CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

ORNL-2889
UC-4 Chemistry-General

# NONNUCLEAR USES FOR DEPLETED URANIUM

J. C. Bresee

E. D. Arnold
S. D. Clinton
B. R. Fish
P. A. Haas
J. R. Muir
C. R. Patterson
S. Peterson
C. D. Scott
C. M. West

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price $2.25. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D.C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-2889

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Unit Operations Section

# NONNUCLEAR USES FOR DEPLETED URANIUM


J. C. Bresee

E. D. Arnold
S. D. Clinton
B. R. Fish
P. A. Haas
J. R. Muir
C. R. Patterson (Y-12)
S. Peterson
C. D. Scott
C. M. West (Y-12)



Date Issued

FEB 17 1960



OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

A survey was completed of nonnuclear uses for depleted uranium. Included in the survey was a description of uranium health protection practices and a listing of potential commercial chemical and metallurgical uses for uranium. The nuclear market for depleted uranium was briefly reviewed in order to establish the availability of depleted uranium for nonnuclear purposes. It was concluded that no outstanding use for depleted uranium exists today, but that many potential uses may be uncovered by extensive chemical and metallurgical development programs. The most important present use for depleted uranium hexafluoride is as a source of HF.

CONTENTS


| | | Page |
|---|---|---|
| 1.0 | SUMMARY | 4 |
| 2.0 | INTRODUCTION | 5 |
| | 2.1 Background of the Depleted Uranium Utilization Program | 5 |
| | 2.2 History of Uranium | 7 |
| | 2.3 Future Nuclear Uses for Depleted Uranium | 10 |
| | 2.4 References | 15 |
| 3.0 | DEPLETED URANIUM HEALTH PROTECTION PRACTICES | 16 |
| | 3.1 Hazards | 16 |
| | 3.2 Hazard Control and Evaluation | 21 |
| | 3.3 Typical Industrial Experience | 23 |
| | 3.4 References | 26 |
| 4.0 | NONNUCLEAR USES FOR URANIUM AS A METAL | 29 |
| | 4.1 Properties of Uranium Metal | 29 |
| | 4.2 Uses for Uranium Metal | 35 |
| | 4.3 Uses for Uranium Alloys | 45 |
| | 4.4 References | 49 |
| 5.0 | CHEMICAL USES FOR DEPLETED URANIUM | 52 |
| | 5.1 Utilization of Fluoride Value of Uranium Hexafluoride | 52 |
| | 5.2 Survey of Uranium Compounds | 57 |
| | 5.3 Catalytic Uses of Uranium Compounds | 63 |
| | 5.4 Uranium as a Reducing Agent | 64 |
| | 5.5 Uses of Uranium Compounds Depending on Their High Densities | 65 |
| | 5.6 Uses Depending on Chemical Properties | 67 |
| | 5.7 Uses Depending on Physical Properties | 68 |
| | 5.8 References | 70 |

## 1.0 SUMMARY

The factors controlling the present and future nonnuclear uses of uranium were reviewed. The amount of uranium discharged as gaseous diffusion plant bottoms depleted in U-235 greatly exceeds any anticipated nuclear uses as a source material for at least forty years. Governmental regulation of the use of depleted uranium appears unavoidable because of the monopoly on supply and the health physics hazards.

Radiation and chemical toxicity of depleted uranium appear to be hazards of about equal importance. The hazards are similar to those encountered in many heavy metal industries and do not make remote handling of uranium necessary. The maximum permissible concentrations for air-borne uranium dusts are in excess of 200 $\mu g/m^3$ for depleted uranium compared to 500, 200, and 100 $\mu g/m^3$ for arsenic, lead, and mercury dusts, respectively.

The high atomic weight and density of uranium metal suggest uses for radiation shields, x-ray tube targets, and counterweights. For example, uranium metal provides protection equal to that of lead with 70% less weight for point gamma sources. The use of depleted uranium metal as an alloying metal and as a strong reducing agent appears promising but is not yet of commercial importance.

The most important potential use for depleted $UF_6$ is as a source of fluorine. Several processes under development produce 100% yields of HF containing a variable amount of water, and process improvements can be expected to minimize the dilution. The other product, uranium oxide, has two important commercial uses, as a ceramic pigment and as a refractory. The present use for uranium oxide as a pigment should continue or expand slightly, while present extensive research on the ceramic properties of $UO_2$ (carried on to develop improved reactor fuels) should provide valuable data for a greatly increased use of $UO_2$ as a refractory.

The nonnuclear uses of depleted uranium could be effectively promoted by the following administrative actions of the AEC:

(1) Simplify and explain to the maximum degree practical the licensing requirements and the health physics and safety regulations necessary for the commercial use of depleted uranium.

(2) Make available positive information on the availability of, the requirements and regulations for, and the properties of uranium and uranium compounds.

(3) Encourage and support applied development studies on a limited number of the most promising nonnuclear uses for depleted uranium including: (a) recovery of concentrated HF by conversion of $UF_6$ to uranium oxides; (b) fabrication of uranium metal into special shielding configurations; (c) use of uranium compounds, particularly oxides, as refractories; (d) use of uranium metal for cathodic protection or as a constituent of steels (now under investigation by the U. S. Bureau of Mines).

# 2.0 INTRODUCTION

J. C. Bresee, E. D. Arnold, P. A. Haas

## 2.1 Background of the Depleted Uranium Utilization Program

The purpose of this first phase of a Depleted Uranium Utilization Program was to survey the potential nonnuclear uses for depleted uranium and to describe those uses which might be worthy of further consideration or development. We have chosen to call any use of depleted uranium metal or compounds for other than as fertile nuclear material a "nonnuclear use." This definition is meant to include consideration of depleted uranium as a shielding material for nuclear radiation and other potential uses that might use the natural radioactivity of uranium.

In spite of the obvious long-term attractiveness of using depleted uranium in breeder reactors, the burgeoning stockpile of uranium accumulated yearly as tails from the gaseous diffusion plants shows that there is a place for the consideration of nonnuclear uses for depleted uranium. Since natural uranium is 99.3% U-238 and conversion of more than 1% of the U-238 to Pu-239 by neutron capture may be impractical in a single reactor irradiation cycle, most of the uranium recovered from ore each year ultimately accumulates as a reject stream from reactor operation or from the gaseous diffusion uranium isotope separation process. Some measure of this accumulation rate is given by the domestic production rate of $U_3O_8$, now approximately 15,000 tons/year.[1] Most of this uranium accumulates as raffinate from which it is not economical either to recover U-235 or to use it as a fuel-fertile material in plutonium production reactors of current design. Obviously, this depleted store of uranium, primarily U-238, has long-term value as a fertile material for plutonium production in reactors using plutonium as the fissile material, such as a plutonium recycle or plutonium breeder reactor. But such reactors are now only in the experimental stage and a rapid expansion in this demand for depleted uranium is not likely.

Uranium has not been considered seriously as a material of commerce, other than in the atomic energy program, for almost twenty years; for this reason the problems of radiological safety that would result from any widespread large-scale use of a naturally radioactive material have not been evaluated. As part of this report a summary has been prepared of the restrictions that would have to be used with uranium for safety and the protection of health.

The maximum prewar consumption of uranium for nonnuclear uses was 100 tons/year. Detailed consideration of the probable requirements for depleted uranium in nuclear reactors for the next forty years, presented later in this chapter, shows that less than six years' domestic production should be sufficient for all uses of depleted uranium as a fuel.

It was the intention of the ORNL survey to select and describe potential uses for depleted uranium regardless of size. It was not the intention to prepare a market survey of potential depleted uranium uses. On the contrary, it was the opinion of those taking part in the program that the development of familiarity in American industry with uranium as a commercial chemical was more important than attempts to achieve a unique use for uranium which might consume tens of thousands of tons per year.

AEC Program. The Oak Ridge Operations Office of the U.S. Atomic Energy Commission was assigned the responsibility early in 1959 of conducting a limited program of research and development on uses for depleted uranium. The AEC program was divided into three phases. Research programs were sponsored jointly with the Department of Interior at two experimental stations of the Bureau of Mines (Rolla, Mo. and Boulder City, Nev.), and close liaison was established between the AEC and the Bureau of Mines-sponsored research programs at Albany, Ore. and Laramie, Wyo. A subcontract was negotiated with Battelle Memorial Institute to conduct a market survey on the uses for depleted uranium.[2] This survey was to expand and bring up to date a market survey made two years previously by the Armour Research Foundation of the Illinois Institute of Technology.[3] Finally, the Oak Ridge Operations Office of AEC established the survey program at Oak Ridge National Laboratory.

ORNL Program. The ORNL program was divided into three major areas of review: a survey of the health physics aspects of depleted uranium utilization, a review of the metallurgical uses for depleted uranium, and a careful study of the chemical uses of depleted uranium and uranium compounds, in particular, uranium hexafluoride.

A modest effort went into an attempt to estimate the requirements for depleted uranium in an expanding nuclear power economy between now and the turn of the century. The major responsibility for the depleted uranium program was assigned to the Chemical Technology Division of the Oak Ridge National Laboratory, but major contributions were made to the program by the Health Physics Division of Oak Ridge National Laboratory and the Radiation Safety Department of the Oak Ridge Y-12 Plant.

Acknowledgments. In addition to the authors, the following people made substantial contributions to the assembly of this report: from Argonne National Laboratory, A. Jonke, I. E. Knudsen, N. M. Levitz, and W. A. Rodger; from the Atomic Energy Commission, Oak Ridge Operations Office, G. Rennich, J. W. Ruch, and J. Vanderryn; from the Bureau of Mines, W. Anable and C. Tout of the Albany, Ore. Station, R. V. Lundquist of the Boulder City, Nev. Station, P. L. Cottingham of the Laramie, Wyo. Station, and J. Rowland and D. S. Walsh of the Rolla, Mo. Station; from Mallinckrodt, Weldon Springs, J. A. Fellows, C. W. Kuhlman, W. C. Philoon, and L. G. Weber; from the Paducah Gaseous Diffusion Plant, S. Bernstein, J. C. Gillespie, W. R. Golliher, V. Katzel, R. W. Levin, W. Pedigo, E. W. Powell, and W. Rossmassler; from the Oak Ridge Gaseous Diffusion Plant, D. C. Brater, W. S. Dritt, H. L. Kaufman, C. H. Mahoney, J. H. Pashley, and S. H. Smiley; from Oak Ridge National Laboratory, L. C. Emerson, J. L. Gregg (Consultant), and E. G. Struxness; from the Oak Ridge Y-12 Plant, C. P. Coughlen.

## 2.2 History of Uranium

Uranium is widely distributed in nature, and the estimated abundance of 4 ppm in the earth's crust is greater than for bismuth, silver, mercury, or cadmium. However, it has a comparatively short history due to its complex, difficult chemistry and limited usefulness. Prior to 1942, the industrial requirements for uranium were met as a by-product of mining primarily intended to produce radium and/or vanadium. The principal use was as coloring agents in ceramics with small-scale uses as analytical reagents, electrical resistors, and vacuum tube applications. From his investigation of the mineral pitchblende, Klaproth in 1789 reported the preparation of a new element which he named uranium after the planet Uranus. Reduction of $UO_3$ in a carbon crucible gave him $UO_2$, which he believed to be the elemental material. This misconception persisted for over fifty years, until 1841 when Peligot observed that the yield of "uranium" (actually $UO_2$) and chlorine from anhydrous $UCl_4$ exceeded the weight of the starting salt. He heated anhydrous $UCl_4$ with potassium in a closed platinum crucible (and survived the resulting reaction), and obtained a black, metallic powder after dissolution of the KCl. This is considered the first preparation of uranium metal. Although atomic weights of 120 had been reported for uranium, Mendeléeff correctly positioned it in his periodic chart as the heaviest known element, with an atomic weight of about 240.

a. Preparation of Important Compounds. The reactions that give the important compounds were reported very early in the history of uranium, although the compositions and mechanisms were not always accurately known. Observations for many compounds, particularly the oxides, chlorides, sulfates, oxalates, and nitrates, were reported between 1789 and 1842 in a confused manner because of the belief that $UO_2$ was an element. In 1842 Peligot[4] gave an accurate report on the appearance and reactions of a number of uranium compounds, including $UO_2(NO_3)_2 \cdot 6H_2O$, $UO_2C_2O_4 \cdot 3H_2O$, $UCl_3$, $UO_2$, $U_3O_8$, $U(SO_4)_2 \cdot 8H_2O$, $UO_2Cl_2$, and $Na_2UO_4$.

The chemistry of uranium and fluorine compounds with the exception of $UF_6$ was extensively reported, confirmed, extended, and documented prior to the discovery of natural radioactivity. Early studies were described by Bolton in 1866.[5] The preparation of $UF_6$ was an exception to the above in that its preparation was first clearly reported by Ruff and others in 1909-1910[6] and little was known about $UF_6$ prior to 1940.

The chemistry of uranium and its compounds was completely re-examined, extended, and confirmed as part of the World War II development of the atomic bomb and postwar development of nuclear technology. This is apparent in the rarity of pre-1940 references in present books on uranium chemistry.[7,8]

b. Preparation of Metal. Peligot's first preparation of uranium metal in 1841 was basically the process used today—by the reaction of anhydrous $UCl_4$ with potassium metal in a nonreactive container. The preparation

of uranium powder by reduction of halides with active metals was extensively investigated, and the process developed during the early days of the Manhattan Project for bomb reduction with magnesium has since been scaled up to the present metal production plants.[9]

All the principal methods for producing uranium metals start with an oxide or halide salt, which is reduced chemically with carbon or an alkaline or alkaline earth metal, reduced electrolytically, or decomposed thermally. Of the eight possible combinations of feed salt and reducing mechanism, reduction of halide salts with carbon, electrolysis of uranium oxide, and thermal decomposition of oxides are not technically feasible. The reduction of a halide salt with active metals (Sec. 4.0) became the preferred production method because it gave a high-purity massive uranium product from $UF_4$ in one simple step. Thermal decomposition of a halide as applied by van Arkel for $UI_4$ does not scale up to low-cost, large-scale production.

Lack of product purity was a major limitation of pre-1940 uranium reduction procedures. Reduction of uranium oxides with carbon requires extremely high temperatures and was reported by Moissan who used electric arc furnaces. This procedure has recently been described as used to prepare uranium metal for steel alloys about 1920;[10] avoiding appreciable amounts of uranium carbide appears difficult. Uranium metal powders were prepared by several methods: (1) reduction of uranium oxides with calcium, magnesium, or aluminum; (2) reduction of uranium halides with sodium, potassium, calcium, magnesium, or aluminum; and (3) electrolysis of fused halide salts containing uranium halides. The difficulty of consolidating the metal powder into a high-purity product made these processes noncompetitive as production procedures.

c. Discovery of Radioactivity. The discovery of natural radioactivity started with observations by Henri Becquerel on the darkening of photographic plates and the discharge of electroscopes by uranium compounds. These studies were continued by the Curies to the discoveries of polonium, radium, radon, and the existence of radioactive decay chains. The names of the contributors to knowledge on radioactivity during 1900 to 1920 are almost a roll call of the noted scientists of this period. The changes in atomic number as a result of alpha and beta emissions were noted and formulated into rules by several investigators as early as 1913. The interest in natural radioactivity and its unusual properties compared to the chemical properties of elements resulted in studies of atomic physics.

d. Discovery of Fission. The observation of the natural radioactivity of uranium by Becquerel in 1896 was followed by a crescendo of interest in an active study of the internal structure of atoms. Fifty years later, a climax was reached in the use of nuclear weapons in World War II. The history connecting these two events is one of the most fascinating examples of the progress of science.

The model proposed by Rutherford in 1911 for the nuclei of atoms and the demonstration of the existence of neutrons as proposed by Chadwick were two important milestones leading to the discovery of nuclear fission. Rutherford's model was an explanation of radioactive decay chains and led to the idea of particle bombardment to produce nuclear transformations. The discovery of neutrons explained the existence of isotopes and provided a new type of projectile for causing nuclear transformations.

Fermi and his coworkers irradiated uranium with neutrons as part of studies which included irradiations of practically all the known elements. The lighter elements produced radioactive materials which decayed to elements of one or two higher or lower atomic numbers. Therefore the radioactive products of uranium irradiations were assumed to be isotopes of elements 93, 94, or 91. Since the chemical properties of these elements were not known and only a few thousand atoms of the radioactive products were produced, the identifications were difficult to prove or disprove. Meitner and Hahn were able to show by chemical separations that a "13-minute" product was not protactinum, uranium, thorium, or actinium. Meanwhile, uranium irradiation products of other half-lives were found. Finally, Hahn, Meitner, and Strassmann were forced to the then remarkable conclusion that they had radioactive barium by the fact that they could make chemical separations of all the natural radioisotopes from barium, but they could not separate this irradiation product from barium. The publication of the existence of fission processes explained and released a flood of information; a bibliography on nuclear fission one year later totaled over 100 publications.

e. Regulations and Federal Control. The history of uranium in the United States since 1942 has been one of complete federal regulation and control. The primary justification has been its importance as a military material. A secondary justification has been the health and radiation hazards (Sec. 3.0). Today the Atomic Energy Commission has a supply of depleted uranium as a by-product which completely overwhelms any probable immediate demand. Therefore nonnuclear uses of uranium will remain federally regulated because of the public welfare and monopoly supply situations involved.

Depleted uranium would be a source material as defined and regulated by the Atomic Energy Act of 1946[11] and succeeding amendments and revisions. The history of these acts and the presently effective Atomic Energy Act of 1954 as amended have been published.[12] The AEC is authorized to issue commercial licenses by Sec. 103B of the 1954 Act reading as follows: "The Commission shall issue such licenses on a nonexclusive basis to persons applying therefor (1) whose proposed activities will serve a useful purpose proportionate to the quantities of special nuclear material or source material to be utilized; (2) who are equipped to observe and who agree to observe such safety standards to protect health and to minimize danger to life and property as the Commission may by rule establish; and (3) who agree to make available to the Commission such technical information and data concerning activities under such licenses as the Commission may determine necessary to promote the

common defense and security and to protect the health and safety of the public. All such information may be used by the Commission only for the purposes of the common defense and security and to protect the health and safety of the public." The restrictions and regulations found necessary for implementing the above and other sections of the Atomic Energy Act are discussed in more detail in Sec. 3.0.

## 2.3 Future Nuclear Uses for Depleted Uranium

a. Role of U-238 in Nuclear Reactors. The primary use of U-238 in a nuclear reactor is as a "target" for neutron captures in order to produce plutonium. This production scheme is

$$\text{U-238} + n \longrightarrow \text{U-239} \xrightarrow[23.5\ m]{\beta} \text{Np-239} \xrightarrow[2.33\ d]{\beta} \text{Pu-239}$$

The first nuclear reactors used natural uranium of which isotope 238 constitutes 99.28%. These reactors are loaded so that a nuclear chain reaction is maintained. Neutrons which are not needed to maintain the chain reaction, are not absorbed by structural material, coolant, or moderator, or do not leak out are absorbed by the U-238.

If more Pu-239 is produced than U-235 or other fissile material is consumed, the reactor is a breeder; if more fissile material is consumed than Pu-239 is produced, the reactor is a converter and the conversion ratio is less than 1. The first reactors were thermal reactors using natural uranium and are classed as converters.

The only type of nuclear reactor using U-238 that will breed is the fast reactor. Here ~ 2.9 neutrons are produced per fission of Pu-239 and ~ 2.5 neutrons per fission of U-235. In a fast reactor the ratio of capture for fissile materials is much lower than it is in thermal reactors. Also, the number of neutrons lost to structural materials is less for the fast reactor. Thus of the original 2.9 or 2.5 neutrons per fission approximately 1.5 or 1.2 neutrons are available for absorption in U-238.

One big nuclear advantage of U-238 over Th-232 is the fast effect. Uranium-238 is fissionable with fast neutrons to a greater extent than Th-232. Thus there is a net gain of neutron production in both thermal and fast reactors using U-238. This fast effect accounts for approximately 3% of the total neutron production rate in a thermal reactor and for 10-20% of the total neutron production in a fast reactor.

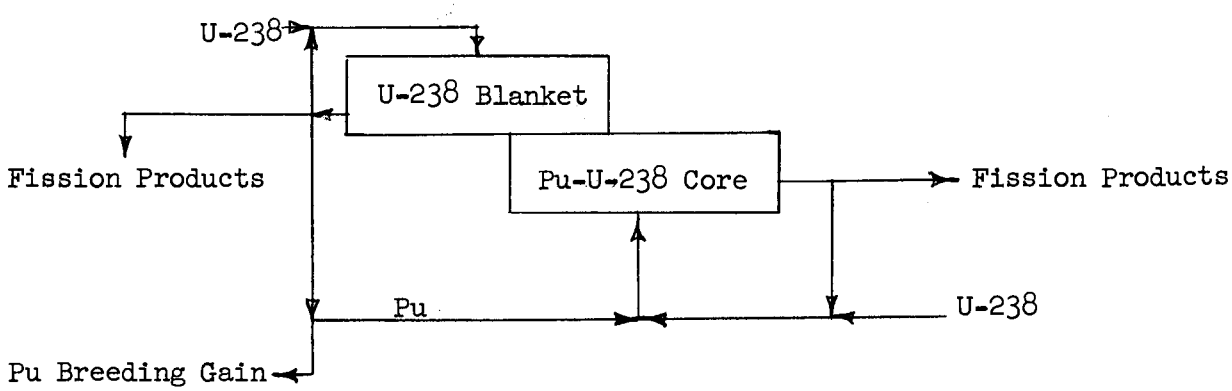
b. Use of Depleted Uranium as a Reactor Blanket or Core Diluent. Depleted uranium can best be used as the blanket material for a fast reactor or as a diluent for plutonium in the core of a fast reactor. It is very unlikely that depleted uranium will be used as the blanket of a heterogeneous thermal reactor. However, depleted uranium as uranyl sulfate has

been considered for the blanket of a dual purpose homogeneous reactor designed for the production of low Pu-240 content plutonium. As far as fast reactors are concerned, depleted uranium uses are:

1. As a core diluent: Fast reactor cores operate best with a U-238 to fissile material ratio of at least 3 to 1. This consideration is based on such nuclear properties as Doppler temperature coefficients (positive for fissile material, negative for U-238) and internal conversion ratios. A fast reactor core containing 6.67 kg of U-238 per kilogram of Pu-239 would have a negative net Doppler temperature coefficient and an internal conversion ratio of ~ 0.6. In other words, 0.6 atom of new Pu-239 will be produced in the core for each atom of Pu-239 burned in the core. The expected specific power for fast reactor cores should be 0.5-2.0 $Mw_t$ per kilogram of plutonium or 13.3-3.3 kg of U-238 per thermal megawatt.

2. As a fast reactor blanket: Fast reactor blankets would require 50-75 kg of U-238 per kilogram of plutonium as loaded in the core. Thus the expected specific power based on U-238 should be 6.7-40 $Mw_t$ per ton of U-238. The conversion ratio for the blanket would be ~ 0.9 atom of new Pu-239 formed in the blanket per atom of Pu-239 burned in the core. Thus the total conversion ratio (core + blanket) would be ~ 1.5 atoms of new Pu-239 formed per atom of Pu-239 burned in the core.

c. Recycle of Depleted Uranium in Entire Reactor Complex. Depleted uranium can be fed to a reactor complex in several possible ways. Probably the most economical method is to feed it to the blanket and core of a two-region plutonium fast breeder as follows:




A single-region fast reactor would decrease the complexity of the flowsheet but would also decrease the breeding gain and increase the size of the system.

The core is processed for fission product purging, and the blanket is processed to separate the plutonium gained by breeding, which is used in another reactor. Enough plutonium is also sent from the blanket to the core to make up for plutonium burned in the core. Makeup U-238 to the blanket and core is required to replace burnup and losses.

If the function of the blanket is primarily to make plutonium and power production is secondary, depleted uranium is preferred to higher priced normal uranium. With depleted uranium, for a given plutonium production per unit weight of uranium, less fission will have occurred in the blanket to cause fuel damage. Because of the lower heat generation rate, thicker sections and/or less coolant can be used with depleted uranium. In power production economics natural uranium competes with depleted uranium for use in the blanket because of its higher burnup rate. The choice is a function of the price difference between natural and depleted uranium.

In a similar way depleted uranium could be fed to a thermal reactor as a blanket for an enriched core or as a single-region system after enrichment with a fissile material, for example, the breeding-gain plutonium of a fast reactor. Again, there is economic competition with natural uranium either directly or after some diffusion plant enrichment. In the thermal reactor there is no clear cost advantage for fueling with low-cost depleted uranium and fissile material worth $12 to $17 per gram over fueling with natural or slightly enriched uranium worth $5 to $12 per gram (including the associated fertile material).

If the price of natural uranium increases markedly, the competitive position of depleted uranium will probably improve, since the cost of enriched U-235 increases less than linearly with normal use cost for constant cost of separation work. This statement assumes that the plutonium price will vary linearly with the U-235 price, and neglects the possible cost-reducing influence on enriched uranium if depleted uranium is saleable.

d. Requirements for Depleted Uranium in an Expanding Nuclear Economy. If it is assumed that the nuclear power industry expands at a rate indicated by the heavy line of Fig. 2.1, a total depleted uranium supply of 150,000 to 1,529,000 tons, depending on the reactor type, would fill the entire needs for the nuclear power industry until AD 2000 if fast reactors produced all the nuclear electricity. Assuming reactor type 2 or 3 as given in Table 2.2* the most probable requirement for U-238 by 2000 would be 72,000 tons. In this case fast reactors produce 25% of the total electrical requirements and operate at 1.5 $Mw_t$ per kilogram of plutonium in the core. The total requirement for U-238 for the next forty years could be supplied by the depleted uranium available from domestic uranium production in approximately six years at the current production rate of 15,000 tons of $U_3O_8$ per year.

The total requirements for raw materials up to AD 2000 for fast reactors supplying 100% of the total nuclear electricity are given in Tables 2.1-2.3. These tables list the reactor characteristics and the fissile and fertile material requirements.

---

*Nomenclature: R = inventory ratio = $\frac{\text{total fuel inventory}}{\text{inventory in reactor}}$; E = thermal efficiency; S = specific power, $Mw_t$/kg fissile material; C = conversion ratio.

UNCLASSIFIED
ORNL-LR-DWG 35030R

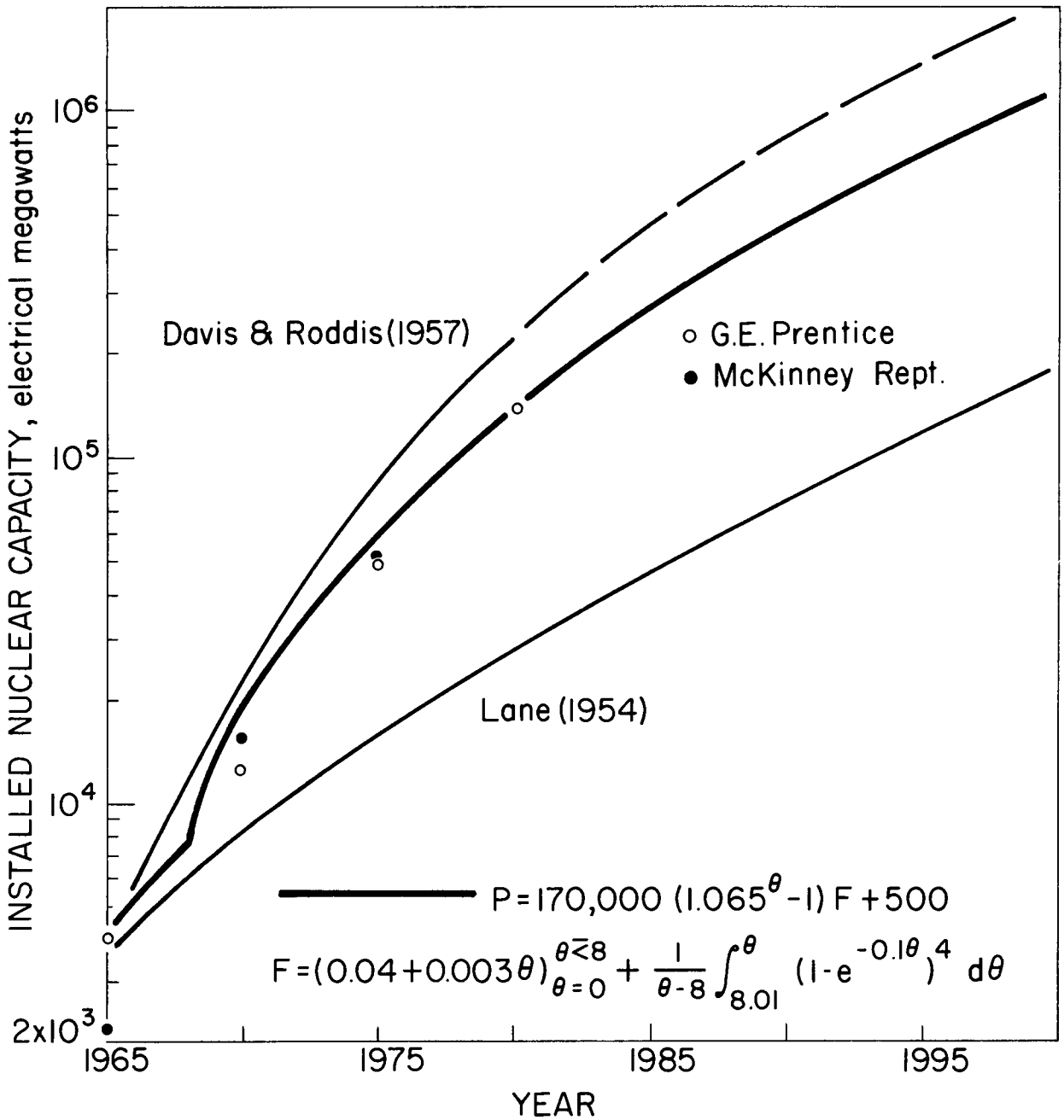



Fig. 2.1. Buildup curves for growth of nuclear power in the United States. For 1960 $\theta = 0$ (see references 13 - 15).

2.1 Net Raw Materials Required by AD 2000 to Supply Fissile Material to Various Reactor Types

| Fast Reactor Type[a] | R | S, Mw/kg fissile | R/SE[b] | C | Doubling Time, years | U-235, tons | Natural U, tons |
|---|---|---|---|---|---|---|---|
| 1 | 3 | 0.5 | 17.15 | 1.85 | 20 | 13,800 | 1,934,000 |
| 2 | 2.5 | 1.5 | 4.76 | 1.60 | 8 | -1,650 (362[c]) | -231,000 (50,700[c]) |
| 3 | 2.5 | 1.5 | 4.76 | 1.45 | 10.6 | 612 (890[c]) | 85,700 (125,000[c]) |
| 4 | 2.5 | 2.0 | 3.57 | 1.45 | 8 | -1,238 (272[c]) | -173,300 (38,100[c]) |
| 5 | 1.75 | 2.0 | 2.50 | 1.25 | 10 | 114 (385[c]) | 16,000 (54,000[c]) |

[a]E = 0.35. [b]R'/S'E for breeders. [c]Peak value.

Table 2.2 Net Raw Materials Required by AD 2000 to Supply Fertile Material to Various Reactor Types

| Fast Reactor Type | R | S, Mw/kg fissile | Fertile/Fissile | Mw Reactor Heat/ton Fertile | Depleted U Req'd, tons |
|---|---|---|---|---|---|
| 1 | 3.0 | 0.5 | 75 | 6.7 | 1,529,000 |
| 2 | 2.5 | 1.5 | 50 | 30 | 285,000 |
| 3 | 2.5 | 1.5 | 50 | 30 | 285,000 |
| 4 | 2.5 | 2.0 | 50 | 40 | 213,000 |
| 5 | 1.75 | 2.0 | 50 | 40 | 150,000 |

Table 2.3 Total Raw Materials Required by AD 2000 to Supply Various Reactor Types

| Fast Reactor Type | Natural U Required, tons: For Fertile | Natural U Required, tons: For Fissile | Total Raw Materials, tons |
|---|---|---|---|
| 1 | 1,529,000 | 1,934,000 | 1,934,000[a] |
| 2 | 285,000 | 50,700 | 285,000[b] |
| 3 | 285,000 | 125,000 | 285,000[b] |
| 4 | 213,000 | 38,100 | 213,000[b] |
| 5 | 150,000 | 53,900 | 150,000[b] |

[a]Fertile material used supplied at same time and from same source as fissile.

[b]Fertile material determines total natural U requirements since fissile material production rate (at some date prior to AD 2000) is greater than the fissile inventory addition rate. (Turnover point of fissile requirement curve reached before AD 2000.)

## 2.4 References


1. U.S.A.E.C. 25th Semiannual Report to the Congress (July-Dec., 1958), "Atomic Industrial Progress and Second World Conference," p 5.

2. H. W. Nelson and R. L. Carmichael, "Survey of Potential Industrial Uses and Markets for Depleted Uranium," BMI-1362 (July 16, 1959).

3. Armour Research Foundation of Illinois Institute of Technology, "Market Study and Development of a Pricing Plan for Depleted Uranium," Final Report, ARF Project P 014 (Aug. 1, 1957).

4. E. Peligot, "Research on Uranium," Ann. 43: 255-86 (1842).

5. H. C. Bolton, "On the Fluorine Compounds of Uranium," Dissertation, Univ. of Göttingen (1866); also Bull. soc. chim. France, (2)6:450-2 (1866).

6. O. Ruff and A. Heinzelmann, "Uranium Hexafluoride," Z. anorg. Chem. 72: 63-84 (1909).

7. J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," National Nuclear Energy Series, Div. VIII, Vol. 5, McGraw-Hill Book Co., Inc., New York, 1951.

8. J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons Inc., New York, 1957.

9. H. A. Wilhelm, "The Preparation of Uranium Metal by the Reduction of Uranium Tetrafluoride with Magnesium," P/817, Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva 1955, 8:162 (1956), UN, New York.

10. C. T. Patterson, "The First Ferro-Uranium Made in America," Metal Prog., 71(6): 85-9 (1957).

11. Atomic Energy Act of 1946 and Succeeding Amendments and Revisions.

12. Public Law 585, 79th Congress, 60 stat. 755-75; 42 U.S.C. 1801-1819.

13. R. McKinney, "Report of the Panel on the Impact of the Peaceful Uses of Atomic Energy to the Joint Committee on Atomic Energy," Vol. 2, pp 27, 117-118, U.S. Gov. Printing Office, Washington, 1956.

14. W. K. Davis and L. H. Roddis, Jr., "A Projection of Nuclear Power Costs," 5th Annual Conference Atomic Energy in Industry (1957), National Industrial Conference Board, Inc., New York.

15. J. A. Lane, Nucleonics 12 (10): 65 (1954).

## 3.0 DEPLETED URANIUM HEALTH PROTECTION PRACTICES

C. R. Patterson, Y-12, C. M. West, Y-12, B. R. Fish, J. R. Muir

Uranium compounds were known to be toxic to humans long before the radioactive properties of the element were discovered. Reports dating back to the 1860's describe the use of uranium as a nephrotoxic agent in studies of kidney function. In the ensuing years a considerable body of literature has accumulated, representing studies of the various aspects of uranium toxicity.[1] The health hazards associated with processing of large quantities of uranium were poorly understood in the early days of the Manhattan Project. Beginning in 1943, a great effort was put forth to assess the toxic effects of many compounds of uranium on a broad spectrum of animal species. The greater portion of this research was carried on at the University of Rochester,[2] N. Y., where considerable emphasis was placed on effects after inhalation. Another group at Michael Reese Hospital,[3] Chicago, Ill., concentrated on the toxicology of uranium compounds after ingestion or injection. More recently a cooperative study of uranium distribution and excretion was conducted by the Health Physics Department of Union Carbide Nuclear Company's Y-12 Plant and Dr. W. H. Sweet of the Massachusetts General Hospital,[4,5] Boston, Mass.

### 3.1 Hazards

Uranium presents a twofold hazard: first, from its chemical toxicity; and second, from the ionizing alpha, beta, and gamma radiation emitted in the process of radioactive decay. The ionizing radiations are hazardous when small amounts of uranium are taken into the body or when relatively large amounts are present in close proximity to the body. However, the chemical properties of uranium present a hazard only after it is absorbed into the blood stream. Fortunately, uranium is absorbed to a very limited extent through unbroken skin or the gastrointestinal tract, and its specific activity is quite low in comparison with most other radioactive elements. Harmful exposures to either hazard can be prevented by careful handling techniques and common sense.

a. External. The isotopes of uranium found in normal or depleted mixtures emit alpha particles accompanied by very low energy gamma radiation in the process of radioactive decay. The alpha radiation presents no hazard unless the uranium gets into the body. The gamma radiation is of such low energy that it constitutes no hazard except to parts of the body in contact with large quantities of uranium for extended periods of time. After chemical refining the beta particle emissions of $UX_1$ and $UX_2$ ($_{90}Th^{234}$ and $_{91}Pa^{234}$), the first two daughters of $_{92}U^{238}$, make up nearly all the penetrating radiation associated with either normal or depleted uranium.

The radiation dose rate at the surface of a uranium metal slab has been measured.[6,7] The 2.32-Mev $\beta^-$ from $_{91}Pa^{234}$ contributes 240 mrem/hr and the 0.1- or 0.2-Mev $\beta^-$ from $_{90}Th^{234}$ adds another 20 mrem/hr. The gamma rays are all quite soft and add only 2.7 mrem/hr, to make a total of

approximately 263 mrem/hr at the surface of a bare metal slab.[6] The beta ray surface dose rate for uranium and some of its compounds is given in Table 3.1. It should be noted that some operations, such as the casting

Table 3.1 Beta Radiation Surface Dose Rate[7]

| | mrem/hr | | mrem/hr |
|---|---|---|---|
| U metal | 239 | $UO_3$ (orange oxide) | 208 |
| $UO_2$ (brown oxide) | 212 | $U_3O_8$ (black oxide) | 207 |
| $UF_4$ (green salt) | 183 | $UO_2F_2$ (cliptite or uranyl fluoride) | 181 |
| $UO_2(NO_3)_2 \cdot 6H_2O$ (yellow uranyl nitrate hexahydrate) | 114 | $Na_2U_2O_7$ (soda salt or sodium diuranate) | 171 |

of molten uranium, result in migration of the $UX_1$ and $UX_2$ daughters to the surface of the casting. The concentration of these beta emitters on the interior surfaces of molds and crucibles, on the exterior surfaces of castings, and in the slag gives rise to much higher radiation dose rates than are listed above. This is likely to be a problem only when working with rather large castings. These surface deposits can be removed quickly and easily by nitric acid pickling. The radiation from the treated metal then will be essentially as given in Table 3.1.

One possible use for compounds of depleted uranium is as a constituent of ceramic glaze. Uranium enhances the color of the glaze when it is present in concentrations of a few per cent, whereas in higher percentages it seems to have a detrimental effect on the color. Dose rate measurements were made by the Instrument Assays Group, ORNL Health Physics Division, on a series of tile samples containing different proportions of uranium in the glaze. The dose rate at 1 in. ranged from 0.5 mrem/hr for an attractively colored tile containing 4% uranium, up to 2.6 mrem/hr for a muddy colored tile containing 20% uranium. These dose rates could result in an individual receiving 84 mrem and 436 mrem, respectively, in seven consecutive days of close proximity to a wall tiled with this material. Section 20.102b.2 of the Federal Regulations[8] prohibits the licensee from creating in an unrestricted area a radiation level that could result in an individual receiving over 100 mrem in seven days. Thus it is seen that the use of ceramic materials bearing low concentrations of depleted uranium is permissible under existing federal regulations. However, considerable caution should be exercised to ensure that glazes containing large amounts of uranium will not be released to uncontrolled use.

b. Internal. Uranium can gain access to the body by way of injection, ingestion, or inhalation. Absorption through unbroken skin is negligible; absorption via injection is likely to occur only in such cases as contamination of open wounds; and absorption via ingestion[9] is approximately 1% of intake. Inhalation of uranium compounds is the significant mode of entry. Once in the body, uranium can cause damage by radiation and by chemical toxicity.

c. Chemical Toxicity. Uranium is one of the most toxic elements. Once uranium enters the blood stream in a chemically active form, its toxicity is comparable to that of arsenic, lead, or mercury. Fortunately, the dusts most likely to be encountered in industrial processing of uranium are relatively insoluble and so inert physiologically that they are considered as radiological hazards rather than toxic chemicals. These are deposited primarily in the respiratory system, from which they are mobilized slowly. The more soluble compounds of uranium are quickly taken into the blood stream via lungs or contaminated wounds and may result in significant deposits of $UO_2^{++}$ in the kidney. There some of the uranium combines with the protein of cell walls, poisoning the cells and interfering with the vital functions of waste elimination and maintenance of electrolyte balance. The uranium does not remain fixed in the kidney, but is eliminated at the rate of about half every two weeks. Moderately severe damage to the kidney as a result of acute exposure is reparable, and a return toward normal kidney function may occur even during continued exposure.

It has been pointed out that inhalation is the most likely avenue by which uranium compounds may enter the body. It is interesting, therefore, to compare the permissible limits for air-borne uranium dusts with those for three other well-known toxic metals. The maximum permissible concentration, $(MPC)_a$, recommended in National Bureau of Standards Handbook 69[10] for soluble uranium of either normal isotopic distribution or completely depleted (pure U-238) is equivalent to about 210 $\mu g/m^3$. The threshold limits recommended by industrial hygienists[11] for arsenic, lead, or mercury dusts are 500, 200, and 100 $\mu g/m^3$, respectively.

The MPC's[8,10,12] of radioactive materials are stated in units of radioactivity permitted in a given volume of air or water. This is true for depleted uranium whether the hazard is chemical or radiological. These units are used because counting the alpha activity of collected dust samples is the simplest means of measuring air-borne uranium concentrations. Conversion from microcuries to mass units requires a knowledge of the radioactivity per gram of the particular mixture of uranium isotopes in question.*

---

*It should be noted that the internal dose handbooks[10,12] define a special "curie" for the specific case of natural uranium: $7.49 \times 10^{10}$ disintegrations per second represents 1 curie. However, in order to avoid the use of ambiguous units, the curie is considered to correspond to $3.7 \times 10^{10}$ disintegrations per second for any isotopic mixture discussed in this report.

Chemical toxicity depends primarily on the mass of uranium absorbed and not on the mixture of isotopes. In Fig. 3.1 the amount of radioactivity, in microcuries per cubic centimeter of air, equivalent to approximately 210 μg of uranium per cubic meter, is plotted as a function of the per cent by weight of U-235 in the mixture, the customary way to express degree of depletion. It was assumed that the uranium was depleted by means of the gaseous diffusion process.

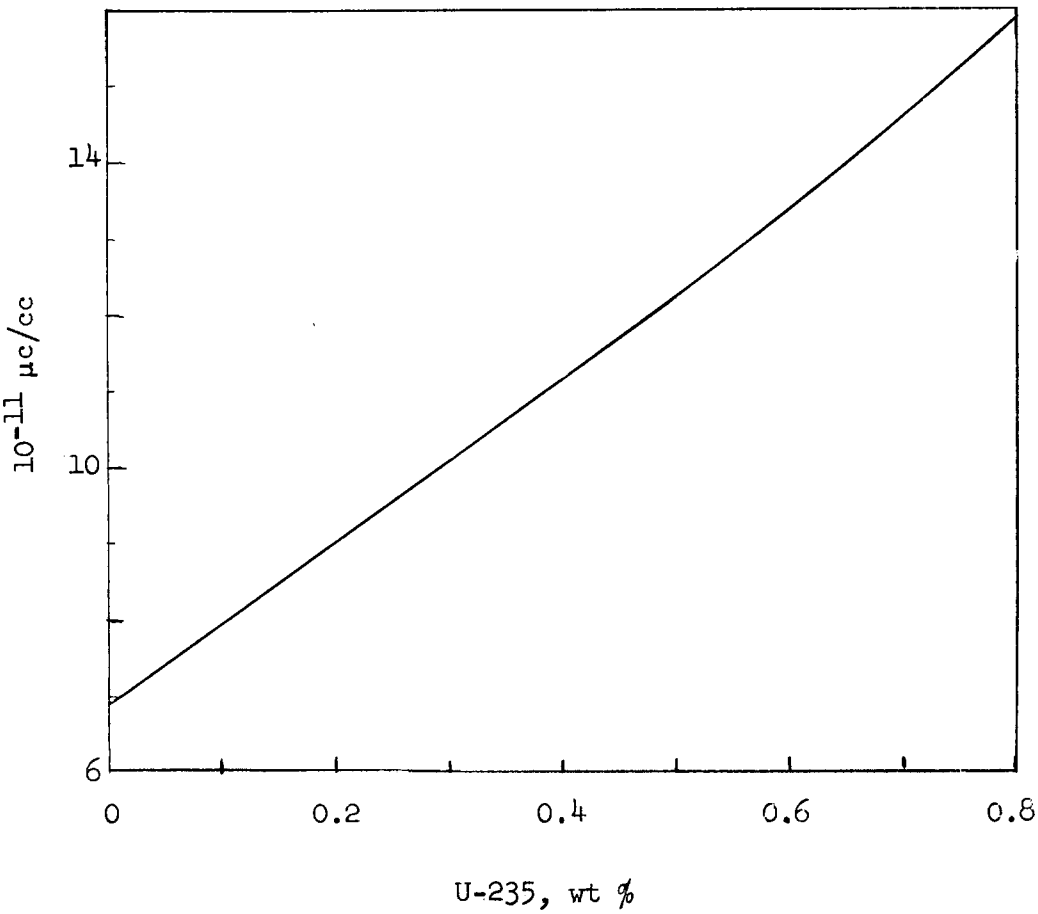



Fig. 3.1. Radioactivity equivalent of 210 μg/m$^3$ with increasing U-235 content.*

*See footnote on page 18.

d. Radiation Hazards. The principal radiation hazard from internal deposits of uranium is the intense ionization in tissue produced by the alpha particles emitted during radioactive decay. The more than 4,000,000 ev energy of the alpha particles is absorbed in the first 0.1 mm of tissue, resulting in localized cellular damage. On the other hand, gamma rays and beta particles dissipate their energies in relatively larger volumes of tissue and produce comparatively little damage.

Many industrial uranium dusts are relatively insoluble and are deposited primarily in the respiratory system. A "fixed" deposit of uranium in the lung is eliminated at the rate of about half every 120 days. One of the premises on which the MPC's of radioactive isotopes are established is that no damage that can be attributed to the radioactivity of the isotope should be evident even after continuous intake at the MPC level for periods up to a working lifetime (50 years). In the case of insoluble compounds of uranium, the MPC is established on the basis of the radioactivity; hence, the equivalent permissible weight of uranium per cubic meter varies with the relative abundance of each isotope. A plot relating the permissible weight concentration to the relative amount of U-235 is shown in Fig. 3.2. It is seen that the MPC for insoluble uranium would be

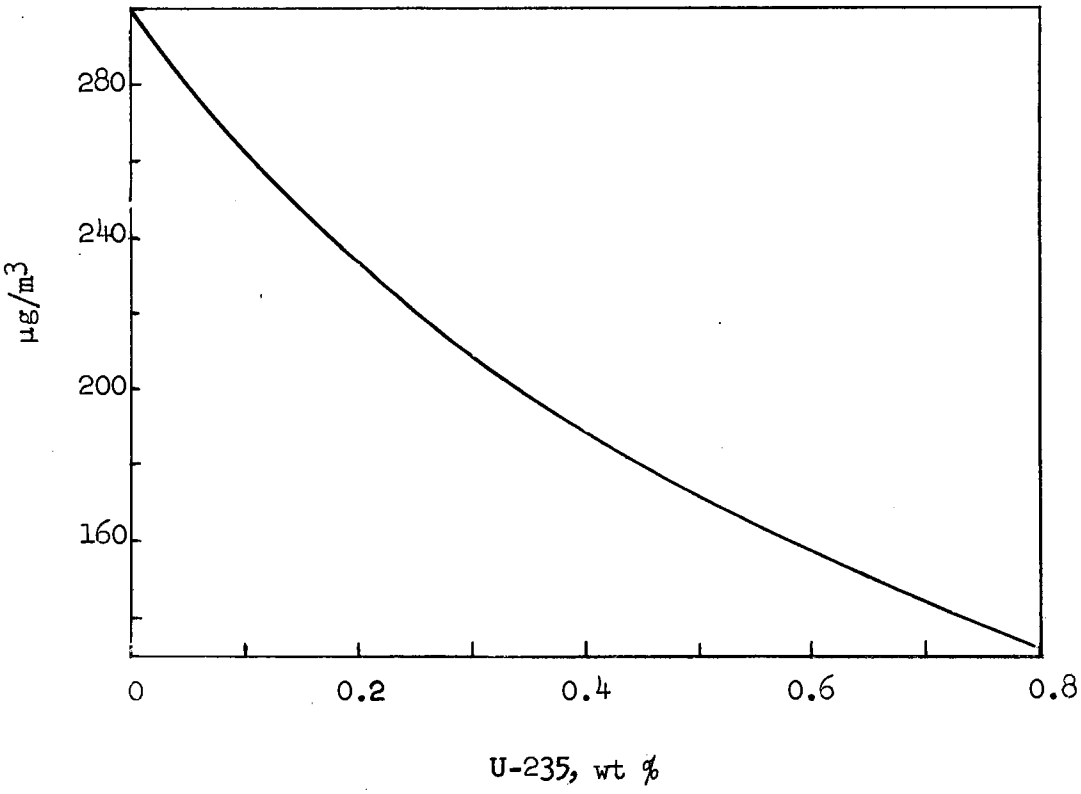



Fig. 3.2 Weight equivalent of radioactive MPC for insoluble uranium ($10^{-10}$ μg/cc).*

*See footnote on page 18.

roughly the equivalent of 140 μg of normal uranium per cubic meter of air or 300 μg of depleted uranium (0.0% U-235) per cubic meter of air. These may be compared with the 500, 200, and 100 $\mu g/m^3$, respectively, for arsenic, lead, and mercury.[11]

## 3.2 Hazard Control and Evaluation

The aim of any industrial hazard control program is to ensure that plant operations with the hazardous material will not cause injury to employees or the general population. A minimum program will consist of evaluation and control of the hazard and a continuing assessment of the control measures. The methods used to determine how well the control measures are functioning will include personnel monitoring as well as some of the same procedures used in the initial evaluation. The control measures discussed here are primarily those which have been used in the depleted uranium processing areas of the Y-12 plant of Union Carbide Nuclear Company at Oak Ridge.[13]

a. External. Since uranium does not constitute a serious external radiation hazard, it is seldom necessary to use stringent measures to control this type of exposure. The time-honored methods for controlling exposure to external sources of radiation are distance, time, and shielding. The intensity of gamma radiation from a point source rapidly decreases with distance away from the source. Beta radiation intensity is decreased even more rapidly with distance. In the case of uranium there is relatively little radiation exposure at a few feet from the material. The length of time a person may remain in any given area or at any particular job can be limited on the basis of instrument evaluations of the radiation conditions.[14] It is not necessary to use massive shielding or special manipulating devices to decrease exposures in working with normal or depleted uranium. The 2.32-Mev betas from these materials will be stopped completely by about 0.5 in. of water, even less plastic (Lucite), or less than 0.25 in. of glass.[15] A horsehide leather glove can decrease the radiation dose to the hands as much as 80%.[16]

Personnel monitoring may be accomplished with photographic film.[17,18] The pocket ionization chambers used for monitoring gamma radiation exposures are of little value in beta monitoring because the walls of the chambers are too dense for the beta particles to penetrate. Some progress has been made toward developing beta monitoring pocket chambers,[19,20] but they are not yet available for widespread use. On the other hand, complete film monitoring services, including supply of the film meters, interpretation of exposure, and recording of data, are available from several commercial organizations. Each person monitored in a film program wears a small meter or case which contains a dental x-ray film packet and metal filters, usually lead, cadmium, or silver. The meter case has an open window or a portion cut out to admit the beta radiation. After photographic development of the film under closely controlled conditions, the darkening of the film is determined with a densitometer or light transmis-

sion meter. The degree of darkening of calibration films exposed to known amounts of radiation provides a basis for estimating the amount of exposure received. Comparison of the darkening of the portion of the film covered by the metal filters with that of the unshielded portion permits determination of dose due to beta and to gamma radiation. The film meters in use at the Y-12 Plant are worn for one month before being processed; other AEC installations use quarterly[24] or monthly[25,26] periods.

b. Internal. Since the principal health hazard in dealing with uranium compounds is that of inhalation, the basic methods of control are enclosure and ventilation. Depleted uranium processing areas should be provided with adequate general ventilation and special or local ventilation appropriate for the kind of operations being performed. In the Y-12 depleted uranium areas, general ventilation provides an average of five air changes per hour, and may range from two to twelve as needed. Special local ventilation is furnished at operations that may produce high concentrations of uranium in the air. Commercially available respiratory protective devices are used for protection against short-term high concentrations. Educational programs and administrative procedures that place emphasis on proper handling techniques are necessary to supplement mechanical controls. Usually the sampling of uranium particulates in the atmosphere, the standard method of evaluating inhalation hazards, is accomplished by drawing air through a filter at a measured rate. The amount of uranium collected on the filter from a known volume of air is determined by measurement of the alpha radioactivity.[13,21]

Air samples are collected in most of the Y-12 depleted uranium processing areas by a system of samplers in fixed locations connected to a central vacuum system. The sampler positions are chosen so as to determine a general air level rather than the localized concentrations associated with any specific operation. Sample collection units are suspended from a wall, a post, or an overhead beam at heights of from 5 to 6.5 ft above the floor. These samplers may be operated continuously or intermittently according to the air-borne hazard potential. To supplement the information from the general air samples, a relatively small number of samples are taken with portable equipment near specific operations. Such samples are valuable for estimating potential exposures, evaluating techniques, equipment, or ventilation, and pointing out sources of air-borne contamination.

The extent of exposure of an individual frequently is estimated by analysis of urine samples for uranium content. Y-12 personnel who work in depleted uranium handling areas participate in a routine urinalysis program. They submit urine specimens at regularly scheduled intervals--at least once per quarter. Estimates of the quantity of uranium in the body are based on interpretation of the urinary uranium excretion rate. To prevent incidental contamination, the sample is collected before the employee changes into work clothing or goes into the work area. The urine samples are analyzed by a photofluorometric method.[21]

## 3.3 Typical Industrial Experience

The experience gained in evaluating hazards and exposures at the Y-12 Plant may be considered typical for an installation handling metals and oxides on a large scale. The plant limits for exposure to external radiation are those set forth by the National Committee on Radiation Protection and Measurement.[22] To simplify administrative control, exposures are limited to one-fourth the suggested annual dose (5 rem/year penetrating radiation or 10 rem/year to the skin of the whole body) in any quarter-year. These control criteria are the same as the limits specified in the Federal Regulations that apply to licensees.[8] Experience with uranium processing has shown that radiation to the skin is the limiting criterion. In Y-12 experience, an individual would exceed the limit on exposure to the skin of the whole body before he received an overexposure to the skin of the extremities.[23] This might not be true if operations required barehanded contact with uranium for significant periods of time.

Figure 3.3 shows the average external radiation exposure per quarter for foundry and machine shop employees expressed in terms of per cent of

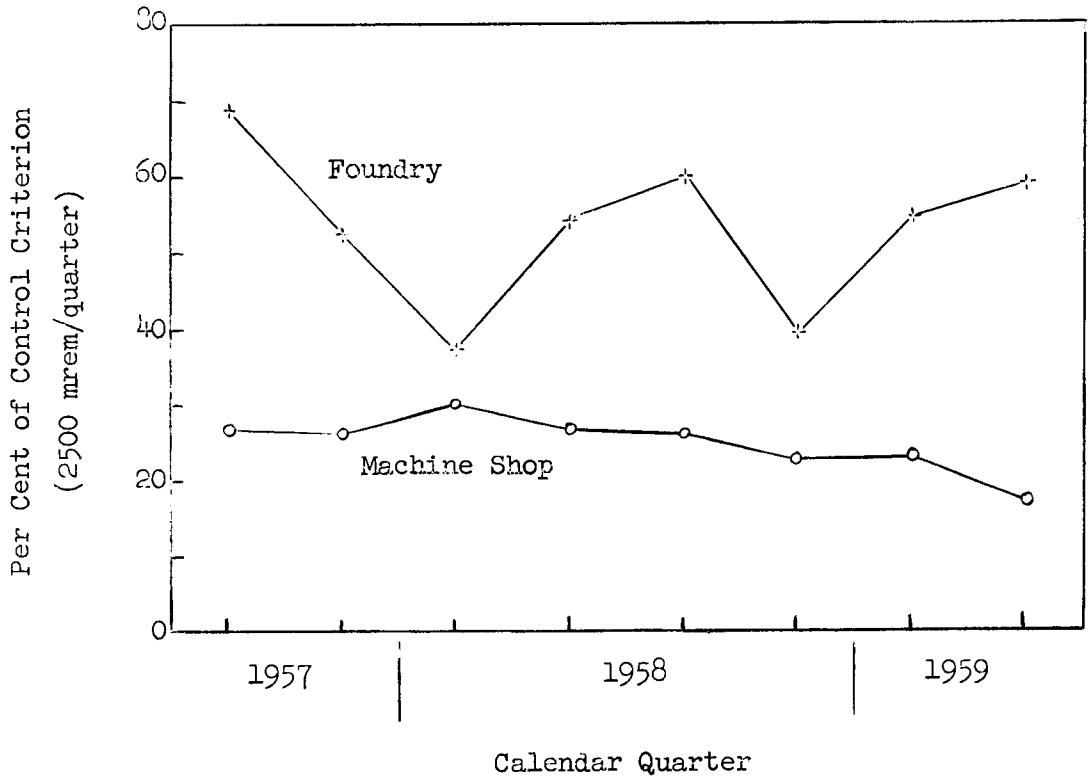



Fig. 3.3 Film badge exposure experienced in a depleted uranium foundry and machine shop.

the control criterion for radiation dose to the skin. The higher potential for exposure to be expected from $UX_1$ and $UX_2$ brought to the surface in casting metal is evident in the level of exposure shown for foundry employees. Surface treatment of the casting, among other factors, reduces the radiation level to which the machine shop employees are exposed. During the calendar years 1957 and 1958, less than 2% of the employees in depleted uranium areas received indicated radiation exposures which exceeded the maximum permissible level of 10 rem per year. The highest integrated dose, as determined by film dosimeters, was 12.7 rem in one year.

The average general air contamination levels found in the depleted uranium foundry and machine shop are shown in Fig. 3.4, in terms of the

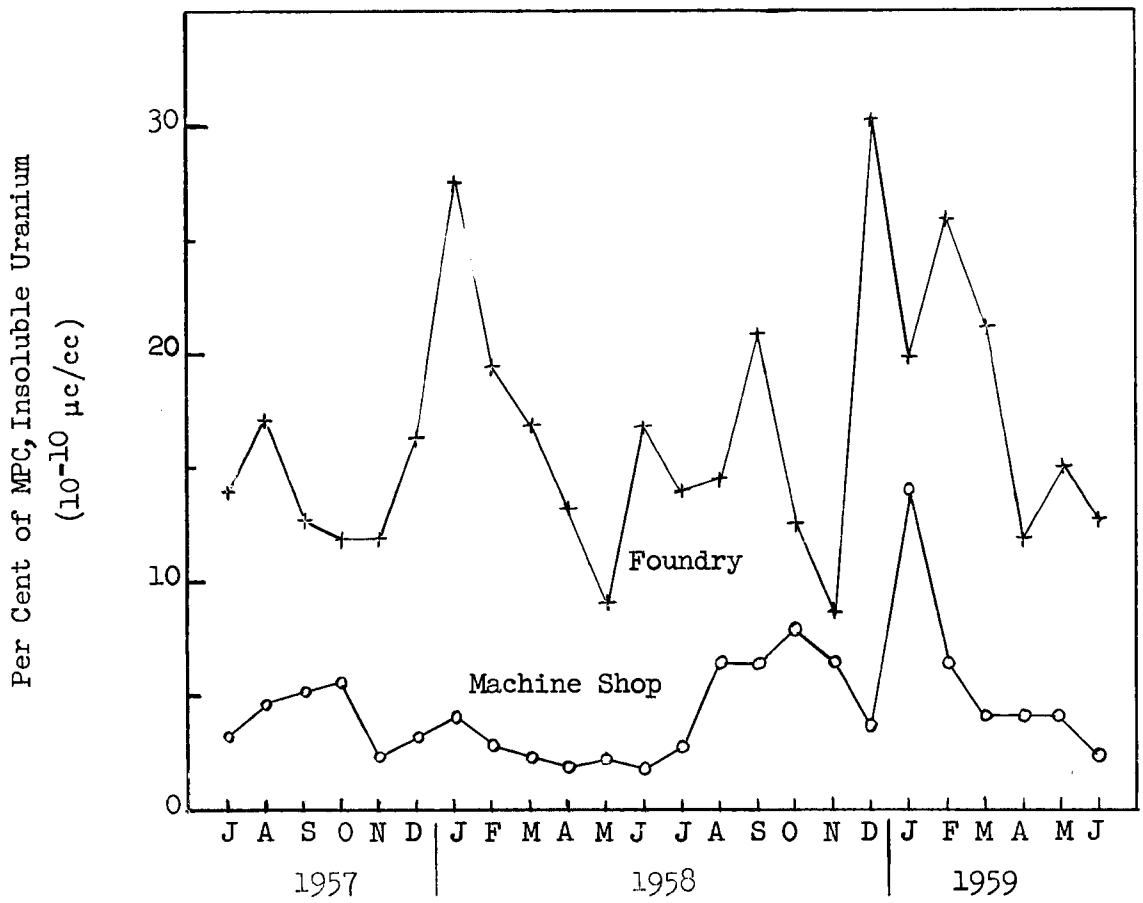



Fig. 3.4. Monthly average concentration of uranium in general air.

per cent of the MPC for insoluble uranium. The average concentrations for the entire period covered were 16.3 and 4.4% of the MPC for the foundry and machine shop, respectively. The regulations[8] do not specify the air contamination concentration above which air samples should be taken, but if the policy should be established on a basis similar to that requiring personnel film monitoring, this concentration might be of the order of 20% of the MPC. Experience at Y-12 indicates that operations involving abrasion of metal or transfer of hot or finely divided compounds are the most troublesome producers of air-borne contamination. Persons directly involved in these operations are afforded adequate protection by local ventilation or respiratory equipment.

Control criteria for the interpretation of urinalyses are based on conservative assumptions relating the urinary uranium excretion rate to the amount in the critical organ. The maximum amount permitted in the critical organ may be determined from data in the handbooks.[10,12] The Y-12 Plant control criterion is 50 μg of depleted uranium excreted in the urine per 24 hr and averaged over a period of 13 weeks. Voegtlin and Hodge[2] suggest that this limit is valid for exposures to soluble normal uranium for which the kidney is the critical organ, as well as to insoluble uranium for which the lung is the critical organ. The fact that depleted uranium has a specific activity lower than that of normal uranium provides an additional safety factor for the lung. Fig. 3.5 shows the

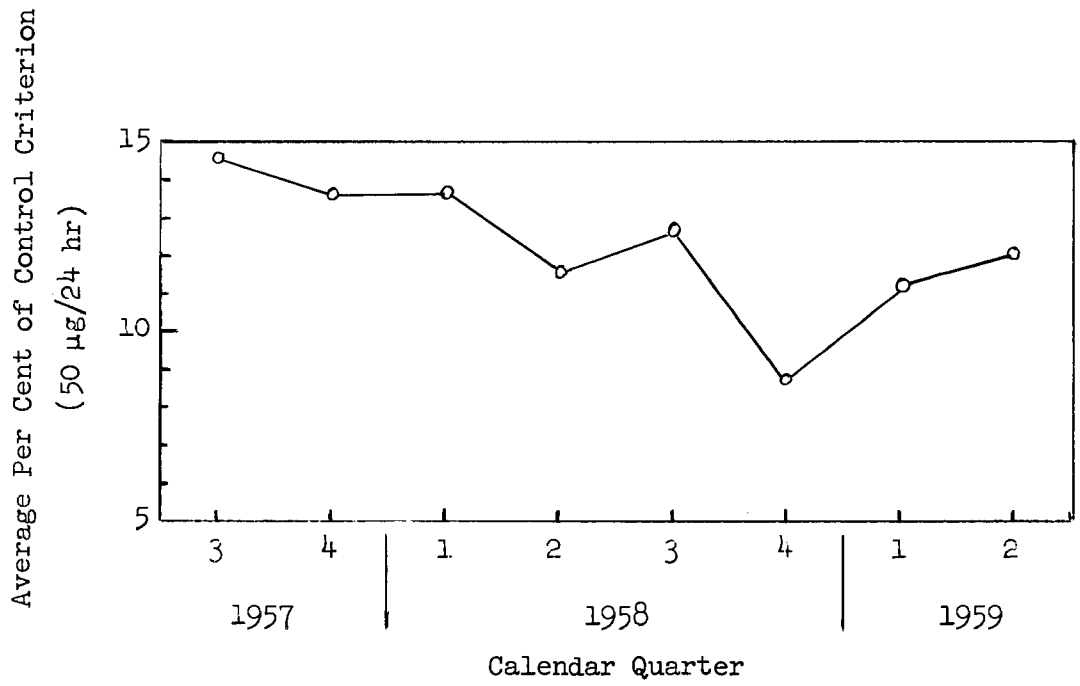



Fig. 3.5 Average urinary uranium excretion rate for employees working with depleted uranium.

13-week average results of urinalyses for the Y-12 employees working with depleted uranium. Data are plotted in terms of per cent of 50 μg per day averaged for all samples submitted during the 13-week period. During the fiscal years 1958 and 1959, less than 0.5% of the employees in depleted uranium areas exceeded the plant control criterion for urinary excretion of uranium. Y-12 experience has shown that work with depleted uranium can be carried on successfully without severe restrictions.

## 3.4 References


1. C. Voegtlin and H. C. Hodge, "Pharmacology and Toxicology of Uranium Compounds," Part 4, pp 2269-2289, McGraw-Hill, New York, 1953.

2. Ibid, Parts 1 and 2, 1949, Parts 3 and 4, 1953.

3. A. Tannenbaum, "Toxicology of Uranium," McGraw-Hill, New York, 1951.

4. S. R. Bernard and E. G. Struxness, "A Study of the Distribution and Excretion of Uranium in Man," ORNL-2304 (1957).

5. A. J. Luessenhop et al., "The Toxicity in Man of Hexavalent Uranium Following Intravenous Administration," Am. J. Roentgenol., Radium Therapy, and Nuclear Med., 79: 83-100 (1958).

6. K. Z. Morgan and H. M. Parker, "Health Control and Nuclear Research," Chap. VI, sect. 6.24 (in publication).

7. H. Bass, H. DiGiovanni, and H. D. LeVine, "Extrapolation Chamber Determination of Beta Ray Surface Dose Rate for Uranium and Some Uranium Compounds," AECD-2753 (NYOO-57) (1949).

8. Code of Federal Regulations, Title 10, Chap. 1, Part 20, Standards for Protection Against Radiation, AEC reprint containing the Amendments issued through July 30, 1958.

9. B. R. Fish, J. W. Hollis, Jr., and J. L. Thompson, "Absorption of Uranium from the Gastrointestinal Tract of Dogs Following Ingestion of $UO_2F_2$" (in manuscript).

10. National Committee on Radiation Protection and Measurement, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure," Natl. Bur. Standards Handbook 69 (1959).

11. "Threshold Limit Values for 1958," Adopted at the 20th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Atlantic City (April 19-22, 1958).

12. International Commission on Radiological Protection, British Institute of Radiology, British Journal of Radiology, Supplement 6, London (1955).

13. G. R. Patterson, Jr., et al., Y-12 Health Physics Program, Y-1186, Union Carbide Nuclear Company, Oak Ridge, 1957.

14. J. S. Handloser, "Health Physics Instrumentation," International Series of Monographs on Nuclear Energy, Division V, Vol. 1 (in preparation at Pergamon Press, London).

15. S. Kinsman, "Radiological Health Handbook," p 154, U. S. Public Health Service, Cincinnati, 1957.

16. M. Eisenbud and J. A. Quigley, in Proc. Internatl. Conf. Peaceful Uses of Atomic Energy, Geneva, August 8-20, 1955, Vol. 13, p 222.

17. E. Stone, "The Response of Sensitive 552 du Pont Film to Beta Radiation," LA-1284 (Aug. 13, 1951).

18. D. M. Davis and J. C. Hart, "A Review of Film Dosimetry" (unpublished report).

19. H. H. Hubbell, Jr., et al., "Pocket Ion Chambers for Beta Radiation Dose," ORNL-2158 (April 26, 1957).

20. A. P. Hull, "A Small Personnel Dosimeter for Beta and Gamma Radiation," paper presented at 3rd Annual Meeting Health Physics Society, Berkeley, California (June 9-11, 1958).

21. Laboratory Division Procedure Manual, Y-B72-145, Vol. V, Y-12 Plant, Union Carbide Nuclear Company, Oak Ridge (1958-1959).

22. National Committee on Radiation Protection and Measurement, "Addendum to National Bureau of Standards Handbook 59, Permissible Dose from External Sources of Ionizing Radiation" (1958).

23. E. O. Wollan, ORNL, unpublished data.

24. Applied Health Physics Semiannual Report, July-December, 1956, ORNL CF-57-1-173.

25. H. F. Henry et al., "Radiation Practices at the Oak Ridge Gaseous Diffusion Plant," KSA-81, Union Carbide Nuclear Company, Oak Ridge (1957).

26. R. G. Jordan, "Paducah Plant Health Physics Program," KY-204, Union Carbide Nuclear Company, Paducah (1957).

# 4.0 NONNUCLEAR USES FOR URANIUM AS A METAL

S. D. Clinton

Before the discovery of nuclear fission, metallic uranium was somewhat of a laboratory curiosity with an insignificant market value. In comparison with other metals, uranium has so many undesirable properties that in all likelihood it would have remained economically unimportant except for the naturally occurring U-235 isotope. In this section the important properties of uranium and probable nonnuclear applications for the metal and its alloys are reviewed. A brief discussion of the preparation, fabrication, corrosion, physical and mechanical properties, and alloys of uranium precedes a description of the proposed nonnuclear uses. At present the most promising uses for depleted uranium metal depend on its high atomic number and high density. Uranium is a more efficient material for shielding gamma photons than either lead or tungsten, and it may be competitive for making weights and ballast when volume is an important consideration. The Bureau of Mines is presently engaged in developing the use of depleted uranium metal for cathodic protection of iron or steel, to give a hard, dispersed phase in soft bearing metals, and as an additive in high-strength steels.

At the beginning of the Manhattan Project, uranium powder was produced in the United States by the reaction of uranium dioxide with calcium hydride and by the electrolysis of potassium-uranium fluoride, $KUF_5$, dissolved in a bath of fused alkali and alkaline earth chlorides. The resulting metal powder could be melted and cast into desired shapes, but the high cost and low yield of both processes influenced the development of a more efficient and economical production method. The present largest commercial production of uranium metal is by the bomb reduction of $UF_4$ with magnesium. Magnesium and $UF_4$ powders are mixed and put into a dolomite-lined steel reaction vessel, which is then heated to 600-640°C to initiate the highly exothermic reaction. The reaction proceeds rapidly to completion, the molten uranium metal collecting at the bottom of the container under a layer of magnesium fluoride slag. After having cooled and solidified, the uranium is vacuum-remelted to remove impurities and consolidate the metal into an ingot. Since all the impurities in uranium form lighter compounds than the metal, they float to the top of the molten ingot. The purity of the uranium may be improved considerably by repeated melting and cropping of the ingot top. A high-purity uranium powder can be made by reacting uranium metal and hydrogen at 220-230°C and thermally decomposing the resulting metal hydride (after sifting from the unreacted impurities) in a vacuum furnace at 480°C.

## 4.1 Properties of Uranium Metal

a. Physical Properties. The properties of uranium have been difficult to determine exactly because of the large effects of varying amounts of impurities contained in the metal. Probably the most significant physical property of uranium is its high density, which ranges between 18.7 and 19.0 g/cc depending on the method by which the metal is formed.

The theoretical density of uranium at room temperature has been calculated from the lattice data of Bridge, Schwartz, and Vaughn[1] to be 19.060 g/cc.

Below its melting temperature uranium metal exists in three distinct allotropic forms, namely, alpha, beta, and gamma. The room-temperature structure or alpha phase is stable up to 665°C. Alpha uranium has an orthorhombic crystal lattice containing four atoms per structure cell, which can also be visualized as a distorted hexagonal close-packed structure. The binding between $\gamma$-uranium atoms is largely covalent, which is reflected in some of its properties such as a low thermal and electrical conductivity and a rather limited solubility with most metals. Since alpha uranium is highly anisotropic, most of its properties are affected significantly by crystal orientation.

The beta phase of uranium is stable between the temperatures of 665 and 771°C, and the gamma phase is stable from 771°C to the melting point. Beta uranium has a tetragonal structure containing 30 atoms per structure cell, while gamma uranium has a body-centered cubic crystal structure containing two atoms per unit cell. Neither the beta nor the gamma phase can be stabilized by quenching pure uranium,[2] but both phases can be quenched and retained at room temperature by alloying with small amounts of either chromium or molybdenum.[3,4]

The melting point of uranium is 1130°C, and the boiling point (determined by the extrapolation of vapor pressure data) is approximately 3818°C. At 1420°C the vapor pressure of uranium becomes equivalent to (assuming the ideal gas law) the maximum permissible concentration of natural uranium in air for a 40-hr week, 175-200 $\mu g/m^3$.[5]

The thermal conductivity of uranium at room temperature is about 0.06 cal/cm·sec·°C (14.5 Btu/ft·hr·°F), comparable in magnitude with that of the 400 series stainless steels. The conductivity of uranium increases with increasing temperature and at 500°C is approximately 0.09 cal/cm·sec·°C. There is a wide variation in the reported conductivity data at higher temperatures, which is probably related to its anisotropic nature.

The electrical resistivity of uranium is high for a metal, ranging between 25 and 35 $\mu$ohms-cm at room temperature. The resistivity of uranium increases almost linearly with temperature and is between 50 and 55 $\mu$ohms-cm at 500°C.

The thermal expansion of uranium is a prime example of the anistropy exhibited by the alpha phase (Table 4.1).[6] The volume expansion coefficient of alpha uranium, calculated from the 25 to 300°C data in Table 4.1, is $37 \times 10^{-6}$ cc/cc·°C.

Table 4.1 Coefficient of Linear Thermal Expansion of Alpha Uranium in the Three Main Crystallographic Directions as Found by High-temperature X-ray Studies

| Direction Parallel to Axis | Average Expansion Coefficient $\times 10^6$, cm/cm.°C | |
|---|---|---|
| | At 25 - 300°C | At 25 - 650°C |
| (100) | 23 ± 3 | 28 ± 2 |
| (010) | -3.5 ± 2 | -1.4 ± 1 |
| (001) | 17 ± 2 | 22 ± 1 |

b. Mechanical Properties. Because of the anisotropic nature of alpha uranium, mechanical properties are strongly affected by grain orientation which, in turn, is controlled by the fabrication history. The grain size and purity of the metal also tend to alter the mechanical properties of uranium. Because the important variables on a uranium metal specimen are not often clearly indicated, many of the results reported from mechanical testing are of little significance.

Since uranium metal shows a rather poorly defined proportional limit, the elastic constants are difficult to determine accurately from a stress-strain diagram obtained by the conventional tensile test. The elastic properties of a solid are related to the velocity of propagation of sound in an infinite medium of that solid, and the most reproducible values of the elastic constants for uranium have been determined by a dynamic method:[7]

Young's modulus = $29.7 \times 10^6$ psi
Shear's modulus = $12.1 \times 10^6$ psi
Poisson's ratio = 0.23

Because of the poorly defined elastic portion of the uranium stress-strain diagram, it is difficult to judge the yield stress. There is a wide variation in the reported uranium tensile data; the most likely ranges of values for yield strength, tensile strength, and elongation for uranium in various conditions are given in Table 4.2.[8] As the temperature is increased, uranium rapidly loses its strength. For example, the yield stress (0.2% offset) of a 300°C rolled, alpha-annealed uranium specimen decreased from 43,300 psi at room temperature to 5100 psi at 500°C.

Hardness data for uranium show surprisingly little scatter between gamma-extruded, alpha-rolled and annealed, and as-cast uranium.[8] The hardness of uranium decreases very rapidly with increasing temperature, from a 200 VHN* (10-kg load) at room temperature to an approximate value of 10 VHN at the alpha-beta phase transformation temperature. At this

*Vickers Pyramid Hardness Number.

Table 4.2 Typical Tensile Properties of Uranium

| Material | Yield Strength (0.2% offset), $10^3$ psi | Tensile Strength, $10^3$ psi | Elongation, % |
|---|---|---|---|
| Cast ingot, coarse-grained | 27 - 35 | 60 - 85 | 5 - 10 |
| Gamma extruded | 18 - 38 | 85 - 120 | 10 - 18 |
| Alpha-rolled, alpha-annealed | 30 - 40 | 80 - 110 | 10 - 15 |
| Beta-annealed | 25 - 35 | 55 - 65 | 6 - 10 |
| Beta-quenched | 30 - 35 | 70 - 95 | 10 - 15 |
| Gamma-quenched | 17 - 26 | 60 - 80 | 8 - 15 |
| 600°C | 30 - 35 | 85 - 100 | 10 - 18 |
| Beta-rolled | 30 - 35 | 80 - 95 | 10 - 15 |

temperature the hardness of beta uranium increases abruptly to a VHN of 40, and then it decreases instantaneously at the beta-gamma phase transformation temperature to a value of less than 1 VHN.[8] The hardness of gamma uranium at 800°C is approximately the same as that of pure lead at room temperature. Uranium may be work-hardened by swaging or rolling.[9]

In general, pure uranium metal is considered a rather ductile metal. Between room temperature and 100°C, the metal exhibits a brittle transition temperature in which the elongation in a 2-in. specimen increases from 5-10% to 30-40%.[8] In this temperature region the tensile properties of uranium change rapidly with temperature, which may partially explain the wide variations in the tensile data reported.

c. Corrosion. In several ways the corrosion behavior of uranium has been shown to be similar to that of iron.[10] Both uranium and iron are quite resistant to corrosion in dry atmospheres, but they corrode rapidly in the presence of moisture. Under conditions of varying oxygen concentrations, the oxygen-depleted region on uranium becomes anodic. Uranium is attacked to only a limited extent by strong nitric acid, although it is dissolved readily by other acids. The passive behavior of iron in strong nitric acid appears to be analogous to that of uranium, but despite these similarities the subject of uranium corrosion is very complex and reproducible data are difficult to obtain.

The experience of the Los Alamos Scientific Laboratory has been that the best atmosphere for storing uranium is freely circulating air and that surrounding the metal with an inert gas tends to increase the uranium corrosion rate.[10] Uranium metal stored out of contact with air for several months develops corrosion products, evidently from reaction with moisture, which ignite spontaneously in air at room temperature. This behavior is not understood, but it is probably influenced by the formation of uranium hydride. Corrosion products tend to adhere to the metal in freely circulating air, whereas considerable spalling occurs under oxygen-depleted conditions. In summary, the moisture and oxygen content of the surrounding atmosphere have the most effect on the corrosion of stored uranium.

Uranium reacts readily with aqueous media, and only under limited conditions is a protective film of $UO_2$ formed and retained on the metallic surface. In distilled water saturated with air, protective films are formed at temperatures up to 70°C for a significant period of time (i.e. at 70°C there is little corrosion for approximately 50 days' exposure), but at temperatures above 80°C there is apparently no protection provided by the corrosion product. It has been postulated that the thin oxide film breaks down as a result of ionic hydrogen diffusing through the film and forming uranium hydride between the metal and the oxide. This hydride causes the loss of oxide and metal adherence with the subsequent loss of corrosion protection.[11]

Because of the poor corrosion resistance of uranium, considerable effort has been made to develop a suitable protective coating. Uranium can be electroplated with a number of metals by using conventional techniques, but difficulty has been experienced in cleaning the metal surface prior to plating. The foil cladding of uranium with a number of metals has been perfected in connection with making nuclear reactor fuel elements.

d. Fabrication. Prior to fabrication uranium must be melted and cast into a desired shape. The melting and casting of uranium is complicated by the high degree of chemical reactivity of uranium with the atmosphere and most crucible materials. The metal may be melted satisfactorily in either a high vacuum or an inert atmosphere (highly purified argon or helium). For the casting container material thoria, alumina, and beryllia are adequate below 1350°C, but only beryllia crucibles are satisfactory above 1700°C.[12] High-purity graphite is a satisfactory crucible material up to 1400°C, but above this temperature the molten metal becomes considerably contaminated with carbon.[13]

Uranium may be extruded in the high alpha and gamma temperature ranges. Extrusion in the gamma range requires less applied load than in the alpha phase because of the soft, plastic nature of gamma uranium. The major difficulty with the gamma extrusion process is finding a suitable die material since uranium reacts readily with most of the commonly used metals at high temperatures. By using refractory alloys for the dies, the problem is minimized. In general, extruded uranium shapes have better physical properties than similar cast shapes.

Uranium wire and tubing may be cold-drawn successfully using specially prepared lubricants.[14] With proper lubrication size reductions of the order of 20% per pass are possible.

Uranium may be rolled in all three of its allotropic forms; however, most rolling is done with alpha uranium between room temperature and 600°C. Rolling in the beta phase requires about twice as much force as rolling at 600°C because of the abrupt increase in hardness at the alpha-beta phase transformation temperature. Gamma uranium, on the other hand, is so soft that it is almost impossible to handle a long rod emerging from the rolls. The recrystallization temperature of heavily cold-worked uranium is

approximately 450°C, and rolling below this temperature is therefore accompanied by work-hardening. Large size reductions are possible on each rolling pass, and uranium metal foil as thin as 0.0005 in. has been produced by cold rolling.

Uranium metal may be forged at about 600°C with metal oxidation protection necessary only during preheating. Swaging can be done either hot or cold. Size reductions of the order of 10 to 15% per pass are possible at 560°C.

Uranium powder, produced by the thermal decomposition of $UH_3$, may be hot pressed in an inert atmosphere to approach theoretical density. A powder compact, made at 40,000 psi at a temperature slightly below the alpha-beta transformation temperature, shows complete densification and a fine grain structure with essentially random orientation. One of the major problems encountered in pressing is the pyrophoricity of uranium powder, which immediately starts to burn when exposed to any oxidizing conditions. The fire hazard can be inhibited by the addition of either paraffin wax or paraffin oil to the powder.

Uranium metal may be machined by standard shop practices provided certain precautions are taken. Extra rigidity and power are required of the machine tools because of the high density of uranium. The metal work-hardens rapidly, and a heavy flow of lubricant is necessary to prevent the machined fines from burning. In general, heavy cuts and high tool speeds are recommended when uranium is machined.[14]

The techniques of metallurgically joining uranium have been hindered by the high reactivity of uranium with the atmosphere. Uranium has been welded by the Heliarc process and by the consumable-electrode shielded arc process using uranium wire as an electrode, an argon atmosphere, and a copper or graphite back-up bar. Brazing or soldering of uranium is complicated by the formation of brittle compounds between uranium and most of the brazing or soldering alloys.[14]

e. Alloys. Because of the chemical activity of uranium, its anisotropic alpha phase, and its unpredictable mechanical properties, there is great interest in the development of new uranium alloys. Thirty binary uranium alloys have been studied sufficiently to permit the drawing of phase diagrams (see Appendix of reference 8). Several other binary systems and a few ternary systems have been studied partially.

The orthorhombic crystal structure of alpha uranium is not found in any other metal, and, since the electron bonding in the alpha phase is largely covalent, it would be expected that formation of solid solutions would be restricted even though the atomic size and valence of the solute elements were favorable. Assuming a valence of IV for alpha uranium, quadrivalent elements, such as titanium, zirconium, and hafnium, should tend to stabilize alpha uranium relative to the beta phase. This effect has been observed in the uranium-titanium and uranium-zirconium systems although there is limited solubility of both titanium and zirconium in the alpha phase.

The complex tetragonal structure of beta uranium, which is also unique among metals, shows some degree of nonmetallic bonding. As in the alpha phase, solid solubilities are limited in beta uranium. Vanadium, niobium, chromium, and molybdenum are capable of stabilizing beta relative to alpha uranium and retaining the beta phase during quenching.

The gamma phase of uranium is the most metallic state and can be regarded as having a valence of VI. On the basis of size factor, crystal structure, and valence, the following elements should form extensive solid solutions with gamma uranium: titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten. It has been observed that titanium, zirconium, niobium, and molybdenum form extensive solid solutions in gamma uranium. Vanadium and chromium have solubilities in gamma uranium of 12 and 4 atom per cent, respectively, while tantalum and tungsten are progressively less soluble.

Many elements form one or more intermetallic compounds when alloyed with uranium with only limited solid solubility in either of the terminal phases. Elements that are known to form intermetallic compounds with uranium are antimony, arsenic, beryllium, bismuth, boron, carbon, cobalt, copper, gallium, germanium, gold, hydrogen, indium, iron, lead, manganese, mercury, nickel, nitrogen, oxygen, palladium, phosphorus, platinum, selenium, silicon, sulfur, tellurium, thallium, tin, and zinc. Similar behavior is indicated in the available portions of the ternary systems of uranium with aluminum and silicon, beryllium and carbon, bismuth and lead, cobalt and iron, chromium and iron, and cobalt and nickel.

Several elements alloyed with uranium neither show extensive solubilities nor form intermetallic compounds but exhibit eutectic, peritectic, or monotectic reactions. The uranium-vanadium and uranium-chromium are binary systems which form a simple eutectic. A peritectic reaction is found in both the uranium-tantalum and uranium-tungsten systems. A monotectic system is shown by uranium-magnesium, uranium-thorium, and uranium-silver. It is probable that cerium, lanthanum, neodymium, and praseodymium also form monotectic systems with uranium.

Titanium, zirconium, and niobium show complete solid solubility with uranium at elevated temperatures, and approximately 30-40 atom per cent molybdenum is soluble in gamma uranium. In all these binary uranium systems except niobium, an intermediate (delta) phase is formed from a metastable gamma phase. These intermediate phases are metallic in nature and are therefore not considered intermetallic compounds.[11]

## 4.2 Uses for Uranium Metal

a. Gamma Shielding. Gamma ray photons may be attenuated in matter primarily by three processes in which all or part of the photon energy is given to electrons. The resulting electrons have a relatively short range, producing heat in the immediate vicinity of the photon interaction. The three gamma attenuation processes are known as the "photoelectric effect," "pair production," and the "Compton Effect."

The photoelectric effect can be accurately treated as an absorption process in which all the photon energy is transferred to an atom. The photon-atom interaction causes the ejection of an electron from one of the inner orbits of the atom, and the ensuing x-ray from the readjustment of the orbital electrons is usually replaced by the emission of a second or Auger electron. The photoelectric effect is dominant for low-energy gammas, and its cross-section varies approximately as $Z^5$ (where Z is the atomic number of the attenuating matter).

The pair production process may be treated effectively as an absorption process in which an energetic photon creates a positron-electron pair. The positron is subsequently annihilated nearby, creating two additional photons each with an energy of 0.51 Mev; however, they are less penetrating than the original photon. Pair production does not occur for photons of energy less than 1.02 Mev. The cross-section for the process increases with increasing photon energy and varies from element to element as $Z^2$.

In the Compton effect the photon interacts with a loosely bound atomic electron, transferring some of its energy to the electron and proceeding with a lower energy in a different direction. The Compton cross-section decreases with increasing energy and varies directly with Z. It is the dominant effect for photons in the intermediate energy range (0.5 to 5.0 Mev).[15]

Since all the gamma attenuation processes vary directly with Z or higher powers of Z, it follows that uranium with an atomic number of 92 (highest of the naturally occurring elements) is the most effective available material for shielding gamma photons. At present, lead, with an atomic number of 82, dominates the gamma shielding market, mainly because of its availability and low cost. Uranium costing between \$5 and \$7 per pound must show special gamma shielding advantages in order to compete with lead costing less than 20¢ per pound.

The maximum weight saving attainable by replacing lead with uranium would occur when shielding a small-volume gamma source or, ideally, a point source. The dose rate from a point source of photons may be calculated from the equation

$$D = K \frac{\mu_a}{\rho} E B \frac{Se^{-\mu t}}{4 \pi R^2} \qquad (1)$$

where D = dose rate, rads/hr (the rad is the quantity of radiation that deposits 100 ergs per gram of the specified material)

$$K = \text{conversion factor, } \frac{\text{g rads}}{100 \text{ ergs}} \frac{1.6 \times 10^{-6} \text{ erg}}{\text{Mev}} \frac{3600 \text{ sec}}{\text{hr}}$$

$$= 5.76 \times 10^{-5} \text{ rad/hr per Mev/sec} \cdot \text{g}$$

$\mu_a/\rho$ = energy-absorption mass attenuation coefficient for the source energy and the material in which the dose is to be measured, $cm^2/g$

E = photon energy of radiation source, Mev/disintegration

B = dose rate buildup factor to account for the Compton-scattered photons, dimensionless

S = gamma source strength, disintegrations/sec

R = distance from the source, cm

$\mu$ = probability per unit distance for a photon interaction with the attenuating material, cm

t = thickness of attenuating material, cm

Using the above equation and assuming a Co-60 point source (zero cavity volume), the dose rate in tissue per unit source strength was calculated for various spherical shield thicknesses of uranium and lead at both the shield surface and 1 meter distance from the source (Fig. 4.1). The spherical shield weights for uranium and lead were calculated at various shield thicknesses assuming densities of 18.8 g/cc for uranium and 11.3 g/cc for lead (Fig. 4.2). The ratio of uranium to lead shield weights and thicknesses were then determined at equal values of dose rate in tissue per unit source strength at both the shield surface and 1 meter distance from the source (Fig. 4.3).

The effect of increasing the cavity volume from zero to 34 cc (spherical cavity of 2 cm radius) is also shown in Fig. 4.3, comparing equivalent dose rates at the shield surface. Probably the most noteworthy facts of these calculations are that, for a Co-60 source with at least 1 curie of activity, the weight saved by using uranium instead of lead is of the order of 60-70 per cent, and the shield volume saving is greater than 75 per cent.

By saving approximately 60 per cent of the required shield weight for point gamma sources, uranium may be able to compete with lead in such applications as shipping carriers and shields for Co-60 teletherapy units. Keleket X-Ray Corporation has estimated that the savings on structural support for a cobalt teletherapy unit using a uranium shield would pay for the difference in cost between uranium and lead.[16] A late 1953 announcement by the University of Chicago disclosed that a rotating device for treating cancer tumors with gamma rays from a Co-60 source in its Argonne Cancer Research Hospital required 850 lb of uranium to shield the cobalt, whereas if lead should be used about 3300 lb would be necessary, making the device much more cumbersome, if not impractical.[17] From Figs. 4.1 and 4.2, a uranium shield weighing 850 lb would permit a dose rate at 1 meter from the source of $1.5 \times 10^{-5}$ mrad/hr-curie. Using this dose

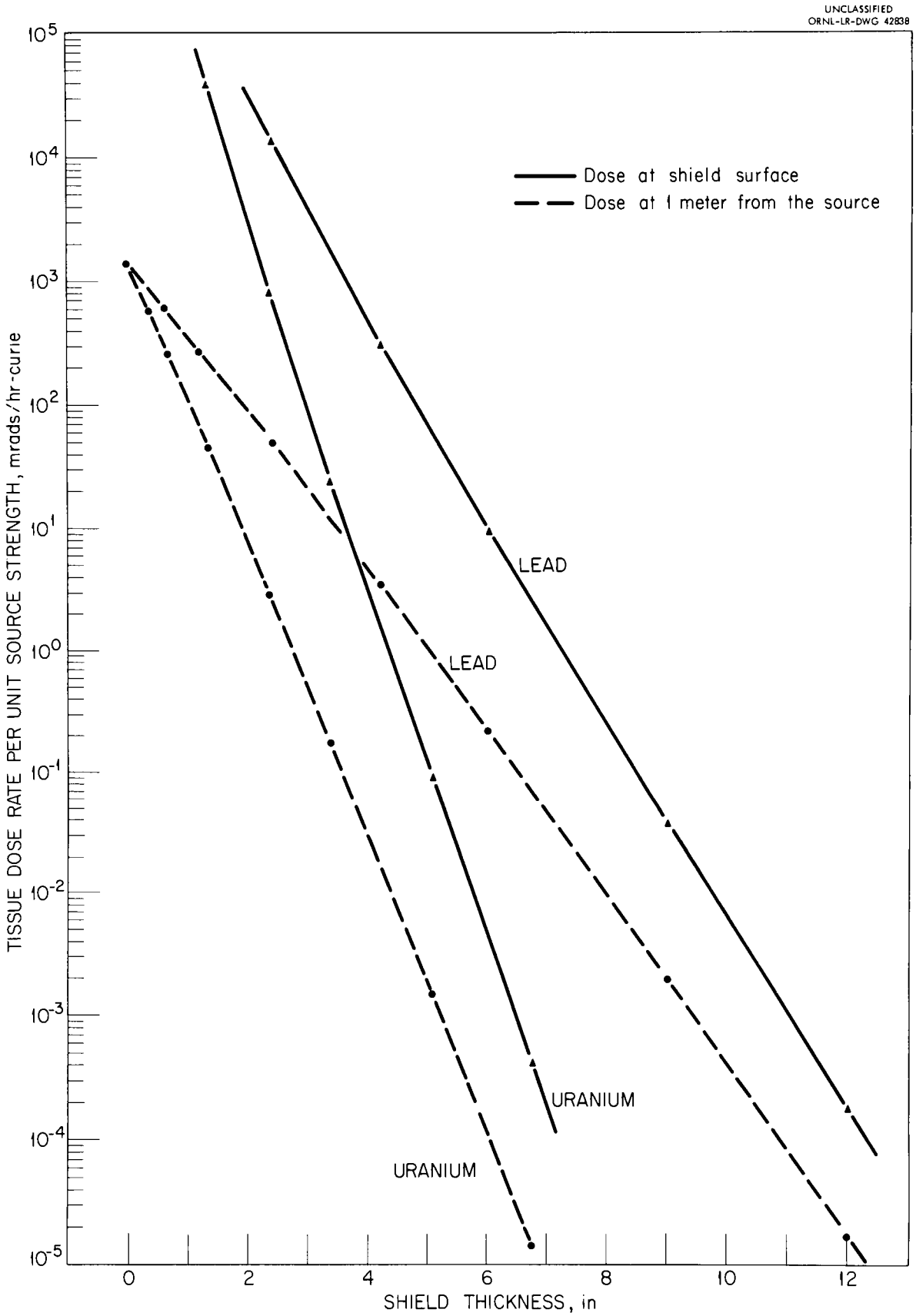



Fig. 4.1. Dose rate in tissue per unit source strength vs shield thickness. Co-60 point source, zero cavity volume.

UNCLASSIFIED
ORNL-LR-DWG 42839

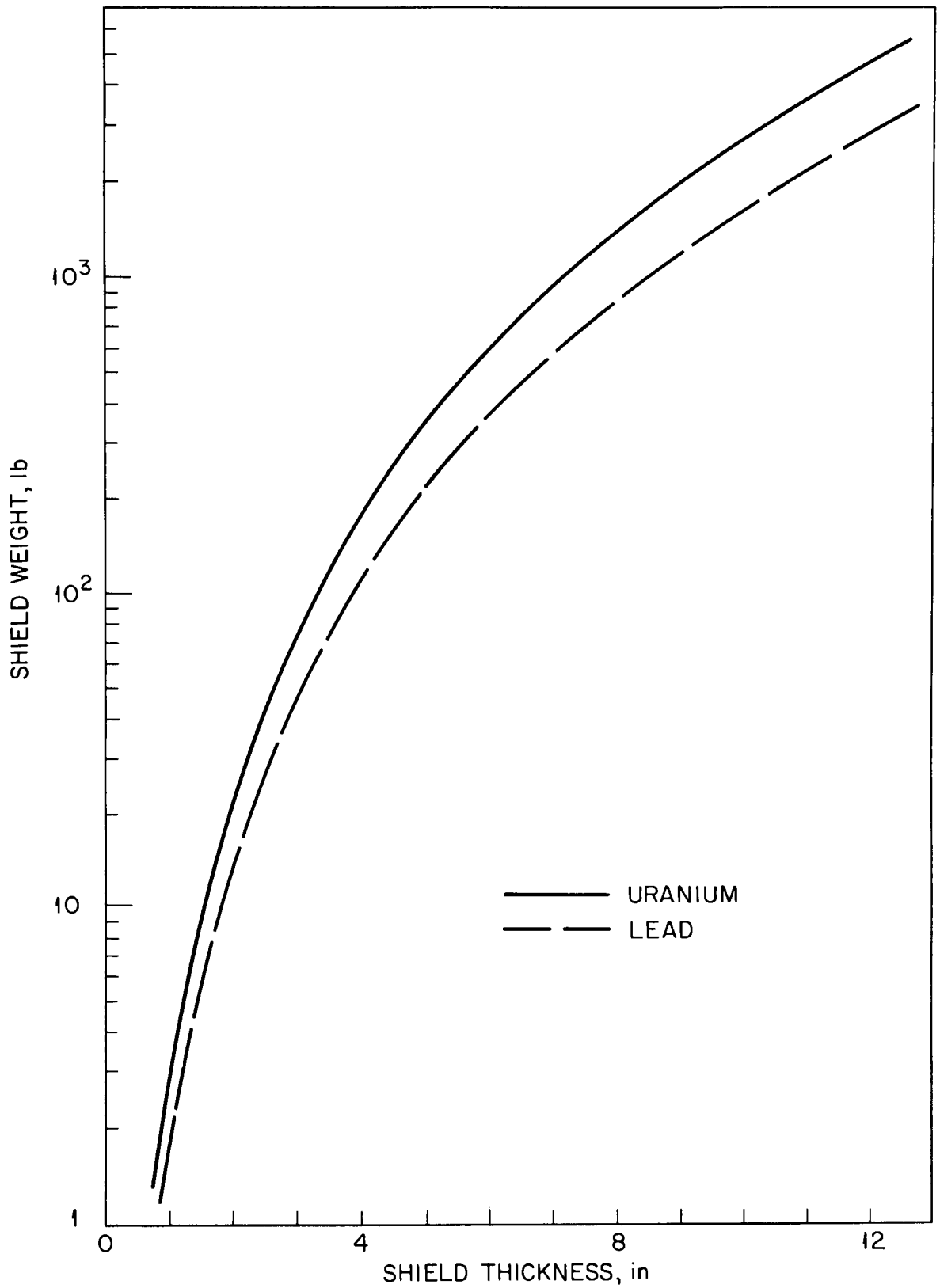



Fig. 4.2. Weight of shield vs shield thickness. Co-60 point source, zero cavity volume.

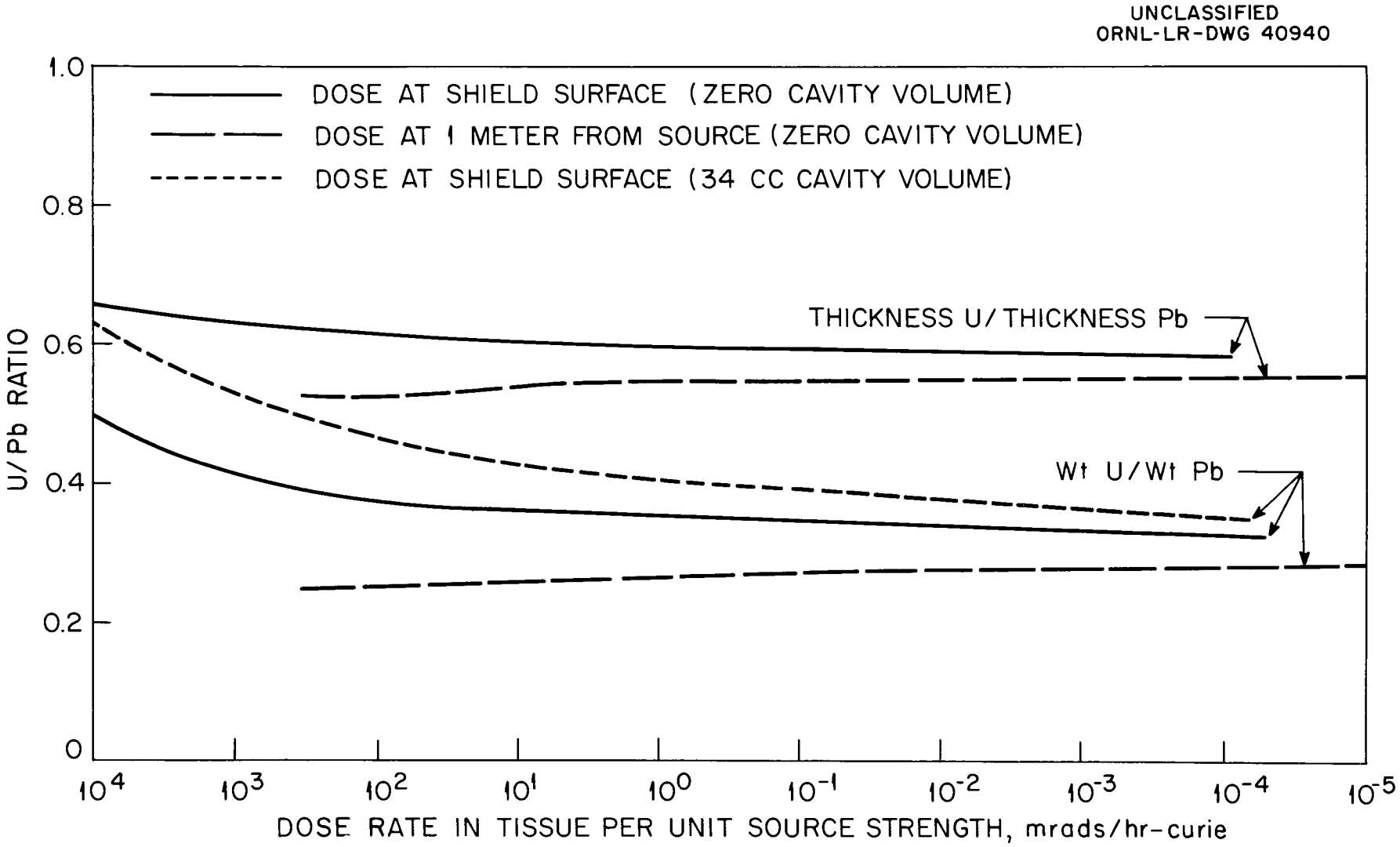



Fig. 4.3. Ratio of uranium to lead shield weights and thicknesses vs dose rate in tissue per unit source strength. Co-60 source.

rate per unit source strength measured at a 1-meter distance, the ratio of uranium to lead shield weights of 0.26 reported by the University of Chicago is comparable to the ratio of 0.28 shown in Fig. 4.3 (assuming a zero cavity volume).

Uranium has been considered as a possible shielding material to be used in shipping containers for irradiated nuclear fuel elements. In one example of a 70-ton shipping cask for the Savannah River plant, uranium was considered for the shielding material.[18] Its greater effectiveness per unit weight for absorption of gamma radiation would result in a lighter cask and consequently lower freight costs. The use of uranium was rejected, however, because of time-consuming fabrication problems and complications involving the development of a firm raw material cost.

A preliminary study was made at the Oak Ridge Y-12 plant in 1957 by C. P. Coughlen on the possible use of depleted uranium for shielding shipments of spent reactor fuel elements.[19] As a result of this study, a development program for fuel element shipping casks was proposed with the three following objectives: (1) To determine the cask design that requires the least ratio of structural and shielding weight to cargo cavity volume; (2) to develop and demonstrate a heat removal system whose capacity would permit the maximum benefits from such factors as optimum cask geometry and selection of shielding material; and (3) to study fabrication techniques. In Coughlen's preliminary shipping cask study, the following assumptions were made: All the gamma heat would be removed by conduction through the cask wall and rejection to the atmosphere; criticality considerations would impose no restrictions on the cask size or shape; design evaluations would be restricted to the shield mass; and biological shielding requirements would be satisfied by 5.5 in. of depleted uranium or 9 in. of lead. For all geometrical configurations regardless of the cask size, the shield mass investment per cargo cavity volume was smaller with depleted uranium for the shielding material than with lead (Figs. 4.4 and 4.5).

b. Special Reactor Shielding. Depleted uranium may prove to have certain specific applications in reactor shielding where a high-performance shield is required. For mobile reactors where weight is one of the more important considerations, depleted uranium may compete favorably with lead. Adequate consideration, however, must be given to depressing the neutron flux in the uranium shield region in order to minimize the amount of activity induced within the shield.[20]

c. X-ray Tube Target, Ammunition, Weights, and Ballast. Because of the high atomic number of uranium it is not only an efficient gamma shield but is also an excellent target material in an x-ray tube. When fast electrons are decelerated in the Coulomb fields of uranium nuclei, hard characteristic x rays of very short wavelength are produced;[21] however, tungsten will probably continue to dominate the market for x-ray tube target materials because of its high melting temperature.

UNCLASSIFIED
ORNL-LR-DWG 40941

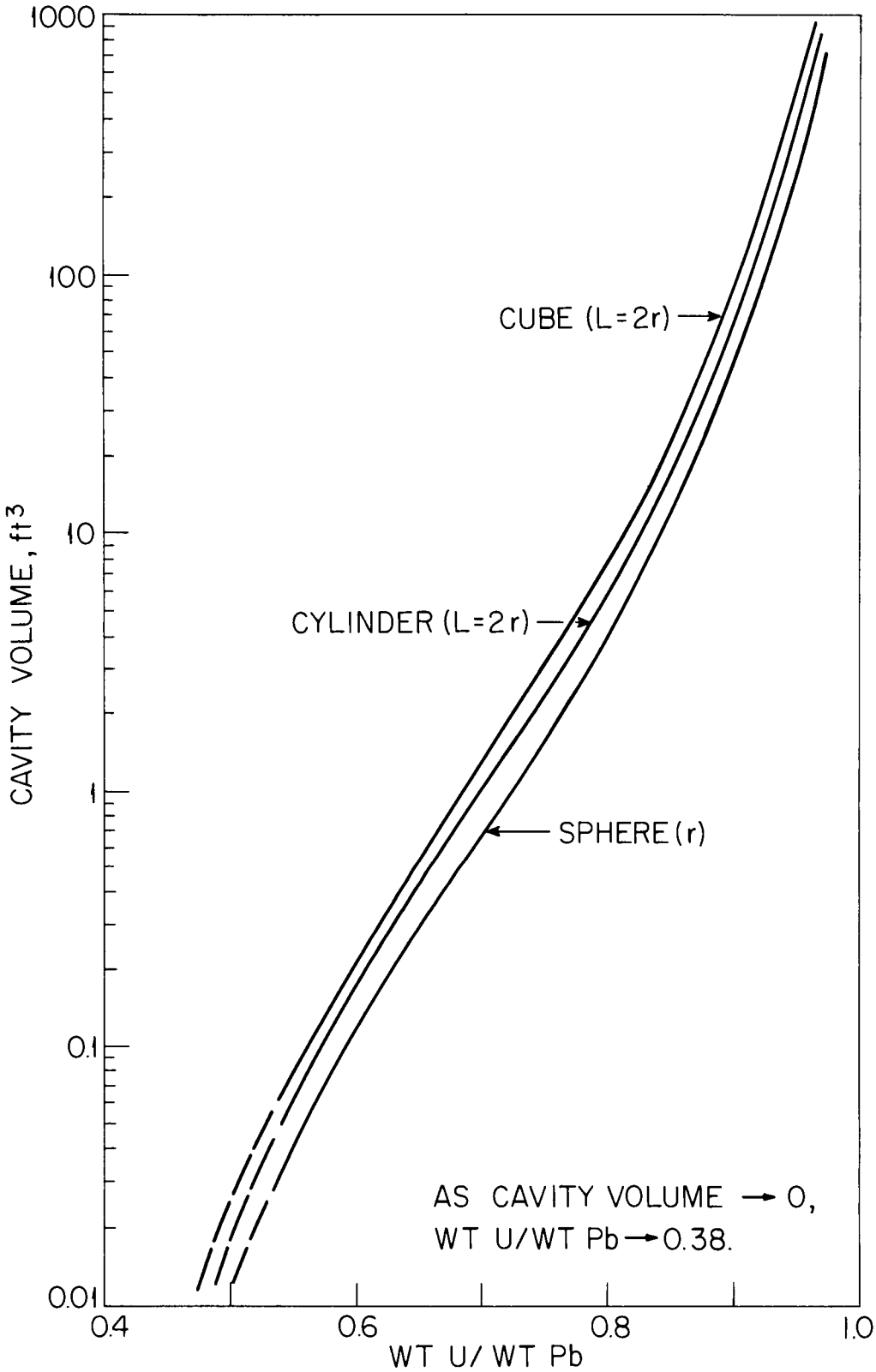



Fig. 4.4. Cavity volume of shield vs U/Pb weight ratio in shield. U thickness 0.458 ft, Pb thickness 0.750 ft.

UNCLASSIFIED
ORNL-LR-DWG 40939

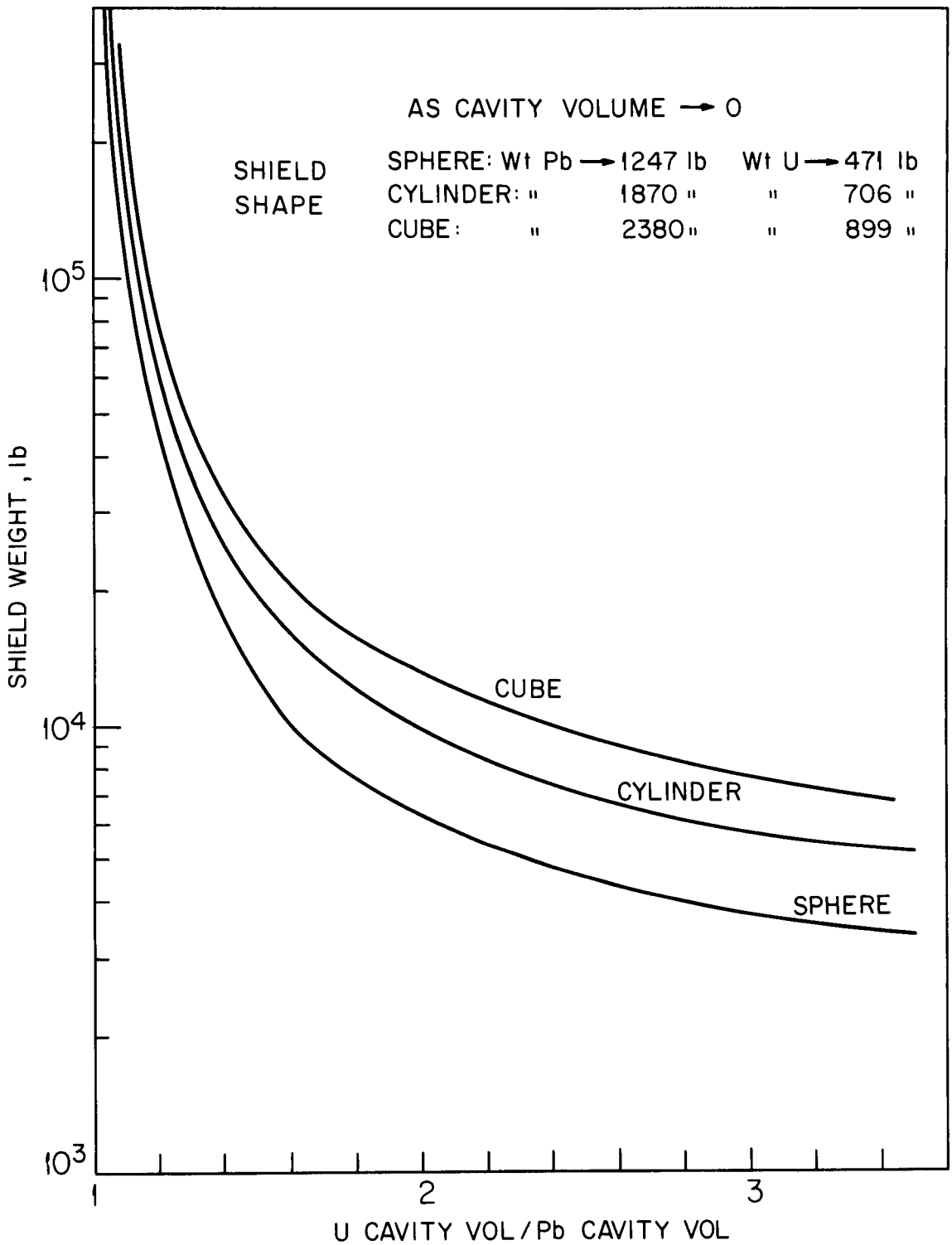



Fig. 4.5. Weight of shield vs ratio of U to Pb cavity volumes. U thickness 0.458 ft, Pb thickness 0.750 ft.

Because of its high density, uranium could replace part of the lead market in ammunition, weights, and ballast; however, at present the cost of uranium would probably have more influence on such a replacement than the advantage of increased density. The yearly consumption of lead in the United States for these products is quite high. In 1957, 42,509 short tons of lead was used in making ammunition, and 7526 short tons was used in weights and ballast.[22]

One interesting application for depleted uranium, developed by National Lead Company, is its possible substitution for tungsten alloys as counterweights for airplane ailerons. This use for uranium, although economically feasible, has not been widespread due to certain restrictions imposed by federal licensing regulations.[23]

d. Cathodic Protection. Cathodic protection is one method of suppressing the anodic reaction (oxidation) that occurs in electrochemical corrosion. When two dissimilar metals are in contact in a corrosive environment in which the more active metal (the one higher in the electromotive force series) does not become passive, the more active metal will be anodic. As the more active metal is corroded by the environment, the less active metal (acting as the cathode) is protected. The amount of protection and the distance over which the protection extends is dependent on such factors as the conductivity of the environment and the solution potential of the anodic metal.

The Bureau of Mines Station at Rolla, Missouri, initiated a program on April 1, 1959, to study the various possibilities of using depleted uranium for cathodic protection. The station hopes to develop information that will lead to such uses for depleted uranium as consumable anodes for underground pipe line protection. The advantages in using uranium rather than magnesium might be the decrease of the space required for the anodic metal and the increase in the time interval between replacement of the anodes.

In the electromotive series of metals uranium has a positive electrode potential of 1.4 volts, which is higher than that of a number of active elements (manganese, zinc, iron, etc.). Assuming a valence of II for magnesium, zinc, and iron and a valence of IV for uranium, it can be shown (using Faraday's law of electrolysis) that 1 in.$^3$ of uranium in a galvanic couple with iron could supply approximately the same amount of protection as 2 in.$^3$ of magnesium or 1.5 in.$^3$ of zinc. On a weight basis, however, it would require almost five times as much uranium to provide the same protection as magnesium.

The Rolla station has determined that in a strongly aerated 3.5 wt per cent NaCl solution, uranium performs satisfactorily as an anodic material in a galvanic couple with copper, iron, steel, and zinc. With the aerated NaCl electrolyte the galvanic current from the uranium anode was characterized by an initial rapid decay, which leveled out at a lower and almost constant value within 40-50 hr. This current decay was probably due to an oxide layer formed on the uranium surface which increased the cell resistance.

For the uranium—high carbon steel and uranium—iron galvanic couples the electromotive force or cell potential also experienced an initial rapid decay; however, there is no reason to assume that a similar decrease in electromotive force would occur in all electrode environments. Furthermore, the emf in these tests persistently favored the anodic decomposition of uranium in favor of those metals or alloys which are grouped below uranium in the electromotive series. Based on these results the Bureau of Mines will continue research on the possible use of uranium as a sacrificial anode.[24,25]

## 4.3 Uses for Uranium Alloys

a. Corrosion-resistant Alloys. There are three general classes of uranium alloys which appear to form and retain protective oxide films, even in oxygen-free water at temperatures up to 350°C: (1) certain metastable gamma-phase alloys, (2) certain supersaturated alpha-phase alloys, and (3) certain intermetallic compounds.[11]

Uranium alloys that contain more than 7 wt per cent molybdenum or niobium are examples of the first class and appear to have the lowest corrosion rates at elevated temperatures. The alloying element is dissolved in gamma uranium and retained as a metastable solid solution by cooling at a moderate rate. As long as the gamma phase is stable the corrosion rate remains low. By mildly heat-treating the alloy after rapid cooling, the corrosion resistance may be further increased. These metastable gamma-phase alloys are, however, susceptible to failure after long periods of time in air-saturated water at low temperatures. This failure is probably caused by the internal formation of uranium hydride.

The supersaturated alpha-phase alloys are typified by a uranium alloy containing approximately 3 wt per cent niobium. This particular alloy shows moderate corrosion rates (e.g., at 300°C in degassed or air-saturated water the weight loss is from 0.7 to 1.3 $mg/cm^2 \cdot hr$).[26] These alloys undergo a martensitic transformation upon cooling from the solid solution gamma phase; however, if the cooling is too slow, the normal alpha uranium is formed with the alloying elements precipitating in the form of compounds. These alloys are corrosion-resistant only so long as the martensitic structure is maintained. The supersaturated alpha-phase alloys are also susceptible to failure, as in the gamma-phase alloys, as a result of hydrogen penetration into the alloy structure.

The stable epsilon phase in the uranium-silicon system, $U_3Si$, is typical of the corrosion resistant intermetallic compounds. In the pure state $U_3Si$ shows corrosion rates similar to those for the supersaturated alpha alloys. The formation of $U_3Si$ requires that the temperature be maintained near the maximum for which the epsilon phase is stable for an appreciable time. This alloy has the advantage of providing stable corrosion resistance at temperatures where both the gamma phase and supersaturated alpha-phase alloys have overaged and thus lost their corrosion resistance. Other intermetallic compounds that show corrosion-resistant behavior similar to $U_3Si$ are $U_6Ni$, $U_6Fe$, and $UAl_2$. The application of these compounds is limited because of difficulties in fabrication.[11]

b. Alloys with Improved Mechanical Properties. Several elements, when added in small amounts, increase the high-temperature strength of uranium. Additions of approximately 0.5 per cent chromium or 2 per cent zirconium will increase the yield strength of uranium by a factor of 3 to 5. Silicon and aluminum also improve the properties of uranium when added in small amounts; however, as larger quantities are added, brittle intermetallic compounds are formed which decrease the fabricability.

In the uranium-base solid-solution-type alloys, very high strengths may be developed by means of a martensite-type transformation. Uranium alloys containing 5 to 10 wt per cent zirconium can be quenched from the gamma phase with the resultant formation of a martensitic alpha-like structure in which essentially all the zirconium is in a metastable solid solution. This martensitic or alpha-prime structure is very hard and strong. The precipitation of excess zirconium from the solid solution can be controlled by proper annealing or tempering to give a wide range of properties. Similar behavior is shown by the uranium binary systems with molybdenum, niobium, and titanium. Although these four binary systems appear to offer the best means of improving the high-temperature mechanical properties of uranium, it should be noted that the alpha-prime structure, and consequently the high strength, is lost by tempering or overaging during extended service at high temperatures.[11]

c. High-strength and Tool Steel Alloys. In a review of alloying elements used in the manufacture of steel, uranium applications have been summarized as follows: "Uranium holds no advantage over cheaper alloying constituents, but is sometimes used to replace part of the tungsten in tool steels. Additions of the order of 0.6 per cent to carbon steels impart increased strength and toughness without serious detriment to their ductility."[27] Although some uranium-containing steels were produced before World War II, the behavior of uranium in these steels was not understood, and consequently reported observations on the steel properties are almost worthless.[28]

From the binary phase diagram for uranium-iron, there is a negligible solubility of uranium in alpha iron, and the solubility of uranium in gamma iron is very small. A brittle intermetallic compound, $UFe_2$, occurs in the iron-rich alloys and forms a eutectic with gamma iron which melts at 1080°C. This temperature is below the normal hot-working temperature for carbon steels. If the iron-rich portion of the phase diagram is correct, there is no reason to believe that useful structural alloys would result from the addition of small amounts of uranium to iron.[28]

Uranium will dissolve in liquid iron, and since the free energy of formation of $UO_2$ is quite high, the uranium would deoxidize iron and its alloys. Since the density of uranium is higher than that of iron, the use of uranium as a satisfactory deoxidizer is questionable. The oxide

products would not rise to enter the slag as do $SiO_2$ and $Al_2O_3$. If uranium is to be added to iron or steel, it should be added to the deoxidized bath.[28]

Experimental work on high-speed uranium steels was done when uranium was placed below tungsten in the periodic table by people who expected uranium to be quite similar to tungsten and molybdenum. A popular high-speed steel contains 18 per cent W, 4 per cent Cr, 1 per cent V, and 0.70 to 0.75 per cent C. A portion of the tungsten is found in the hardened steel as complex carbides of iron and tungsten. The tungsten, which remains in solid solution, slows down the rate at which the steel softens when heated to a red heat. Molybdenum behaves similarly to tungsten and may be used to replace much of the tungsten in several grades of high-speed steel. Uranium added to a high-speed steel would probably be found in the carbide phase. There is no reason to believe that the presence of uranium as a carbide would be beneficial; however, experimental evidence may indicate otherwise.[28]

The Bureau of Mines station at Albany, Oregon, has undertaken a project to develop techniques for producing uranium alloy steels and subsequently to evaluate the effect of various uranium additions on the steel properties. The first steel which the Albany station has been trying to duplicate is a high-strength steel produced by C. T. Patterson at the close of World War I.[29] The composition of this steel is 1.4 per cent U, 2.0 per cent Ni, 0.3 per cent Si, 0.4 per cent C, and 0.6 per cent Mn. Approximately 40 years ago a steel of this composition was reported to have a tensile strength of 330,000 psi; however, the Albany group has not yet been able to produce steel specimens containing 1.4 per cent U which are amenable to heat treatment. Grain boundary stress cracks appear in the specimens upon forging. Steel specimens have been made containing 0.7 per cent and 0.35 per cent U which do not exhibit stress cracks after forging, but no data have yet been obtained on the mechanical properties of these specimens.[30]

To date, the Bureau of Mines has produced uranium steel by placing slugs of uranium and nickel in steel bar electrodes and melting in a consumable electrode-arc furnace. This method should be ideal for making small rapid melts and allows maximum control over the radiation health hazard. The uranium steel specimens, however, show uranium segregation at the grain boundaries, even after double and triple remelts including melting in a vacuum-induction furnace. Plans are underway to prepare a 40 per cent ferrous-uranium alloy by adding slugs of uranium to an iron rod and melting in the consumable electrode-arc furnace. If the ferrous-uranium alloy shows no uranium segregation, attempts will be made to duplicate the original Patterson steel by adding the ferrous-uranium alloy to steel electrodes and again melting in a consumable electrode-arc furnace.

If no positive results are obtained with the consumable electrode method, pellets of depleted uranium will be added to molten steel in a vacuum induction furnace. In the event that this method is also unsuccessful, the Bureau will try to duplicate Patterson's original process for making uranium steel, in which uranium oxide and excess coke were put in an open crucible lined with $U_3O_8$. A carbon electrode was lowered into the furnace, and an electric arc was formed between the carbon electrode and a steel nail driven through the bottom of the $U_3O_8$ crucible. Under the influence of the high temperature created by the electric arc, the uranium oxide was reduced by the coke to form molten uranium. A change in the sound of the arc indicated when oxidation of the coke was complete. Iron was added to the molten uranium to form a 40 per cent ferrous-uranium alloy. This alloy was then added to steel under closely controlled conditions in an electric-arc furnace to produce uranium steel.[29,30] It has been reported from different sources, however, that uranium produced by the reduction of its oxides with carbon contains appreciable amounts of uranium carbide.[17]

d. Bearings. Another investigation being made at the Bureau of Mines station at Rolla, Mo., is the possibility of using depleted uranium as one constituent of the hard compound in lead-base, tin-base, or copper-base alloys to be used as bearing metals. The Bureau hopes to develop a uranium-containing bearing that will have a unique property compared with other bearing metals and that would lead to practical applications.[24]

The Bureau has completed metallographic studies of lead-uranium alloys, cast under controlled conditions, containing up to 20 wt per cent uranium. These studies show that the lead-uranium alloys containing up to 8 wt per cent uranium consist of a lead matrix containing distinct angular cube crystallites of an intermetallic compound, $UPb_3$. The $UPb_3$ crystallites tend to lose the cuboidal shape and become rounded and partially agglomerated in alloys containing greater than 12 wt per cent uranium. The volume of uranium-lead compound occurring in the lead matrix increases from approximately 5 vol per cent for an alloy of 2 wt per cent uranium to about 80 vol per cent for an alloy containing 20 wt per cent uranium. The $UPb_3$ crystallites distribute themselves rather randomly through the lead matrix, and their distribution is not affected significantly by any moderate variation in cooling rate. There is a slight tendency for the $UPb_3$ crystallites to settle in the liquid lead; however, this effect should not create any significant fabrication problem.

The microstructures of the uranium-lead alloys containing between 2 and 8 wt per cent uranium suggest that these alloys may be useful in certain antifriction applications. The $UPb_3$ crystallites in these alloys are probably relatively hard, and it is known that the lead matrix containing these crystallites is very soft and malleable. The size and shape of the crystallites should be acceptable for a bearing alloy of the antimony-lead type.

The lead-uranium alloys must be evaluated by certain mechanical and physical tests before making a definite statement on the practical applications of the alloy. On the basis of available data the Rolla group will continue a study of the lead-uranium alloys, particularly in the range up to 8 wt per cent uranium. The Bureau also hopes to explore the possibilities of uranium in tin-base and copper-base alloys.[31]

## 4.4 References


1. J. R. Bridge et al., "X-ray Diffraction Determination of the Coefficients of Expansion of Alpha Uranium," J. Metals, 8 (Sec. II): 1282 (1956).

2. N. Allen, "Fourth and Fifth reports of Work on X-metal Carried out for the Metals Subcommittee of the Directorate of Tube Alloys," BR-579 (1945); BR-592 (1945).

3. C. W. Tucker, Jr., "The Crystal Structure of the Beta Phase of Uranium," Acta Crystallographica, 4: 425 (1951).

4. A. S. Wilson and R. E. Rundle, "The Structures of Uranium Metal," Acta Crystallographica, 2: 125 (1949).

5. K. Z. Morgan et al., "Report of Committee on Permissible Dose for Internal Radiation," 1958 revision (prepublication copy).

6. J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Natl. Nuclear Energy Series, Div. VIII, vol 5, McGraw-Hill, New York, 1951.

7. H. L. Laquer, W. E. McGee, and M. F. Kilpatrick, "The Elastic Constants of Uranium," Trans. Am. Soc. Metals, 42: 771 (1950).

8. A. N. Holden, "Physical Metallurgy of Uranium," Addison-Wesley, 1958.

9. A. H. Compton, "Metallurgical Project Report for Month Ending December 15, 1942," CT-393.

10. J. T. Waber, "A Review of the Corrosion Behavior of Uranium," LA-2035 or TID-4500 (includes 32 references), 14th ed. (1958).

11. C. O. Smith, "Notes on Reactor Materials Engineering for ORSORT Students," Part II, pp 527-75 (1958).

12. P. C. L. Pfeil, "The Constitution of Uranium-Molybdenum Alloys," J. Inst. Metals, 77: 553 (1950).

13. E. W. Colbeck, "The Metallurgy of Uranium," Metal Industry, 81: 361, 387 (1952).

14. "The Reactor Handbook," vol. 3, Sec. 1, AECD-3647, Technical Information Service, pp 383-436 (1955).

15. E. P. Blizard, "Nuclear Engineering Handbooks," Sec. 7, pp 60-116, McGraw-Hill, New York, 1958.

16. J. F. O'Sullivan, Keleket X-ray Corporation, letter to R. Armstrong, June 1, 1959.

17. C. A. Hampel, "Rare Metals Handbook," Reinhold, pp 501-61, 1956.

18. W. H. Piper and J. W. Langhaar, "70-Ton Shipping Cask for the Savannah River Plant—Design and Fabrication," DP-357 (1959).

19. L. B. Emlet, Union Carbide Nuclear Co., letter to S. R. Sapirie, September 9, 1957.

20. C. L. Storrs and J. M. Miller, "Shielding Properties of (Natural) Uranium," ORNL CF-53-9-96 (1953).

21. J. W. Marden, "The Production and Utilization of Thorium and Uranium," Trans. Electrochem. Soc., 66: 39 (1934).

22. Bureau of Mines, "Minerals Yearbook, 1957," vol. 1, U. S. Govt. Printing Office, Washington (1958).

23. A. Stewart, National Lead Co., personal communication, April 22, 1959.

24. J. Rowland and D. S. Walsh, Bureau of Mines Station, Rolla, Missouri, personal communication, June 25, 1959.

25. "Depleted Uranium for Cathodic Protection," (Bureau of Mines—Atomic Energy Commission Cooperative Research), unnumbered progress report for June, 1959.

26. H. A. Saller and F. A. Rough, "The Alloys of Uranium," Proc. Internatl. Conf. on Peaceful Uses of Atomic Energy, vol. 9, pp 33-68 (1955).

27. E. C. Pigott, "Cast Iron and Steel—Influence and Commercial Applications of Constituent Elements." Iron and Steel (London), 20: 519 (1947).

28. J. L. Gregg, Metallurgy Consultant at Oak Ridge National Laboratory, letter to John H. Frye, Jr., July 10, 1959.

29. C. T. Patterson, "The First Ferro-Uranium Made in America," Metal Prog., 71(6): 85-89 (1957).

30. W. Anable and C. Tout, Bureau of Mines Station, Albany, Oregon, personal communication, June 19, 1959.

31. "Depleted Uranium as a Constituent of Bearing Metals" (Bureau of Mines—Atomic Energy Commission Cooperative Research), unnumbered progress report for June, 1959.

# 5.0 CHEMICAL USES FOR DEPLETED URANIUM

S. Peterson, P. A. Haas, C. D. Scott

This section deals with the chemical uses of uranium and the uses of chemical compounds of uranium. Since depleted uranium is produced as uranium hexafluoride, it appears wise to consider using the fluoride value as well as the uranium; this is considered in the first part of the section. Uranium forms a tremendous number of compounds with many unique chemical and physical properties. There are a variety of known minor uses of uranium compounds; the most important uses have probably not yet been discovered. For this reason a survey of the chemistry of uranium and its compounds is included. The known uses of uranium and areas of probable use are grouped according to the catalytic properties, reducing ability, density, and other chemical and physical properties of uranium and its compounds.

## 5.1 Utilization of Fluoride Value of Uranium Hexafluoride

The present stockpile and future accumulations of depleted uranium hexafluoride represent a large capital investment in fluorine. Also, the storage of depleted uranium as uranium hexafluoride is more expensive than storage of a uranium compound (such as an oxide) which is less volatile, corrosive, and bulky. It would be desirable to recover and use the fluoride value from the uranium hexafluoride, while at the same time converting the uranium to a form usable for other applications and cheaper to store. Considering only the economics of storage and interest on capital investment in the fluorine, several years' storage of uranium hexafluoride would be more expensive than recovery of the fluoride content and storage as an oxide, even if after the storage period the oxide required reconversion to uranium hexafluoride. The fluoride value of the depleted uranium hexafluoride, if available, could be used in the present AEC program, reducing unit cost in the preparation of natural uranium fluorides for either metal production (uranium tetrafluoride) or for cascade feed (hexafluoride). There would probably be a commercial market for the recovered fluoride also.

The use of uranium hexafluoride directly as a fluorinating agent is one means of using the fluoride content. There is some knowledge fundamental to this use, and it appears that there could be limited application to the fluorination of organic compounds after sufficient development effort. It would be desirable to recover the fluoride content of uranium hexafluoride as elemental fluorine which could be used in the production of cascade feed and for which there would be a ready commercial market. Neither electrolytic nor thermal decomposition of uranium hexafluoride into its elements is at present technologically feasible or under investigation. Electrolysis of uranium hexafluoride is limited by lack of a satisfactory electrolyte below 590°K and of a satisfactory anode material at higher temperatures (graphite anodes can be used below 590°K .[1] Appreciable decomposition of uranium hexafluoride is expected above 2000°K at atmospheric pressure,[2] but a process taking advantage of this does not seem feasible at the present.

Technology is available for recovery of the fluoride value of uranium hexafluoride as both aqueous and anhydrous hydrogen fluoride. If this hydrogen fluoride is to be used in the present production scheme for the preparation of cascade feed uranium hexafluoride, at least one third of it should be anhydrous. Anhydrous hydrogen fluoride is needed for production of elemental fluorine, which in turn is required for the production of uranium hexafluoride from tetrafluoride. A small amount of anhydrous hydrogen fluoride is also necessary for metal-grade uranium tetrafluoride. It is estimated that aqueous hydrofluoric acid at a concentration as low as 70% could be used in the production of uranium tetrafluoride, but greater than 90% is preferable.[3-5] If lower concentration hydrofluoric acid is recovered, it may be upgraded by distillation or other techniques. Production of uranium hexafluoride by alternative processes, such as the Fluorox process[6] based on oxidation of uranium tetrafluoride with oxygen, could use concentrated aqueous hydrogen fluoride without requiring anhydrous hydrogen fluoride or elemental fluorine.

a. Available Technology for Recovery as Hydrogen Fluoride. There are several possible processes for the recovery of hydrogen fluoride from uranium hexafluoride. Some of these processes have been completely developed and are used in the present production scheme but most are in various stages of development.

Direct Conversion of Uranium Hexafluoride to Uranium Oxide with Recovery of Hydrogen Fluoride. The direct conversion of uranium hexafluoride to oxide and hydrogen fluoride seems to be the most straightforward approach for the recovery of the fluoride value as hydrogen fluoride if oxide is the desired form for the uranium content. Uranium oxide with less than 2% residual fluoride would be a desirable material for inexpensive storage.[3,5]

The simultaneous hydrolysis and reduction of uranium hexafluoride to form uranium dioxide and hydrogen fluoride is feasible, and the technology has advanced to the small pilot plant stage. This method combines hydrolysis of uranium hexafluoride,

$$UF_6 + 2H_2O \longrightarrow UO_2F_2 + 4HF$$

and reduction of the resulting uranyl fluoride,

$$UO_2F_2 + H_2 \longrightarrow UO_2 + 2HF$$

in a single process step. Thus, the over-all stoichiometry of the process is

$$UF_6 + 2H_2O + \longrightarrow UO_2 + 6HF$$

This process has been studied at the Paducah Gaseous Diffusion Plant[4] and Oak Ridge Gaseous Diffusion Plant[65] on a laboratory scale and is currently being investigated by the ORGDP[3] and by Argonne National Laboratory[7,8] in fluid bed reactors which are 6 and 1.5 in. in diameter,

respectively. The work at Paducah and at Oak Ridge is being done with major emphasis on recovery of concentrated hydrogen fluoride, while the work at Argonne emphasizes production of high quality uranium dioxide. The reaction appears to require a temperature in the range 900-1000°K. High concentrations of hydrogen fluoride can be obtained by using less than 100% excess steam, but larger amounts of steam are needed to obtain low residual fluoride content in the solid product. To date, higher than 80% aqueous hydrogen fluoride has been produced in the 6-in. reactor at 980°K with 2% residual fluoride, and 0.05% residual fluoride has been achieved in the 1.5-in. reactor at 870°K with 300% excess steam. Residual fluoride less than 2% indicates fluoride recovery of greater than 90%. Work is progressing on this process and it is probable that better fluoride recovery and higher hydrogen fluoride concentrations will be achieved. The primary reactor for such a process would probably be a continuous fluid-bed reactor with a uranium dioxide bed at 900-1000°K, and fluidization would be achieved with the reactants, uranium hexafluoride, steam, and hydrogen with possibly some nitrogen dilution.

Pyrohydrolysis of uranium hexafluoride results in the formation of $U_3O_8$ and hydrogen fluoride,

$$3UF_6 + 9H_2O \longrightarrow U_3O_8 + 18HF + 1/2\ O_2$$

Preliminary work at Paducah and at Oak Ridge National Laboratory indicates that the process would be feasible at temperatures in the range 1100-1200°K. At Paducah, steam and uranium hexafluoride were contacted in a small tower reactor at 1140°K; approximately 90% of the fluoride content was recovered as 70% hydrogen fluoride. At ORNL a concentrated uranyl fluoride solution was continuously sprayed into a fluid bed of $U_3O_8$ at 970°K, in a 3-in. reactor, resulting in greater than 95% recovery of the fluoride as less than 10% hydrofluoric acid. This method is still in a preliminary investigation-of-feasibility stage. If it proves feasible, it would have the advantage over the simultaneous hydrolysis and reduction process of not requiring hydrogen. The pyrohydrolysis may suffer from higher corrosion rates in the primary reactor since it has to be carried out at a higher temperature. The solid product, $U_3O_8$, would be suitable for economical storage.

Reduction of Uranium Hexafluoride to Uranium Tetrafluoride with Subsequent Reversion of the Uranium Tetrafluoride to Uranium Dioxide. A two-step process that will produce uranium dioxide and hydrogen fluoride is the hydrogen reduction of uranium hexafluoride to uranium tetrafluoride,

$$UF_6 + H_2 \longrightarrow UF_4 + 2HF$$

followed by pyrohydrolysis of the resulting uranium tetrafluoride to uranium dioxide and hydrogen fluoride,

$$UF_4 + 2H_2O \longrightarrow UO_2 + 4HF$$

The first step in this scheme, the so-called "6 to 4" reaction, is well-known and is used extensively on a production scale.

Laboratory thermobalance work done at several sites has shown that the equilibrium hydrogen fluoride concentration in the product of the pyrohydrolysis of uranium tetrafluoride can be as high as 90% at 950-1000°K.[7,8] This so-called "reversion" process (reverting uranium tetrafluoride to uranium dioxide and hydrogen fluoride) has been studied on an engineering scale in fluid-bed reactors at Argonne National Laboratory and at Weldon Spring and in one production-scale test at Weldon Springs. In these tests fluoride recoveries of up to 99% were achieved with hydrogen fluoride concentrations as high as 56%. Several problems of process control have been encountered, indicating that further investigation is needed before the process could be ready for production-scale operation.

One major advantage for this process over the other mentioned is the recovery of one third of the fluoride as anhydrous hydrogen fluoride in the "6 to 4" reaction. The fact that this would be a two-step process rather than a single step is a disadvantage.

Reduction to Uranium Metal with Hydrogen Fluoride Recovery from the Slag. If uranium metal is required from depleted uranium hexafluoride, the best process routes for fluoride recovery appear to be hydrogen reduction to uranium tetrafluoride, magnesium reduction of the uranium tetrafluoride to uranium metal,

$$UF_4 + 2Mg \longrightarrow 2MgF_2 + U$$

and pyrohydrolysis or acid treatment of the magnesium fluoride slag for recovery of the fluoride as hydrogen fluoride. As mentioned previously, the "6 to 4" reaction results in one third of the fluoride content being recovered as anhydrous hydrogen fluoride. It appears that the pyrohydrolysis of magnesium fluoride slag will yield aqueous hydrogen fluoride. This process has been investigated on a laboratory scale by the Oak Ridge Gaseous Diffusion Plant, Weldon Spring, and the Fernald Feed Materials Production Center, and, according to R. Koch of the U. S. Bureau of Mines Experiment Station at Albany, Oregon, it would produce suitable hydrogen fluoride for converting gamma alumina to aluminum fluoride.

Upgrading of Aqueous Hydrofluoric Acid. In several processes under consideration aqueous hydrofluoric acid rather than anhydrous hydrogen fluoride is the fluoride product. If anhydrous hydrogen fluoride is desired, it would be necessary to upgrade the aqueous acid.

For very dilute hydrofluoric acid, an azeotropic still may be used for upgrading to the water-HF azeotrope (38% HF). One of these units is currently in use at the Weldon Spring Plant. To further upgrade the

azeotrope by distillation it would be necessary to add a third component such as sulfuric acid to break the azeotrope. Hydrofluoric acid more concentrated than the azeotrope can be upgraded to near anhydrous HF by distillation.

Some work has been done on use of NaF as a concentrating agent both at Oak Ridge Gaseous Diffusion Plant and at the U. S. Bureau of Mines Experiment Station at Albany, Oregon. In this process, sodium fluoride is contacted with a dilute hydrogen fluoride vapor stream which results in reaction of the hydrogen fluoride with sodium fluoride to form $NaHF_2$ while letting the steam escape. The $NaHF_2$ can be decomposed by heat to the original sodium fluoride and anhydrous hydrogen fluoride. It would be desirable to recycle the sodium fluoride and thus achieve a seemingly inexpensive separation process. Limited work at the Oak Ridge Gaseous Diffusion Plant showed difficulty in recycling the sodium fluoride, and the work at Albany is in a very preliminary stage.

b. Comparison of Hydrogen Fluoride Recovery Processes. It appears that there is technology available for recovering the fluoride value of uranium hexafluoride as either anhydrous hydrogen fluoride or aqueous hydrofluoric acid. The choice of a specific process for this recovery would be dependent on the desired uranium product and on the over-all economics involved. A more thorough investigation would be necessary for good economic evaluation, but it is possible to make a process choice based on the presently available technology.

No present process has been demonstrated on an engineering scale to convert all the fluorine in uranium hexafluoride to 100% anhydrous hydrogen fluoride without HF upgrading. Two major process routes appear to be competitive for production of anhydrous hydrogen fluoride when combined with aqueous hydrogen fluoride upgrading: (1) the two-step process of hydrogen reduction to uranium tetrafluoride and pyrohydrolysis of uranium tetrafluoride to uranium dioxide and hydrogen fluoride, and (2) the direct reaction of uranium hexafluoride to a uranium oxide and hydrogen fluoride, either by simultaneous hydrolysis and reduction or by pyrohydrolysis alone.

The two-step method will produce one third of the hydrogen fluoride as anhydrous hydrogen fluoride; however, it involves one additional process step.

If aqueous hydrofluoric acid is acceptable as the recovered fluoride, the direct conversion of uranium hexafluoride to an oxide either by simultaneous hydrolysis and reduction or by pyrohydrolysis alone would be the most desirable process. It should be emphasized that these processes will be able to produce concentrated aqueous hydrogen fluoride (certainly greater than 70%) although not anhydrous.

c. Use of Uranium Hexafluoride as a Fluorinating Agent. One third of the fluorine in uranium hexafluoride comes from elemental fluorine. The difficulty of recovering this fluorine in the elemental state has been pointed out. Since uranium hexafluoride is very reactive, it appears that some elemental-fluorine value could be recovered by fluorination of organic compounds with uranium hexafluoride. Gibson[10] has considered the possible reactions by which uranium hexafluoride could convert inexpensive organic compounds to Freons and fluorocarbons. Actual experimental effort has not been directed at obtaining useful fluorinated products from uranium hexafluoride, but some knowledge of the fluorination reactions can be derived from investigations of trichloroethylene[11] and carbon tetrachloride[12] as reducing agents for uranium hexafluoride.

The reactions of chlorinated hydrocarbons with uranium hexafluoride, in order of decreasing ease, are: addition of fluorine to double bonds, replacement of hydrogen with fluorine, replacement of chlorine with fluorine, breaking a carbon-carbon bond, and polymerization. The last of these is favored by allowing hydrogen fluoride by-product to remain with the organic products. The difference in ease of these reactions is not great, so a mixture of products is obtained. At 30°C the fluorination product of trichloroethylene is about two thirds $CHFCl\text{-}CFCl_2$ and one third $CF_2Cl\text{-}CFCl_2$. At higher temperatures additional products are more highly fluorinated compounds, one-carbon products, and a high-boiling residue. Carbon tetrachloride is fluorinated to a mixture of one-carbon fluorochlorocarbons. It appears that if these or any other reactions are used to manufacture fluorinated organic compounds, there will have to be a separation process for the mixed products. The carbon tetrachloride reaction gives a very satisfactory uranium tetrafluoride product. The trichloroethylene reaction has been adapted to a continuous pilot plant[12] but is not used in production because the uranium tetrafluoride product is of too low packed density and too high carbon content. These difficulties can be remedied by additional steps in the process.

It appears that reactions of uranium hexafluoride can produce useful fluorinated organic compounds; development work would be needed before such a useful process could be realized. Mixed products would result, requiring separation. There is doubt that uranium tetrafluoride of good quality would result without making the process considerably more complicated than the present hydrogen reduction.

## 5.2 Survey of Uranium Compounds

Being a very active metal, uranium forms compounds with all the nonmetals. For the most part, these compounds exhibit oxidation states from +3 to +6; the same range of states is observed in the solution chemistry of uranium. The complicated chemistry of uranium appears to arise from a combination of the 5f electron orbitals and the large size of the atom; a large number of electronegative atoms or molecular groups can surround and combine with the uranium atom.

A very complete critical compilation of chemical information available in 1949 on the simpler compounds of uranium was made by Katz and Rabinowitch[14]. Less extensive but broader and more recent treatments are in the collection edited by Seaborg and Katz[15] and the volume by Katz and Seaborg.[16]

a. Uranium Aqueous Solution Chemistry. The principal species in acidic aqueous solution of the four oxidation states of uranium are $U^{3+}$, $U^{4+}$, $UO_2^{+}$, and $UO_2^{++}$. The oxidation potentials[17]

$$U^{3+} \xrightarrow{0.631\ \text{volt}} U^{4+} \xrightarrow{-0.605\ \text{volt}} UO_2^{+} \xrightarrow{-0.063\ \text{volt}} UO_2^{++}$$

$$\underbrace{\qquad\qquad -0.334\ \text{volt} \qquad\qquad}$$

point out some important features of uranium solution chemistry. The +3 state is very unstable with respect to evolving hydrogen from solution, and the +5 with respect to disproportionation. Uranium in +4 solutions is a moderately strong reducing agent and the +6 solutions are quite stable.

The +3 oxidation state of uranium in aqueous solution is obtained by dissolution of the trihalides or by reduction of higher states electrolytically or with very powerful reducing agents such as active metals. The resulting solutions are unstable, evolving hydrogen and converting uranium to the +4 state. The persistence of uranium(III) solutions is somewhat improved by high chloride concentrations. Precipitation behavior of uranium(III) is similar to that of rare earth ions.

Dark green uranium(IV) solutions are readily obtained from uranium(VI) by chemical, electrochemical, or photochemical reduction. Solutions are quite stable if protected from air. High acidity or complex formation is necessary to prevent hydrolysis leading to colloid formation or to precipitation of hydroxide or of basic salts. The hydroxide, phosphate, and fluoride are very insoluble and are not dissolved by excesses of the anions. The other halides and the sulfate are very soluble. Sulfate and oxalate form stable complexes; the oxalate is also readily precipitated from solution. Complex formation by chloride is appreciable even at fairly low concentrations. Many common oxidizing agents convert uranium(IV) in solution to uranium(VI).

Uranium(V) in aqueous solution is observed only as an intermediate in oxidation-reduction reactions involving other states.

Solutions of uranium(VI) usually show the bright fluorescent yellow of uranyl ion, $UO_2^{++}$. No acid, complexing agent, or other reagent is capable of separating two oxygen atoms from the uranium except by reduction to the +4 state or lower. Uranyl nitrate, sulfate, and halides are very soluble in water. The uranyl ion forms complexes with all anions, exhibiting a tendency toward a maximum coordination number of 8, including the two oxygens. Nitrate and chloride anions at high concentrations enter the coordination sphere of the uranyl ions. Anions that precipitate uranyl ion, such as oxalate and carbonate, when in excess often form complex anions. Quite numerous are complexes formed from uranyl ion and three oxygenated anions, such as sulfate, sulfite, oxalate, carbonate, acetate and other carboxylates, and even nitrate. Apparently two oxygen atoms from each of three anions are arranged about the uranium atom in a plane perpendicular to the line of the uranium and the uranyl oxygen atoms. Fluoride complexing of uranyl ion is so great that uranyl fluoride is ordinarily considered a weak electrolyte, and uranyl fluoride anions are known. The ability of many organic oxygen compounds to enter the coordination sphere along with anions is responsible for the well-known extractability of uranyl nitrate by organic solvents.

Only under a rather limited set of conditions can uranyl ion be precipitated as the hydroxide $UO_2(OH)_2$ (sometimes written as $H_2UO_4$ or $UO_3 \cdot H_2O$). Bases are ordinarily said to precipitate uranium as "diuranates" such as $(NH_4)_2U_2O_7$ and $Na_2U_2O_7$, but the precipitates are variable in composition and probably complex mixtures. Uranium(VI) can exist in alkaline solution only as complexes including $UO_2(CO_3)_3^{4-}$ and some peroxyuranates. Uranium is very completely precipitated from solutions of low acidity, with good separation from other metals, by hydrogen peroxide.

b. Simple Inorganic Compounds of Uranium. Uranium reacts rapidly with hydrogen at 250°C to form the pyrophoric black or brown hydride, $UH_3$. This in turn decomposes to finely powdered metal on heating in a vacuum or at higher temperatures. The hydride can be stabilized against spontaneous ignition by controlled oxidation. It is a powerful reducing agent and a useful material for the preparation of many pure uranium compounds.

Uranium fluorides containing 3, 4, 4.25, 4.5, 5, and 6 fluorines per uranium are prepared by gas-solid reactions under anhydrous conditions. Those between $UF_4$ and $UF_6$ in composition disproportionate to these on heating. The hexafluoride, well-known for its high volatility, is very reactive, being especially sensitive to water. The other fluorides are high-melting solids. The tetrafluoride can be precipitated from aqueous uranium(IV) solutions as a hydrate. The only well-established oxyfluoride is uranyl fluoride, $UO_2F_2$.

The other halides and oxyhalides of uranium are very hygroscopic and soluble in water, giving solutions of the corresponding oxidation states. Prepared by gas-solid reactions are $UX_3$ and $UX_4$ with all three halogens, $UX_5$, $UO_2X_2$, $UOX_2$, and $UOX_3$, with chlorine and bromine, and $UCl_6$. The uranium(V) compounds in water give a mixture of the +4 and +6 states. The brown oxychloride, $UOCl_3$, has been prepared from an equimolar mixture of $UO_2Cl_2$ and $UCl_4$ at 370-390°C,[18] the red-brown oxybromide from $UO_3$ and $CBr_4$ in dry nitrogen at 110°C,[19] and the black-brown pentabromide from $UO_3$ and excess $CBr_4$ at 126°C in a sealed tube.[20] Except for the uranyl halides, the compounds containing uranium in oxidation states above +4 are decomposed at relatively low temperatures. Several mixed uranium(III) and (IV) halides are known. Uranium(IV) halides are often volatile at temperatures near 600°C. The uranyl halides, as typical uranyl salts, form addition compounds with a variety of basic substances. Their hydrates can be prepared from solution.

The oxides of uranium are numerous and often variable in composition. Three are of greatest interest and importance. Uranium trioxide, $UO_3$, is the "orange oxide" of uranium technology, formed by decomposition of oxygen-rich uranium compounds, such as the nitrate and peroxide, below 450°C. Several hydrates are known, and the color varies from yellow to red depending on hydration and other factors. It dissolves readily in acids to give uranyl salt solutions. The green-black "black oxide," $U_3O_8$, is the usual product of ignition of uranium compounds in air at 700-900°C. It dissolves readily in acids under oxidizing conditions. Various treatments can alter the composition while maintaining the $U_3O_8$ crystal structure. Ignition of uranium compounds in hydrogen or decomposition at extremely high temperatures (>1500°C) leads to the very refractory brown to black "brown oxide," $UO_2$. This compound is a common intermediate in the manufacture of uranium and its compounds; it is readily converted to tetrahalides and other compounds by gas-solid reactions. The crystal structure of the dioxide can accommodate changes in composition, both variations of the O/U ratio above stoichiometric and incorporation of many other metal oxides. Other oxides, of limited ranges of stability, are UO, $U_4O_9$, and $U_3O_7$. The pale yellow peroxide, $UO_4 \cdot 2H_2O$, obtained by precipitation, is said to form $U_2O_7$ on partial decomposition.

Reactions of uranium and its compounds with sulfur and hydrogen sulfide[21] give a polysulfide, $US_3$, three allotropic forms of $US_2$, $U_3S_5$, $U_2S_3$, US, and UOS, all stable solids. Uranyl sulfide is precipitated from solution by ammonium sulfide. Analogous selenides $USe_3$, $USe_2$ (again three forms), $U_3Se_5$, and UOSe are similarly obtained.[22] Uranyl selenide and uranium tellurides have been reported.

Nitrides of uranium are made from the hydride and the calculated quantity of ammonia or nitrogen. The light-gray mononitride is stable to at least 1700°C, but it is attacked by air or water vapor. Any compositions

between $U_2N_3$, which decomposes in vacuum at 700-800°C, and $UN_2$, which requires high nitrogen pressures to exist, are a single solid phase. Uranium phosphides, arsenides, and antimonides are also known.

The excellent refractory UC is made from uranium oxides and graphite at 1800°C or from metal and various sources of carbon. Physical properties have been studied[23] extensively because of the possibility of using uranium monocarbide as a nuclear fuel. The dicarbide is prepared at 2400°C; it is quite reactive at relatively low temperatures. A sesquicarbide is also known. Uranium metal combines with boron and silicon to form the refractory compounds USi, $USi_2$, $USi_3$, $UB_2$, and $UB_4$. Molten-salt electrolysis of $U_3O_8$ and boric acid can also produce the tetraboride and a higher boride, $UB_{12}$. Uranium tetrafluoride reacts with aluminum borohydride to form green volatile crystalline pyrophoric uranium(IV) borohydride, $U(BH_4)_4$. This and its methyl derivatives are probably the most volatile uranium compounds other than the hexafluoride.

c. Uranium Salts. Many normal, complex, and basic uranous, or uranium(IV), salts are known to crystallize from solution. The halides have been described already. The soluble sulfate is known as several hydrates and at least two basic salts. Salts of all the phosphorus oxyacids have been precipitated from solution, as well as double salts of uranous phosphate with fluoride and with perchlorate. There are acid, basic, and normal oxalates. There are many complex phosphates and oxylates of the alkali metals. Basic salts of weak acids such as sulfite and formate are also known.

Uranyl nitrate crystallizes from solution with six, three, or two molecules of water. The latter cannot be dried without decomposition, but the anhydrous nitrate may be obtained by heating $UO_2(NO_3)_2 \cdot 2NO_2$, which is formed by the action of liquid $N_2O_4$ on uranium oxides. Uranyl halides have been described above. Like the halides, the nitrate forms addition compounds with many bases and complex salts with the alkalis. Basic uranyl chloride and bromide may be crystallized from solution, but not basic nitrate or perchlorate. In addition to the normal salts there are many complex salts of uranyl ion with organic anions such as oxalate, formate, acetate, propionate, and salicylate. An especially long series of complex acetates is known, comprising double acetates of several singly and doubly charged cations and triple acetates containing both doubly and singly charged ions of other metals.

Uranates are generally insoluble in water. They are prepared either by precipitation with base from uranyl salt solutions or by ignition of double salts or mixtures of salts containing metals in the correct proportions. Alkali uranates of formula $M_2UO_4$ and $M_2U_2O_7$ and alkaline earth uranates of formula $MUO_4$, $MU_2O_7$, and $M_3UO_6$ are known. The precipitate from sodium hydroxide and uranyl solutions has been found to be, according to one report,[24] a mixture of $Na_2U_2O_7$ and $Na_2U_{16}O_{49}$ (the latter being

converted on washing with water to $Na_2U_7O_{22}$) and according to another,[25] a series of compounds $Na_2U_nO_{3n+1}\cdot nH_2O$ with n ranging from 3 to 16. Uranates of urea, $CO(NH_2)_2$,[26] and of choline, $[(CH_3)_3NCH_2CH_2OH]OH$,[27] can be precipitated from solution.

d. Organic Compounds of Uranium. No compounds are known, in spite of many attempted preparations, with uranium bonded covalently to carbon. In nearly all the known organic uranium compounds the uranium replaces the "active hydrogen" from a number of molecules of alcohol, amine, mercaptan, or chelating agent. An exception is the deep red cyclopentadienyl complex $(C_5H_5)_3UCl$ made from sodium cyclopentadiene and anhydrous uranium(IV) chloride in tetrahydrofuran. It is stable to at least 300°C, melts at 265°C, and sublimes in vacuum at 180°C. It is a weak electrolyte in water and precipitates a number of anions. Uranium pentachloride reacts with pyridine, hydrogen chloride in alcohol, and thionyl chloride to form a pyridinium chlorouranate(V), $(C_5H_6N)_2UOCl_5$.[28]

Anhydrous uranium tetrachloride reacts with the lithium derivative of diethylamine to yield $U[N(C_2H_5)_2]_4$, from which can be obtained uranium tetramercaptides, $U(SR)_4$, and tetraalkoxides, $U(OR)_4$, where R represents a simple carbon radical. These are green liquids or low-melting solids, some of which can be distilled under vacuum but all of which are decomposed on heating or by water. The mercaptides are pyrophoric. Attempted preparation of uranium(IV) dialkyl dithiocarbamates has led to a series of compounds, $[RR'NH_2][UO_2(RR'NCS_2)_3]$.[29]

By oxidation reactions of the tetraalkoxides, by the action of sodium ethoxide on uranium pentachloride, or from alcohol, ammonia, and $(C_5H_6N)_2UOCl_5$ one obtains pentaalkoxides, $U(OR)_5$. Several of these compounds have been prepared by treating the ethoxide with an excess of the appropriate alcohol. The pentaalkoxides are generally green to brown solids or liquids, sensitive to water, and usually volatile under vacuum. The red pentamethoxide sublimes at 200°C without melting. The pentaethoxide is a dark brown liquid, readily distilled at 110°C under high vacuum and quite stable below 170°C. Its physical properties and thermal stability have been thoroughly investigated.[30] The ethoxide reacts with hydrogen chloride to give $UCl_n(OC_2H_5)_{5-n}$, n = 1, 2, or 3, and with metal ethoxides to give $NaU(OC_2H_5)_6$, $Ca[U(OC_2H_5)_6]_2$, and $Al[U(OC_2H_5)_6]_3$. The sodium compound is saltlike; the calcium and aluminum compounds sublime under vacuum at 200° and 111°C, respectively. The trifluoroethoxide, $U(OCH_2CF_3)_5$, forms addition compounds with amines. The pentaalkoxides can be oxidized to the volatile but unstable red hexaalkoxides, $U(OR)_6$. A remarkably stable complex alkoxide is formed from sodium aluminum isopropoxide and uranium tetrachloride:

$$UCl_4 + 4NaAl(OR)_4 \longrightarrow 4NaCl + U[Al(OR)_4]_4$$

where R = $-CH(CH_3)_2$. This compound boils, with slight decomposition, under normal atmospheric pressure at 270°C.

The greatest number of organic uranium compounds are the chelate complexes, of both uranium(IV) and uranyl. They are normally precipitated

or extracted from aqueous solutions of uranous or uranyl salts by treatment with base and the organic reagent. The replacement of hydrogen from four organic molecules by uranium satisfies the coordination number of 8, so uranium(IV) chelates are generally quite stable liquids of appreciable volatility. The two uranyl oxygen atoms plus the two chelating groups do not satisfy the maximum coordination or neutralize the polar force field about the uranium atom, so uranyl chelates are generally fairly high-melting nonvolatile solids and often form addition compounds with water, alcohol, ammonia, organic bases, or extra molecules of chelating reagent. The most extensive series of uranium chelates are those of the dicarbonyl compounds, $R\text{-}CO\text{-}CH_2\text{-}CO\text{-}R'$; the organic radicals can be any of a large variety. Dozens of these compounds have been combined with both uranium(IV) and uranyl. Uranyl chelates with 8-hydroxyquinoline and some of its substitution products precipitate with an added molecule of reagent; this can be removed by heating.

## 5.3 Catalytic Uses of Uranium Compounds

The literature on the use of uranium compounds as catalysts is limited to experimental evaluations with no important commercial applications. Early studies were prompted partly by the placing of uranium in the same group on the periodic chart of the elements as chromium, molybdenum, and tungsten. The correct location in the actinide series is a less promising one as far as catalytic activity is concerned. While catalytic activity has been demonstrated for a number of reactions, there are none for which uranium is a clear-cut first choice on the basis of performance. If any clear superiority of uranium is found, it is likely to be on the basis of selectivity or for use as a promoter for some other catalytic material.

a. Petroleum Refining. Uranium compounds have been found to have catalytic activities of the types necessary in petroleum refining processes. Whether or not these are of economic value can be determined only by experimental studies. Excellent results are claimed for the polymerization of ethylene[31] and for the dehydrogenation of propane to propylene.[32] A general evaluation of transition metal oxides[33] did not disclose any distinctive activity by uranium compounds. Other references indicate a tendency to form cyclic and aromatic compounds. Patents have been issued for the use of uranium oxides as alkylation and catalytic cracking catalysts.[34,35]

Tests being made at the U. S. Bureau of Mines Petroleum Research Center at Laramie, Wyo. on uranium catalysts for oil shale refining will determine the immediate future of petroleum refining applications. Catalysts must be evaluated on a comparison basis, and the previous work on shale oil refining will provide the background necessary for evaluation of uranium compounds. Shale oils are particularly difficult to refine, with hydrogenation, desulfurization, cracking, and re-forming all being necessary, and a high degree of catalytic activity by uranium for any of these processes should be detectable. Initial studies were with about 10% uranium oxides deposited on activated alumina. Reaction conditions were 890-1000°F, 1500-3000 psi total pressure, hydrogen overpressure, and 1 vol of oil per hour per volume of catalyst. Tests of uranium sulfides as catalysts and of uranium compounds as promoters for other catalysts are planned.[36]

b. Organic Synthesis. Uranium compounds are reported to be excellent for certain selective oxidations such as for the production of aldehydes. Examples are oxidation of toluene to benzaldehyde,[37] methane to formalin,[38] and toluene to benzaldehyde and benzoic acid.[39] Application to preparation of butadiene from ethyl alcohol, to selective dehydrogenations, and to Fischer-Tropsch syntheses were tested without notably good or bad results.

c. Inorganic Catalysis. A uranium metal—uranium carbide mixture was suggested by Haber[40] as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. A later reference[41] reported the use at 500°C of uranium carbide made by heating an oxide and resin lampblack in an arc furnace. A $U_3N_4$ compound was suggested as the active catalyst. Uranium metal reacts with nitrogen to give first UN and then $U_2N_3$. The $U_2N_3$ reacts with hydrogen to give ammonia and UN. It is possible to write a set of reactions combining nitrogen and hydrogen to give ammonia with uranium nitrides as intermediate compounds which can be considered catalysts. The traditional ammonia synthesis catalysts are prepared as iron oxides fused with several per cent aluminum oxide and potassium carbonate. In operation, the hydrogen and heat result in a catalyst of iron metal and aluminum and potassium oxides. Avoiding poisoning, particularly by carbon monoxide and hydrogen sulfide, is a major problem for ammonia synthesis and the iron catalyst is considered especially rugged and durable.

Uranium compounds have been tested as catalysts for inorganic oxidations, particularly photochemical oxidations and oxidations of hydriodic acid. None of the results appear promising for commercial uses. $UO_2$ was not a good promoter for $TiO_2$ in the oxidation of carbon monoxide, and $U_3O_8$ was a poor catalyst for the oxidation of sulfur dioxide to sulfur trioxide. Patents have been issued on the use of uranium as a catalyst for the formation of hydrogen cyanide from nitrogen, hydrogen, and carbon monoxide.

## 5.4 Uranium as a Reducing Agent

As a very electropositive metal, uranium is reactive as a reducing agent toward many substances, particularly when heated. Only the inert gases will not combine with uranium. Thus uranium is quite useful in high-vacuum work as a getter or for freeing helium or argon from traces of nitrogen, oxygen, or other gases; it is often favored over other materials by workers in atomic energy laboratories who have ready access to metallic uranium. Research should turn up other applications; it is doubtful whether these uses could ever be a large fraction of production since very-large-scale reductions demand less expensive reducing agents.

Massive uranium metal is difficult to control in its reactions with oxidizing substances. Uranium hydride or uranium powder formed by hydride decomposition probably will find many applications. The metal powder is often pyrophoric, but this can be corrected by treatment with zinc chloride solution.[42] Uranium metal has been useful in the laboratory for purifying hydrogen,[43] either by passing the gas over the powder (from hydride decomposition) at 700-750°C or by forming and decomposing the hydride. The

latter gives purification even from inert gases. Reduction of heavy water by uranium is a convenient laboratory preparation of deuterium gas.[43] Uranium reacts with Tetralin and Decalin to form $UH_3$ and presumably naphthalene,[43] suggesting the use of uranium for dehydrogenation of organic compounds. (Note: Uranium metal might be considered an oxidizing agent in this use.) Uranium hydride reduces maleic anhydride and nitrobenzene to unidentified products.[44]

## 5.5 Uses of Uranium Compounds Depending on Their High Densities

Since uranium is a very heavy element, one would expect some applications of uranium and its compounds to result from their high densities. The metal is denser than any of its compounds and in many applications would be preferred over its compounds. These applications are discussed in Sec. 4. There are a number of cases where the compounds would be preferable; for example, when the metal is not stable to the expected environment and protective cladding either is too expensive, is impossible, or adds excessive low-density material. These eventualities are not unreasonable, considering the high reactivity of metallic uranium. Some binary uranium compounds and their densities, in grams per cubic centimeter, are UN, 14.32; UC, 13.6; $U_2C_3$, 12.88; $UB_2$, 12.71; $UC_2$, 11.68; $UN_2$, 11.3; $U_2N_3$, 11.24; $UO_2$, 10.97; $UH_3$, 10.9; US, 10.87; UOS, 9.60; $UB_4$, 9.38; $USi_2$, 9.25; $UF_3$, 8.95; $U_3O_8$, 8.38; $UO_3$, 8.34. Some metal uranates are also of high density, and uranium compounds are generally denser than analogous compounds of other elements. Many of these could be used for compact weights under conditions where metallic uranium is unsuitable.

a. Heavy Media for Mineral Separation. An application of high-density materials is in the use of heavy media for mineral separations. Liquids of density 3.0 or greater are of special value. Many such liquids are known,[45] but they are so expensive that their use is limited to laboratory investigations. Such liquids include highly halogenated organic compounds such as methylene iodide, $CH_2I_2$; and acetylene tetrabromide, $C_2H_2Br_4$; and concentrated aqueous solutions such as those of thallous formate and thallous malonate. In plant-scale separations[46] aqueous slurries of galena (PbS of density 7.4-7.6 g/cc), ferrosilicon (density 6.3-7.0 g/cc), and magnetite (density 5.0-5.2 g/cc) have been used successfully, although the application is obviously limited to separation of rather coarse ore particles.

Slurries. The technical feasibility of using uranium compounds is being investigated under the direction of R. V. Lundquist at the Boulder City, Nevada, station of the Bureau of Mines. The first experiments planned are with aqueous slurries of dense uranium compounds. As of June 22 no such experiments had been performed, but an apparatus had been built for small-scale evaluation of slurries, and $U_3O_8$ was on hand as the first material to try. Denser uranium compounds will be tried also. Because of the high densities of uranium compounds, less concentrated suspensions would be required, having lower viscosity and thus requiring less agitation. Or, if desired, a higher density could be obtained and thus a wider range of applicabilities.

It has been suggested by Morris Fine of the Bureau of Mines Rolla station that a good solid for heavy-medium slurries would be a uranium alloy that is stable to water, magnetic, hard, and brittle. Magnetic separations are inexpensive and useful for recovering slurry medium—hence the successful application of ferrosilicon and magnetite. Naturally the material must be easily ground to a suitable particle size. It may be wise to examine known uranium alloys for meeting these criteria, although stability to water may be difficult to obtain without such heavy alloying that the high density is sacrificed. Perhaps particles of $UO_2$ or UC coated with iron or nickel may have suitable properties.

Solutions. Since a slurry cannot be used for separating an ore so intimately mixed with gangue that fine grinding is required, a stable liquid of density 3.0 g/cc and of reasonable cost would be useful. One might expect organic uranium compounds, organic solutions of uranium compounds, and aqueous uranium solutions to be possible liquids for this application.

Because of the very high coordination number of uranium, stable organic molecules containing uranium must contain a rather large number of light atoms such as oxygen, carbon, hydrogen, and fluorine. Thus a high-density compound is impossible. For example, the stable liquid uranium pentaethoxide, $U(OC_2H_5)_5$, has a density of 1.7 g/cc. Mixed halide-alkoxide liquids of possibly higher density are known, but their densities are not reported. These include $UCl_n(OC_2H_5)_{5-n}$ where n is 1, 2, or 3. Since the density of $UCl_5$ is only 3.81 g/cc, it is unlikely that the chloroalkoxides are very dense.

Organic solutions of uranium salts are well known from work on solvent extraction processes, but several organic molecules are required to coordinate each uranium ion, so again the over-all density is not high. Uranium tetrahalides (such as $UBr_4$) will dissolve in a number of organic liquids, but the solubility is too low to give a high density. Some uranium salts have extremely high solubilities in water, but in most cases the light anion and the minimum water needed for solution are enough to bring the density below levels of interest. Solutions of uranyl chloride and bromide offer the most promise as uranium-base high-density liquids. The uranous salts should also form solutions of high density, but these would be susceptible to atmospheric oxidation.

The maximum density of a uranyl chloride solution (at 25°C) has been reported[47] as 2.842 g/ml; at ORNL[48] the saturated solution has been found to be of 2.725 g/ml density. No advantage is gained at room temperature by dissolving $UO_3$ in this saturated solution since the basic salt, $UO_2(OH)Cl \cdot 2H_2O$, precipitates.[47] This salt has a high positive temperature coefficient of solubility, so higher density uranyl chloride—uranium trioxide solutions may be possible at slightly elevated temperatures. Uranyl bromide solutions are said to be unstable to oxidation, but concentrated solutions prepared in this laboratory[48] appear to have excellent stability with density up to 3.3 g/ml. This dense solution is very deep red, nearly opaque, very hygroscopic, and of high but as yet unmeasured

viscosity. On repeated evaporation, as might be necessary during use to compensate for dilution by atmospheric moisture or by washings, loss of acidity takes place, leading to precipitation of yellow $UO_2(OH)Br \cdot 2H_2O$, a previously unreported compound. This loss of acidity would have to be compensated for by addition of hydrobromic acid.

There is some question as to the value of a high-density liquid for gravity separation of minerals. Slurries work very well, and if the ore particles are too small for separation in a slurry, their settling rates in a viscous solution would be too slow to be practical. For separation of light minerals where true liquids have been available, their use has not been completely satisfactory. Perhaps the best way[49] to use a dense liquid would be as a medium for centrifugal separation of minerals, in which the finely divided ore, suspended in a liquid of density between those of ore and gangue, is fed to a hydraulic cyclone separator. It should be remarked that uranyl halide solutions, as media for these separations, have application only to acid-resistant minerals; alkaline materials such as limestone would destroy the solution.

b. Uranium Compounds for Radiation Shielding. The use of depleted uranium metal in radiation shielding is discussed in Sec. 4.2. Uranium compounds should similarly be effective as shielding materials, but probably no more so than lead in most cases where uranium metal is unsatisfactory. The use of high-density uranium solutions has been suggested for radioactive-cell windows. The light absorption of these solutions is a great disadvantage for this application. The uranyl bromide solutions described above are opaque at a thickness of only 1 cm. It is possible that the chloride would transmit sufficiently in the yellow part of the spectrum to be used, but it would probably be inferior to existing window materials.

## 5.6 Uses Depending on Chemical Properties

Uranium forms many compounds with a great variety of properties. It is therefore reasonable to expect that making known these compounds and their properties would lead to a variety of uses, although perhaps not tonnage uses. The uses of uranium as a reducing agent, of uranium hexafluoride as a fluorinating agent, and of uranium compounds as catalysts have been considered in previous sections.

a. Analytical Uses. Varied use of uranium has already been found in analytical chemistry. The ability of uranyl ion to form many stable double and triple acetates is useful in the detection of several metal cations, particularly in microchemistry. Noteworthy is the detection of sodium which precipitates as a triple acetate with uranyl and zinc ions without interference by other alkali cations. In volumetric analysis uranous sulfate solutions have been useful as a reducing agent and uranyl nitrate as a precipitant for phosphate and arsenate. Since uranyl ion is coordinatively unsaturated, it forms a large variety of complexes, some of which might have analytical application. One recent example[50] uses uranyl acetate solution to develop paper chromatograms to detect meso-inosotol.

b. Ion Exchange by Uranyl Phosphates. The use of uranyl phosphate has been suggested[51] for the immobilization of fission product wastes. One difficulty with most methods of immobilizing wastes is that one of the main radioactive components of old waste is cesium-137 which, as an alkali metal, forms very few insoluble compounds. Since the double phosphate $CsUO_2PO_4$ is insoluble, uranyl phosphate will carry cesium along with the other fission products which are normally phosphate-insoluble. Thus uranyl phosphate can immobilize cesium as well as other metals. This is related to an observation that precipitation of uranyl ammonium phosphate does not always effectively decontaminate the uranium from fission product cesium. Uranium alkali phosphates exhibit ion-exchange properties, and thus depleted uranium double phosphates could be used as ion exchangers to sorb cesium from radioactive wastes. Uranyl hydrogen phosphate and uranyl sodium phosphate would probably be the best of these exchangers for cesium sorption. These materials may also have other applications as ion exchangers.

c. Miscellaneous Useful Uranium Reactions. Recent preliminary experiments[52] have shown that sulfate solutions containing uranium(III), because of the reducing power of the latter, are excellent for descaling stainless steel and decontaminating it from fission products. Uranium compounds have had some medical application and some use as insect repellants; the pharmacological properties of uranium have been reviewed in an annotated bibliography.[53] Uranium salts have had photographic application, particularly in the toning of prints and the intensification of negatives. Uranium salts have been used as textile mordants and the borate as a rubber additive. Uranyl nitrate crystals in sodium silicate solution produce a rapidly growing yellow column. This could be suggested to the marketers of materials for "inorganic gardens" if the toxicity of uranium can be tolerated. Chlorine can be purified by pass-it over $UCl_4$ at 400°C, during which oxygen impurity reacts to form uranyl chloride.[54] This purification and several other laboratory gas purification methods using uranium and its compounds are described by Newton.[55] Uranyl ion quantitatively sensitizes the photochemical oxidation of oxalic acid in aqueous solution; this reaction has been used to calibrate the intensity of light in photochemical apparatus. It may be that this is a clue to a possible application of uranium in conversion of light to other forms of energy.

## 5.7 Uses Depending on Physical Properties

Uranium and its compounds have unique physical properties which could lead to uses for depleted uranium. A number of properties which are known to afford uses are considered below.

a. Radiation Sources. Depleted uranium can serve as a low-intensity source of radiation, alpha from its own decay and beta-gamma from its daughters, Th-234 and Pa-234. Natural uranium oxide is often used for standards for testing radiation-measuring systems, and depleted uranium could serve as well except where an established isotopic composition is needed to relate mass to intensity; depleted uranium would have a variable U-235 content. While such uses would not consume a great deal of uranium,

it appears that for many cases depleted uranium could be useful for instrument checking, discharge of static electricity, and other purposes calling for low-intensity ionizing radiation.

b. Electrical. Uranium trioxide and uranates have been considered[56] for use as solid conductors for fuel cells, but rejected as having too low conductivity. Uranium metal has been used as electrodes for arc lights, as an ultraviolet-sensitive element in photoelectric tubes, and as a target for x-ray production. Possibly wider electrical applications could arise from the semiconductor properties of uranium dioxide.

The literature reports many conflicting values of the electrical conductivity of uranium dioxide. The crystal structure of the dioxide is capable of accommodating a considerable variation in composition without formation of a new phase, and it is very likely that many samples have contained nonstoichiometric oxygen/uranium ratios or appreciable impurities. A more recent set of measurements[57] gives the effect of added oxygen on the electrical conductivity of $UO_2$ over a wide temperature range. The conductivity of uranium dioxide can also be varied by incorporation of oxides of other metals. A considerable increase in thermal conductivity is obtained[58] by incorporation of 2% $Y_2O_3$ or $Nb_2O_3$; it is logical to expect increases also in electrical conductivity. The dark-blue solid solutions of $UO_2$ and $CeO_2$ have enhanced electrical conductivity over pure $UO_2$.[59] Reported application of these properties has not been extensive. A uranium dioxide element in series with the tungsten filament of high-intensity incandescent lamps smooths out current surges, protecting the filament. Thermistors made of $UO_2$ have been found excellent in sensitivity but poor in reproducibility for the detection of infrared and microwaves.[60]

c. Ceramic Uses. The best known nonnuclear use of uranium has been in ceramic glazes, which can be fired to a variety of brilliant colors with uranium oxides as the coloring agents. This use of uranium has been resumed in spite of the high price and unique restrictions on uranium. Removal of these obstacles could increase the uranium use, although probably not to more than a few tons per year. A more important use of uranium in ceramics is probably the use of $UO_2$ in industrial refractories. Uranium dioxide is stable and maintains its strength to extremely high temperatures except under oxidizing conditions. There are many records in the atomic energy projects, where there has been rather free availability of uranium, of the use of uranium dioxide crucibles for high-temperature operations, such as the melting of uranium. There is no doubt that this usefulness could be made more widespread with greater availability of uranium. Also, the properties of uranium dioxide are readily modified by additives, giving it a wider range of usefulness. The importance of uranium dioxide as a material for reactor fuel elements has led to a very large amount of recent work in the nuclear power reactor field on the physical properties, fabrication, and modification of uranium dioxide. For example, the properties of $UO_2$ powder prepared by many reactions from a variety of starting materials have been compared by Clayton and Aronson.[61] The properties and fabrication of $UO_2$ have

been extensively reviewed by Runnals.[62] Uranium dioxide is not stable to oxygen, but its structural integrity on oxidation can be maintained by the incorporation of lanthanum oxide.[63]

Some metal uranates are very refractory and stable to oxidizing environments; it appears that ceramics fabricated from them could be developed for purposes for which the dioxide is inadequate. Uranium monocarbide also has excellent ceramic properties. Like the dioxide it is useful as nuclear fuel, and thus its properties and fabrication are under active development. Also like the dioxide, it is unsuitable under oxidizing conditions.

The incorporation of uranium oxides in ordinary glass to make a yellow fluorescent glass is well known. Other colors of glass can be made by incorporating uranium in other glasses under various conditions.[64]

d. Uranium Compounds as Pigments. Uranium forms compounds with a wide variety of intense colors, and thus many uranium-based pigments are possible. The application of uranium compounds to coloring ceramics and glass has already been discussed. It is to be expected that the coloring power of uranium compounds should have much wider application if the price is sufficiently low. Naturally the toxicity of uranium will prevent some applications, such as in paints for children's furniture, but similar limitations exist for the use of lead pigments. The luminescence of many uranium compounds should give especially brilliant yellows of far greater stability than organic pigments. Paints for highway marking could very well make use of the brilliance and stability of uranium pigments.

The uranates and different forms of uranium trioxide afford a variety of yellows and oranges. Red forms of $UO_2$ and $UO_3$ have been reported, but they are not stable. Several peruranates are red, but they may be too unstable for pigment use. A stable red oxidation product of uranyl sulfide is known. Uranium tetrafluoride is green, but not of great intensity or brilliance. Solid solutions of uranium and cerium dioxides are a deep blue.[59] The stable oxide $U_3O_8$ is greenish black. Uranium dioxide can be brown or black; browns and blacks are also known among the reduction products of the uranates.

## 5.8 References

1. W. R. Rossmassler, R. L. Harris, and T. J. Mayo, "On the Electrolytic Generation of Fluorine from Uranium Hexafluoride," Report KY-287 (1959) (confidential).

2. L. Brewer et al., "The Thermodynamic Properties and Equilibria at High Temperature of Uranium Halides, Oxides, Nitrides, and Carbides," Report MDDC-1543, p. 69 (declassified 1947); also in TID-5290, p. 234 (1958).

3. Conference between C. D. Scott of ORNL and J. H. Pashley and H. L. Kaufman of ORGDP, at ORGDP, May 26, 1959.

4. Conference between C. D. Scott of ORNL and W. C. Philoon, L. G. Weber, J. A. Fellows, and C. Kuhlman of Weldon Spring Feed Materials Plant, at Weldon Spring, June 29, 1959.

5. Conference between C. D. Scott of ORNL and R. W. Levin, J. C. Gillespie, W. R. Golliher, W. Rossmassler, S. Bernstein, W. Pedigo, V. Katzel and E. W.Powell of Paducah Gaseous Diffusion Plant, at Paducah, July 1, 1959.

6. C. D. Scott, J. C. Bresee, and J. B. Adams, "The Fluorox Process: The Production of $UF_6$ in a Fluid Bed Reactor," ORNL-2797 (1959).

7. Conference between C. D. Scott of ORNL and W. A. Rodger, N. M. Levitz, and I. E. Knudsen of Argonne National Laboratory, at ANL, June 26, 1959.

8. S. Lawroski et al., "Chemical Engineering Division Summary Report, January, February, March 1959," ANL-5996, pp. 183-189.

9. J. W. Simmons, editor, "Summary Technical Report for the Period July 1, 1958 to September 30, 1958," NLCO-760, pp. 51-67 (confidential).

10. J. D. Gibson, "Survey of Reactions by which Useful Fluorocarbons or Chlorofluorocarbons may be Produced by the Fluorination of Available Materials with $UF_6$," Oak Ridge Gaseous Diffusion Plant internal memo, KLI-828 (1951) (secret).

11. H. A. Bernhardt, J. H. Junkins, S. S. Kirslis, and J. C. Posey, "Batch Reduction of Uranium Hexafluoride to Uranium Tetrafluoride by Means of Trichloroethylene," K-348 (1949) (confidential).

12. J. S. Nairn, D. A. Collins, and J. C. Taylor, "The Reduction of Uranium Hexafluoride by Carbon Tetrachloride," Proc. 2nd Internatl. Conf. on Peaceful Uses of Atomic Energy, P/300, vol. 4, p. 191, U.N., New York, 1959.

13. S. H. Smiley and D. C. Brater, "Continuous Processes for the Direct Reduction of Uranium Hexafluoride to Uranium Tetrafluoride of High Purity and Density," ibid, 523, vol. 4, p. 197; "Conversion of Uranium Hexafluoride to Uranium Tetrafluoride," p. 171, Process Chemistry, Series III, vol. II, Pergamon Press, London, 1958.

14. J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Natl. Nuclear Energy Series, Div. VIII, Vol. 5, McGraw-Hill, New York, 1950.

15. G. T. Seaborg and J. J. Katz, editors, "The Actinide Elements." Natl. Nuclear Energy Series, Div. IV, Vol. 14A, McGraw-Hill, New York, 1954.

16. J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen and Co., London, and Wiley, New York, 1957.

17. W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, New York, 1952.

18. S. A. Shchukarev, I. V. Vasil'kova, N. S. Martynova, and Yu. G. Mal'tsev, "On the Heat of Formation of Uranium Chlorides and Monoxytrichlorouranium," Zhur. Neorg. Khim., 3: 2647 (1958).

19. J. Prigent, "A New Uranium(V) Oxybromide," Compt. rend., 236:710 (1953).

20. J. Prigent, "Preparation of Uranium Pentabromide," Compt. rend., 239: 424 (1954).

21. M. Picon and J. Flahaut, "The Sulfides of Uranium," Bull. soc. chim. France, 1958: 772.

22. P. Khodadad and J. Flahaut, "On Uranium Polyselenide," Compt. rend., 244: 462 (1957); P. Khodadad, "On the Selenides of Uranium(IV)," ibid., 245: 934 (1957); "Uranium Oxyselenide," ibid., p. 2286; "Uranium Selenide $U_3S_5$," ibid., 247:1205 (1958).

23. For example, C. A. Smith and F. Rough, "Properties of Uranium Monocarbide," NAA-SR-3625 (1959).

24. J. Sutton, "Hydrolysis of $UO_2^{++}$ and Formation of Sodium Uranates," J. Inorg. and Nucl. Chem. 1:68 (1955).

25. J. Malý and V. Veselý, "Chemistry of Sodium Polyuranates," Jaderná Energie, 4: 371 (1958).

26. P. S. Gentile, L. H. Talley, and T. J. Collopy, "Chemistry of Uranyl Nitrate-Hydroxide-Urea Systems," J. Inorg. and Nuclear Chem., 10: 110 (1958).

27. G. Soye, "On the Preparation of Uranates of Choline," Compt. rend., 248: 3565 (1959).

28. D. C. Bradley, B. N. Chakravarti, A. K. Chatterjee, "Quinquevalent Compounds of Uranium. I. Alkoxides and Complex Chlorides," J. Inorg. and Nuclear Chem., 3: 367 (1957).

29. H. Albers and S. Lange, "Alkylammonium Uranyl Dithiocarbamates," Chem. Ber., 85: 278 (1952).

30. T. I. Taylor, E. R. Smith, J. L. Torgesen, H. Matheson, and J. K. Taylor, "Properties of Uranium Pentaethoxide," AECD-3144 (1946, declassified 1951); also in TID-5290, p. 369 (1958).

31. Y. Konaka, "Catalytic Polymerization of Ethylene under Ordinary Pressures. VI-VII," J. Soc. Chem. Ind. Japan, 41: suppl., p. 22 (1938).

32. M. Kurokawa and Y. Takenake, "Formation of Propylene by Dehydrogenation of Propane," J. Soc. Chem. Ind. Japan: suppl., p. 45 (1941).

33. A. Clark, "Oxides of the Transition Metals as Catalysts," Ind. Eng. Chem., 45: 1476 (1953).

34. G. A. Mills, "Catalytic Conversion of Hydrocarbons," U. S. Patent 2,453,152 (Nov. 9, 1948).

35. E. A. Stahly and E. M. Hattox, "Catalytic Reactions of Olefins," U. S. Patent 2,278,677 (April 7, 1942).

36. "Progress Report on Depleted Uranium Studies," U. S. Bur. Mines unnumbered memo, June 1959.

37. D. Bigalli, "Catalytic Oxidation of Toluene in the Vapor Phase to Benzaldehyde," Engenharia e quim., 2 No. 4: 7 (1950).

38. A. Matsui et al., "Formation of Formalin from Methane and Air by Direct Oxidation," J. Soc. Chem. Ind. Japan, 43: suppl. p. 117 (1940).

39. W. G. Parks and J. Katz, "Vapor Phase Catalytic Oxidation of Organic Compounds-Toluene," Ind. Eng. Chem., 28: 319 (1936).

40. F. Haber, "On the Production of Ammonia from Nitrogen and Hydrogen," Z. Elektrochem., 16: 244 (1910).

41. F. Haber and F. C. Greenwood, "Researches on Ammonia. VII. The Action of Uranium as Catalyzer in the Synthesis of Ammonia from Its Elements," Z. Elektrochem., 21: 241 (1915).

42. J. Dubuisson, A. Houyvet, E. LeBoulbin, and C. Moranville, "Preparation and Sintering of Uranium under Pressure," Rev. met., 56: 55 (1959).

43. F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns, and A. H. Daane, "Uranium Hydride—Preparation, Composition, and Physical Properties," Nucleonics, 4 No. 1: 4 (1949).

44. A. S. Newton, J. C. Warf, F. H. Spedding, O. Johnson, I. B. Johns, R. Nottorf, J. A. Ayres, R. W. Fisher, and A. Kant, "Uranium Hydride—Radiochemical and Chemical Properties," Nucleonics, 4 No. 2: 17 (1949).

45. J. D. Sullivan, "Heavy Liquids for Mineralogical Analysis," U. S. Bur. Mines Tech. Paper 381 (1927).

46. A. F. Taggert, "Handbook of Mineral Dressing," pp. 106-125 of section 11, Wiley, New York, 1945.

47. C. A. Kraus, "Properties of Aqueous Solutions of Some Uranyl Salts," A-360 (1942).

48. S. Peterson, ORNL, unpublished experiments, 1959.

49. Suggestion of Morris Fine, U. S. Bur. Mines, Rolla, Mo., June 25, 1959.

50. P. Meredith and H. G. Sammons, "Reaction between meso-Inosotol and Uranyl Acetate," Analyst, 83: 686 (1958).

51. Howard Whetsel, ORNL, private communication, 1959.

52. A. B. Meservey, ORNL, unpublished experiments, 1959.

53. L. J. LaFrance, "Uranium and its Compounds. Annotated Bibliography with Particular Reference to Pharmacology and Toxicology," UR-166 (1951).

54. O. Johnson, T. Butler, and A. S. Newton, "Preparation, Purification, and Properties of Anhydrous Uranium Chlorides," TID-5290, pp. 1-28 (1958).

55. A. S. Newton, "Use of Uranium and Uranium Compounds in Purifying Gases," TID-5290, pp. 74-80 (1958).

56. E. Bauer and H. Preis, "Fuel Cells with Solid Conductors," Z. Elektrochem., 44: 695 (1938).

57. M. J. Brabers, "Electrical Conductivity of Uranium Oxides," Proc. 2nd Internatl. Conf. on Peaceful Uses of Atomic Energy, P/1474, Vol. 6, p. 122, U. N., New York, 1959.

58. H. Shapiro and R. M. Powers, "Uranium Dioxide with Improved Thermal Conductivity," SCNC-271 (1959).

59. W. Rudorff and G. Valet, "The Mixed-Crystal Series $UO_2$-$CeO_2$," Z. Naturforsch., 7b: 57 (1952).

60. J. Prigent, "A Study of Uranium Oxide Thermistors," J. phys. radium, 10: 58 (1949).

61. J. C. Clayton and S. Aronson, "Preparation and Characteristics of $UO_2$ Powder," WAPD-178 (1958).

62. O. J. C. Runnals, "$UO_2$-Fabrication and Properties," Nucleonics, 17, No. 5: 104 (1959).

63. W. B. Wilson, "Stabilization of $UO_2$ by Valence Compensation," BMI-1318 (1959).

64. W. Colbert and N. J. Kreidl, "Unusual Colors Produced by Uranium in Glasses," J. Optical Soc. Am., 35: 731 (1945).

65. S. Smiley, "Engineering Development Department Contribution to the Quarterly Report, 1st Fiscal Quarter, FY 1959, KL-257 (1958) (secret).

ORNL-2889
UC-4 Chemistry-General
(TID-4500 (15th ed.)

## INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R. C.
28. A. M. Weinberg
29. L. B. Emlet (K-25)
30. J. P. Murray (Y-12)
31. J. A. Swartout
32. E. H. Taylor
33. E. D. Shipley
34-35. F. L. Culler
36. M. L. Nelson
37. W. H. Jordan
38. C. P. Keim
39. J. H. Frye, Jr.
40. S. C. Lind
41. A. H. Snell
42. A. Hollaender
43. K. Z. Morgan
44. M. T. Kelley
45. T. A. Lincoln
46. R. S. Livingston
47. A. S. Householder
48. C. S. Harrill
49. C. E. Winters
50. H. E. Seagren
51. D. Phillips
52. W. K. Eister
53. F. R. Bruce
54. D. E. Ferguson
55. R. B. Lindauer
56. H. E. Goeller
57. C. W. Hancher
58. R. A. Charpie
59. J. A. Lane
60. M. J. Skinner
61. R. E. Blanco
62. G. E. Boyd
63. W. E. Unger
64. A. T. Gresky
65. E. D. Arnold
66. C. E. Guthrie
67. J. W. Ullmann
68. K. B. Brown
69. K. O. Johnsson
70-79. J. C. Bresee
80. P. M. Reyling
81. J. R. Muir
82-83. S. D. Clinton
84. B. R. Fish
85. P. A. Haas
86. W. H. Lewis
87. R. A. McNees
88. S. Peterson
89. C. D. Scott
90. E. G. Struxness
91. M. E. Whatley
92. H. B. Whetsel
93. R. G. Wymer
94. D. L. Katz (consultant)
95. I. Perlman (consultant)
96. M. Benedict (consultant)
97. C. E. Larson (consultant)
98. H. Worthington (consultant)
99. J. H. Rushton (consultant)
100. ORNL - Y-12 Technical Library, Document Reference Section

## EXTERNAL DISTRIBUTION

101. Division of Research and Development, AEC, ORO
102. Montana State College (L. Berg)
103-104. Bureau of Mines, Laramie, Wyoming (H. M. Thorne)
105-108. Union Carbide Nuclear Company (Y-12 Plant, 1 copy each to C. P. Coughlen, J. M. Googin, C. R. Patterson, Jr., and F. S. Patton)
109-114. Union Carbide Nuclear Company (ORGDP, 1 copy each to W. S. Dritt, D. M. Lang, C. H. Mahoney, J. H. Pashley, S. H. Smiley, and P. R. Vanstrum)

115. University of Tennessee (L. C. Emerson)
116-117. Union Carbide Nuclear Company (Paducah, 1 copy each to R. W. Levin and C. Powell)
118. Argonne National Laboratory (A. Jonke)
119-120. Bureau of Mines, Boulder City, Nevada, D. Blue)
121-124. Oak Ridge Operations Office (1 copy each to R. B. Martin, G. Rennich, J. W. Ruch, and J. Vanderryn)
125-126. Battelle Memorial Institute (H. Nelson)
127-128. Mallinckrodt Chemical Works, Weldon Springs, (W. Philoon)
129-130. Bureau of Mines, Albany, Oregon, (L. Banning)
131. Clemson College, (G. C. Robinson)
132. Argonne National Laboratory (W. A. Rodger)
133-134. Bureau of Mines, Rolla, Missouri (J. Rowland)
135. Union Carbide Nuclear Company (Y-12 Plant, C. M. West)
136. National Lead Company, Fernald (J. O. Davis)
137-138. U. S. Department of Interior, Bureau of Mines, Washington, D. C. (1 copy each to J. E. Crawford and T. H. Miller)
139-695. Given distribution as shown in TID-4500 (15th ed.) under Chemistry-General category (75 copies - OTS)