Albuquerque, New Mexico
ROBERT W. YOUNGBLOOD, ISL, Inc., Rockville, Maryland

Board on Radioactive Waste Management Liaison

RODNEY C. EWING, University of Michigan, Ann Arbor

Staff

JOHN R. WILEY, Study Director
DARLA J. THOMPSON, Research Assistant
LAURA D. LLANOS, Senior Project Assistant

BOARD ON RADIOACTIVE WASTE MANAGEMENT

JOHN F. AHEARNE, Chair, Sigma XI and Duke University, Research Triangle Park, North Carolina
CHARLES MCCOMBIE, Vice Chair, Consultant, Gipf-Oberfrick, Switzerland
ROBERT M. BERNERO, U.S. Nuclear Regulatory Commission (retired), Gaithersburg, Maryland
GREGORY R. CHOPPIN, Florida State University, Tallahassee
RODNEY EWING, University of Michigan, Ann Arbor
HOWARD C. KUNREUTHER, University of Pennsylvania, Philadelphia
NIKOLAY LAVEROV, Russian Academy of Sciences, Moscow
MILTON LEVENSON, Bechtel International (retired), Menlo Park, California
JANE C.S. LONG, Mackay School of Mines, University of Nevada, Reno
ALEXANDER MACLACHLAN, E.I. du Pont de Nemours and Company (retired), Wilmington, Delaware
NORINE E. NOONAN, College of Charleston, South Carolina
EUGENE A. ROSA, Washington State University, Pullman
ATSUYUKI SUZUKI, University of Tokyo, Japan
VICTORIA J. TSCHINKEL, The Nature Conservancy, Altamonte Springs, Florida

STAFF

KEVIN D. CROWLEY, Director
MICAH D. LOWENTHAL, Staff Officer
BARBARA PASTINA, Senior Staff Officer
JOHN R. WILEY, Senior Staff Officer
TONI GREENLEAF, Administrative Associate
DARLA J. THOMPSON, Research Assistant
LATRICIA C. BAILEY, Senior Project Assistant
LAURA D. LLANOS, Senior Project Assistant
ANGELA R. TAYLOR, Senior Project Assistant
JAMES YATES, JR., Office Assistant

Contents

Capenhurst, UK; Almelo, Netherlands; and Gronau, Germany. The worldwide inventory of DU is estimated to be about 1.2 million MT (NEA, 2001).

Disposition Options and Challenges

Options for future disposition of the DU, once converted to oxide, are continued storage, reuse, or disposal as waste. There are significant gaps in understanding health effects of uranium and its compounds that need to be resolved before DOE can fully evaluate these options. Beneficial ways to reuse large amounts of uranium have not been identified. Because of uranium's unique chemical and physical properties, the committee believes that this lack of reuse options reflects gaps in current knowledge rather than being an a priori reason for disposing of the material as a waste. There are significant challenges for deciding how the uranium might be disposed if it were declared to be waste.

Potential Health Issues

Surprisingly there are still substantive gaps in knowledge of the non-radiological health impacts of exposure to uranium and its compounds. For example, uranium can cause kidney damage in humans, but information on thresholds and the degree or reversibility of such damage is not available. According to the World Health Organization (WHO), studies in humans performed some 50 years ago cannot be used in quantitative risk estimation because the information on exposure, both qualitatively and quantitatively, is inadequate (WHO, 2001). Recent concerns over health effects of DU used in munitions have led to a resurgence of research in this area (Abu-Qare and Abou-Donia, 2002; McDiarmid et al., 2001; Miller et al., 2002).

Quantitative risk estimates for insoluble uranium have been obtained, albeit with uncertainty. Chemical dose-response and dose-effect relationships have not been investigated to any large degree. The extrapolation of data from animal studies to human response has not been investigated fully and a large degree of conservatism may exist. In fact, there appear to be differences in the sensitivity of different biological species to uranium toxicity, but no general picture has emerged. For humans, only very limited information is available on the inter-individual variation in uranium toxicity.

Reuse

The primary challenges to developing new uses for DU are lack of a scientific understanding of its potential health effects and public concern

NAS/NRC 2003

about its health effects. For example, uranium alloys and compounds are important in some materials applications because of their very high density ($r \sim 20$ g/cm^3). Depleted uranium has been used for shielding radioactivity and in armor-piercing projectiles for this reason.[1] It has also been proposed for counterweights or ballast in aircraft components (e.g., ailerons). However, concerns over the uranium's low-level radioactivity and toxicity have discouraged more widespread utilization.

Finding uses for relatively small quantities of DU will not solve DOE's disposal problem, nor would a use that would simply result in a different disposal problem. A major usage such as high-level waste repository overpacks might provide both a reuse and a disposal route. One proposed large-scale use for depleted uranium is as a component of multipurpose casks for commercial SNF storage, shipment, and disposal—one cask would serve all functions. DU can provide shielding and possibly enhance repository performance. For example, commercial SNF is made of UO_2. If it is surrounded by DUO_2, the DUO_2 can act as a sacrificial material to delay the degradation of the SNF under almost all conditions. The DUO_2 also reduces the potential for criticality in the very long term, after engineered barriers have failed, by isotopic dilution of U-235.

Disposal

The current plans for conversion to oxide will put the DU in a form that will be more stable than the DUF_6 for further storage. If disposal is necessary, it is not likely to be simple. The alpha activity of DU is 200 to 300 nanocuries per gram. Geological disposal is required for transuranic waste with alpha activity above 100 nanocuries per gram. If uranium were a transuranic element, it would require disposal in the Waste Isolation Pilot Plant (WIPP) based on its radioactivity. The chemical toxicity of this very large amount of material would certainly become a problem as well.

One option suggested by the U.S. Nuclear Regulatory Commission (USNRC) is disposal in a mined cavity or former uranium mine (Leeds, 2000). Challenges for this option would include understanding the fundamental differences between uranium ore (see Sidebar 6.1) and the bulk uranium oxide powder.

[1]Munitions fired in Kosovo in 1999 totaled about 9 tons of DU. This has raised new environmental and health concerns (Stone, 2002).

SIDEBAR 6.1 THE ENVIRONMENTAL BEHAVIOR OF URANIUM

Uranium's average natural concentration is approximately 2 ppm in the Earth's upper crust, where it exists in both the uranium(IV) and uranium(VI) oxidation states. Uraninite, UO_2, is the most widespread uranium mineral and the only common one with uranium in the tetravalent form. Pitchblende, UO_2, a major ore of uranium having the same idealized formula as uraninite, always contains some uranium(VI). Thus, a more realistic formula is $(U(IV)_{1-x}U(VI)_x)O2_{+x}$. Natural pitchblendes will have a stoichiometric range of uranium:oxygen from UO_2 to $UO_{2.6}$. Uraninite and pitchblendes vary chemically as a function of whether they are pegmatitic or magmatic uraninite or hydrothermal pitchblende. The first usually exhibits large amounts of rare earths and thorium, while the second does not (Rich et al., 1977). Reduction of the U(VI) can be effected by reducing agents such as sulfides, iron(II), and organic matter. More information regarding the uranium in its ores can be found in many texts and monographs (IAEA 1974, 1976, 1993).

Oxidation of the tetravalent uranium in both the uraninite and pitchblende leads to the introduction of the hexavalent uranium in the form of the uranyl ion, UO_2^{2+}, which can form the basis of an extensive chemistry of its own. In addition to the formation of the ion itself from oxidation, it reacts with many other cations and anions to form other complex molecules. This is attested to by the existence of mixed cation uranyl minerals containing a wide variety of metals ions resulting in minerals such as saleeite ($Mg(UO_2)_2(PO_4)_2$-10(H_2O)), dewindtite ($Pb_3[H(UO_2)_3O_2(PO_4)_2]_2$-12($H_2O$)), and torbernite ($Cu(UO_2)_2(PO_4)_2$-8-12($H_2O$)). Uranium(VI) forms "simple" compounds such as carbonates (i.e., UO_2CO_3). Additionally, the uranyl ion can undergo reactions with many organic compounds to form coordination complexes, including the uranyl ion in conjunction with ammonia, urea, and many oxygen donor molecules. The chemistry of the uranium and its oxides is treated in a number of standard works (Burns and Finch, 1999; Katz et al., 1986; Raran, 1994).

Research Needs and Opportunities

The Environmental Management Science Program (EMSP) should support near-term (1–5-year) research to help ensure safety of the depleted uranium hexafluoride during storage, transportation, and conversion. The EMSP should also support longer-term research that might lead to new, beneficial uses for uranium or that would provide a scientific basis for selecting a disposal option.

Near-Term Research for Managing and Converting the DUF_6

Even though DU is only slightly radioactive, its concentration in large masses in the DUF_6 cylinders produces radiation doses to workers in their vicinity. The radiation levels measured on the outside surface of cylinders are typically about 2 to 3 millirem per hour (mrem/hr)

decreasing to about 1 mrem/hr at a distance of 1 foot.[2] Although the historical dose to cylinder yard workers has been less than 200 mrem/yr, the committee was told during its visit that the cylinder yard is one of the more significant sources of worker doses at the Oak Ridge Reservation (Philpot, 2002).

During its visit, the committee observed that the way the cylinders are stacked restricts the workspace between cylinders and in some cases precludes workers from being able to examine the entire outer surface of each cylinder. Nor is it possible to confidently move and hoist all cylinders because corrosion may have weakened some to the point that they could be damaged by the available handling techniques and equipment (see Figure 6.4). As time passes, more cylinders will fall into this category. If a cylinder is breached the release of UF_6 and its reaction products (e.g., HF), could have serious consequences.

There is need and opportunity for near-term (1–5-year) research that will support DOE's plans for converting its DUF_6 to oxide. Particularly

[2]http://web.ead.anl.gov/uranium/guide/health.

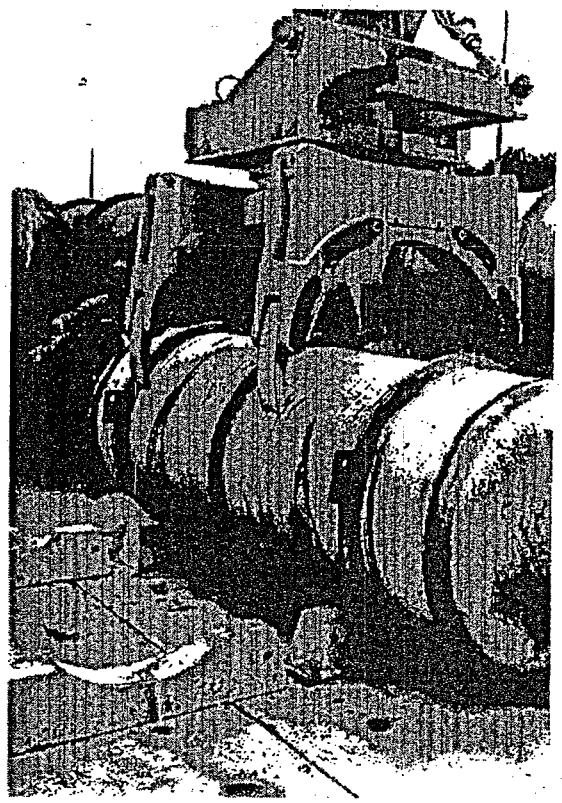

Figure 6.4 Currently available equipment may not be adequate to safely lift severely corroded cylinders. Source: http://web.ead.anl.gov/uranium/guide/.

with emphasis on robotics or remotely operated methods that enhance worker safety, research could lead to new techniques and equipment to

- assess the integrity of DUF_6 cylinders whose exterior surface is partially blocked, and which cannot be handled with confidence;
- extract the DUF_6 from cylinders in the storage yard that cannot be moved to the processing facility, or whose integrity cannot be ascertained; and
- provide field deployable methods to measure contaminants in the DUF_6, which might be important for operator safety or to meet regulatory requirements for transporting or converting the material. For example, some cylinders are contaminated with technetium from recycled uranium.

Longer-Term Research for Reuse or Disposal

WHO has compiled a list of the research needed to better assess chemical and radiological health risks from exposure to uranium compounds.[3] The committee believes that this research will assist DOE in its future decisions for reusing or disposing of its DU:

- Neurotoxicity: Other heavy metals (e.g., lead and mercury) are known neurotoxins, but only a few studies have been conducted on uranium. Studies are needed to determine if DU is neurotoxic. Reproductive and developmental effects have been reported in single animal studies but no studies have been conducted to determine if they can be confirmed or that they occur in humans.
- Hematological effects: Uranium distribution within bone is thought to be such that irradiation of bone marrow and blood-forming cells are limited due to the short range of alpha particles emitted during decay. Research is needed to determine if this view is correct.
- Genotoxicity: Some in vitro studies suggest genotoxic[4] effects occur via the binding of uranium compounds to DNA. Research is needed to determine if uranium is genotoxic by this or other mechanisms.

---

[3]See http://www.who.int/environmental information/radiation/depleted uranium.htm.

[4]Genotoxic refers to materials that are capable of causing damage to genetic material (DNA). DNA damage does not lead inevitably to the creation of cancerous cells, but potentially such damage can lead to the formation of a malignancy.

There are also opportunities to extend current knowledge in the following areas:

- Understanding of the extent, reversibility, and possible existence of thresholds for kidney damage in people exposed to DU. Important information could come from studies of populations exposed to naturally elevated concentrations of uranium in drinking water.
- Better assessments of impacts of exposure of children. This is particularly important given their unique exposure scenarios such as geophagia and hand-to-mouth activities.
- Validation of transfer coefficients for uranium compounds entering the food chain, for example, from soil ingested by livestock during grazing and then to humans.

Investigations are needed on the chemical and physical form, physiological behavior, leaching, and subsequent environmental cycling of specific forms of uranium from various industrial and military sources (e.g., depleted uranium alloys, phosphate by-products). Particular attention should be paid to how the bulk of DU might eventually be disposed.

Aside from the possible presence of contaminants in some of the DU from recycled uranium, the isotope enrichment process leaves a material that initially has a lower radioactivity than natural uranium. Not only U-235 but most of the uranium decay chain isotopes (e.g., radium, radon) are removed. Modeling the long-term behavior of DU should include the fact that these daughter isotopes will gradually reappear over time.

Reuse

Uranium compounds have been used as colorants in ceramic glazes (e.g., "Fiestaware"). DU has been proposed as a diluent for some spent nuclear fuel, to ensure that stored fuel elements do not achieve criticality, and for excess HEU nuclear fuels to render them less attractive as potential weapons material. Uranium silicides are potential fuels, and research into such alloy fuels would be facilitated by the availability of DU for processing and radiation effects stability studies. DU is a candidate fertile material for future breeder reactors. Steel/UO_2 cermets, which were developed as test reactor fuels, are a candidate material for use as gamma-shielding repository containers for spent fuel (Forsberg and Haire, 2002; Haire, 2002). Given its range of chemical valence states and redox potentials, uranium could have important applications in catalysis, optics, and electronics.

Disposal

Returning the DU, as oxide, to former uranium mines is attractive because it does not foreclose recovery and reuse options. The goal of

research directed toward this option should be to understand and hence avoid mechanisms that might lead to rapid migration of uranium from the disposal facility. Research opportunities include the study of the interaction chemistry of uranium and its oxides with reactants that might be found under environmental conditions in a mine or near-surface repository—reactants such as water and carbon dioxide. This can include the identification of reactions to form new uranium phases, in both the U(IV) and U(VI) oxidation states. Some possibilities might be mixed carbonate oxide phases resulting from CO_2 reactions, uranium oxide/metal ion reactions involving other metal ions that are present in a uranium mine setting, and the study of interfacial reactions involving aqueous solutions of metal ions with uranium and its oxides.

These studies can include electronic and magnetic state data, since uranium—under normal environmental conditions—exhibits a $5f^2$ electronic configuration for U(IV) and a $5f^0$ electronic configuration for U(VI). Reactions of importance also encompass chemisorption, reduction/oxidation related to metal ion/uranium ion couplets, and the study of some of these reactions as a function of segregation and diffusion in rock matrices. Saturated aqueous solution studies of uranium oxides with mineral phases that might exist in uranium mine environments are relevant. Oxidation of UO_2 under different chemical conditions is of interest, especially for input into models. Research approaches might ideally combine spectroscopic techniques with microscopy in order to study the chemistry of the uranium system with respect to chemical changes, species, and physical as well as chemical phases.