

DEPLETED-URANIUM USES R&D PROGRAM

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ABSTRACT

The U.S. government has - 500,000 metric tons (t) of surplus depleted uranium (DU) stored at U.S. Department of Energy sites across the country. This material is mostly stored in the form of depleted uranium hexafluoride (DUF_6), resulting from enrichment operations. DOE has decided to convert the DUF_6 inventory to a more chemically stable form. DOE has initiated the DU Uses Research and Development (R&D) Program to ensure the most effective disposition of the converted DU. This program will explore potential beneficial uses of the converted DU, the fluorine associated with the DUF_6 , and emptied carbon-steel DUF_6 storage cylinders, which were used during conversion of the DUF_6 . Additionally, the government will also carry out research activities necessary to ensure the direct disposal of these materials to the extent that cost-effective and realistic beneficial uses are not found. This paper describes the principal activities of the DU Uses R&D Program.

1. INTRODUCTION

The U.S. government has - 500,000 metric tons (t) of surplus depleted uranium (DU) stored at U.S. Department of Energy (DOE) sites across the country. This material, mostly depleted uranium hexafluoride (DUF_6), resulting from enrichment operations, is the largest mass of nuclear material in DOE's inventory. On August 2, 1999, DOE issued a *Record of Decision (ROD) for Long-Term Management and Use of Depleted Uranium Hexafluoride*. This ROD indicated that DOE has decided to promptly convert the DUF_6 inventory to a more chemically stable form.

DOE is subject to a number of requirements that call for research and development (R&D) on DU disposition. Public Law 102-486 [PL 1992] requires DOE to prepare a study that identifies DU tailings available for conversion to commercial use. Public Law 105-204 [PL 1998] requires that DOE undertake a good-faith effort to consider the recycle (i.e., beneficial use) of DU and of the associated fluorine and cylinders associated with it. In response to this legislation, DOE prepared a document, *Depleted Uranium Materials Use Roadmap*, which is a guide to R&D activities for materials associated with its DUF_6 inventory. The roadmap is built upon the analysis performed and documented in the final *Programmatic Environmental Impact Statement for Alternative Strategies for the Long-Term Management and Use of Depleted Uranium Hexafluoride* (DOE April 1999). The roadmap is being implemented by a DOE-sponsored DU Uses R&D Program, the principal activities of which are described in the rest of this paper.

2. REPOSITORY APPLICATIONS

Oak Ridge National Laboratory (ORNL) scientists have proposed a new spent nuclear fuel (SNF) package fill technology in which DU dioxide is placed in the voids of SNF waste containers for storage, transport, or disposal (Forsberg December 1996). This concept is intended to provide shielding, reduce the potential for repository nuclear criticality events, and reduce the long-term release of radionuclides from SNF at the repository. In this concept, empty waste packages (WPs) would be loaded with SNF. The void space between the fuel pins and outer void between SNF assemblies and the inner WP wall, which would ordinarily be filled with helium gas, would instead be filled with small depleted UO_2 particles. The repository WP would then be sealed. The use of fill material (not uranium oxides) has been extensively investigated for Canadian WPs. The thin-walled, particulate-packed containers were selected as the design for the reference engineering study for the Concept Assessment Phase of the Canadian Nuclear Fuel Waste Management Program [Teper and Reid 1989].

The presence of the highly dense UO_2 would reduce the external shielding requirements and radiation dose to repository materials. In addition, the depleted UO_2 has the theoretical potential to provide two additional advantages, which remain to be proven in practice. First, the depleted UO_2 should reduce the probability of short-term and long-term nuclear criticality incidents by lowering the average enrichment inside the WP to well below 1 wt % ^{235}U equivalent. Second, the UO_2 fill has the potential to reduce the long-term release of radioactive constituents of the SNF into the environment by reacting with groundwater before the water reaches the fuel material. Such a reaction should suppress dissolution of the SNF via multiple chemical mechanisms: maintenance of chemically reducing conditions within the WP, saturation of the groundwater in the degraded WP with uranium, and reduction of degraded WP permeability to air and water flow. The use of DU as fill material in SNF packages is estimated to consume approximately one-half of the entire DU inventory.

Some of these improvements may be possible when DU oxide particulates are used as a component of invert and backfill material at the repository. Waste repository “invert” is material placed in the bottom of the tunnel to form a flat foundation for operating equipment and WPs. Once all WPs are placed in the repository and it is decided that in situ monitoring and human activities can cease, the repository tunnels may be loaded with material termed “backfill,” which, according to current plans, will be crushed native rock. Some of the potential advantages of using DU oxides as fill material in WPs listed above may apply to the use of DU oxides as a component of repository invert and backfill materials. Figure 1 shows a schematic of DU applications in a high-level waste repository.

Current research revolves around three sets of technical issues: (1) material characteristics and insertion—optimal particle sizes and shape, chemical form, binder/diluent for backfill and invert, insertion techniques for fill and backfill; (2) performance improvement—determining the nature, extent, and probability of potential benefits to improving crush resistance, and ameliorating shielding, criticality, and radionuclide dissolution and transport issues; and (3) performance degradation—determining the nature, extent, and probability of potential adverse impacts such as increased temperatures or damage caused by insertion of fill or backfill.

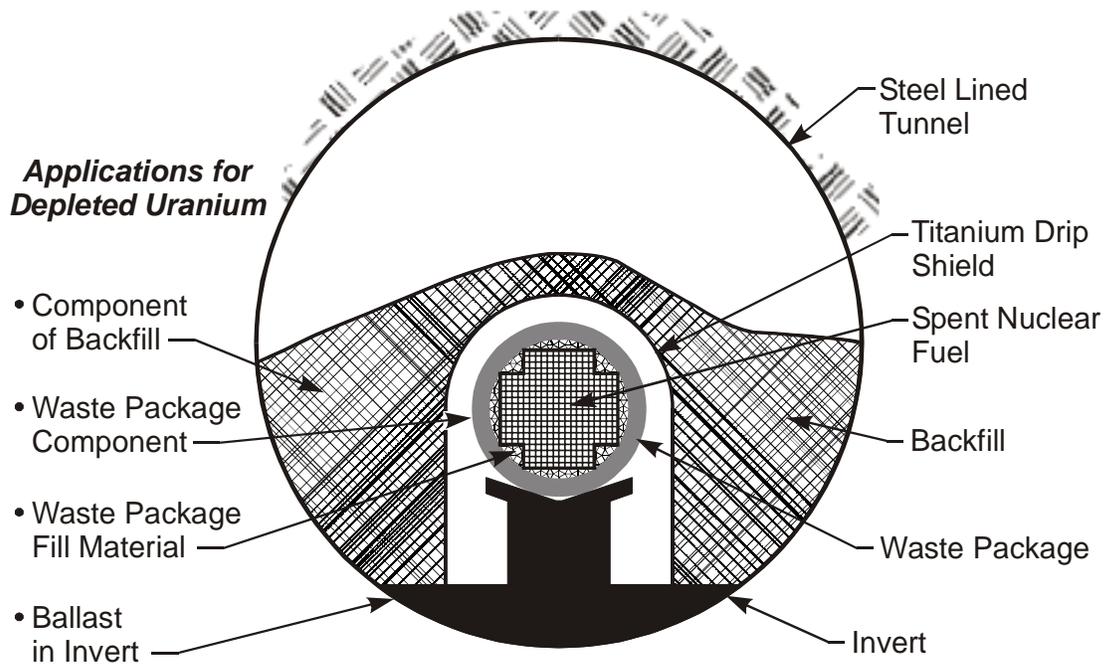


Fig. 1. Schematic of potential depleted uranium uses at a high level waste repository.

3. RADIATION SHIELDING PRODUCTS

Because of its high density, a large potential market for DU exists in radiation shielding from x-rays or gamma rays for radiation protection. DU metal has been used in such applications, but its relatively high cost has justified such use only when its high density can justify the premium. DU in either oxide or carbide form could be used as a component of the primary shielding material in containers designed to store and, in some cases, dispose of SNF, and low-level or high-level radioactive wastes. The high density of uranium compounds makes them excellent components as shields from photon radiation.

One attractive DU shielding concept involves making a “heavy” concrete using a DU compound as one of the components of the concrete. If a DU compound is used to make the concrete, the same shielding performance could be achieved with up to half the thickness required of normal concrete, depending on the form of the DU. In this approach, the uranium compound is substituted for the coarse aggregate in conventional concrete and is enclosed between annular stainless steel shells that make up the body of the container to provide predictable structural strength.

The most advanced DU concrete technology involves converting the DU to uranium dioxide particles, aggregating the particles into briquettes using a special binder, and sintering the briquettes to form a dense aggregate called DUAGG [Lessing September 1995]. The DUAGG is combined with conventional concrete-forming materials (e.g., cement, sand, and water) to form an ultra-high-density concrete named DUCRETE™. This concrete weighs 6,407 kg/m³ (>400 lb/ft³), as compared to 2,114 kg/m³ (- 132 lb/ft³) for conventional concrete [Quapp, Lessing, and Cooley 1995]. DUCRETE™ has been patented in the United States for DOE. Starmet Corp. of Concord, Massachusetts, has entered into an exclusive world-wide license agreement to commercialize the DUCRETE™ process. Starmet has installed pilot-scale equipment at its Barnwell, South Carolina, facility.

DUCRETE™ has also been proposed for use in constructing dry SNF storage shields for on-site storage of civilian reactor fuel. In this application, the use of DUCRETE™ results in smaller shield size and lower weight. Conceptual design studies [Powell April 1995] have shown that a ventilated storage container for dry SNF storage similar to the Sierra Nuclear Corporation VSC-24 can be made from such high-density concrete. Although the fuel load (24 spent pressurized-water reactor fuel assemblies) is the same as a container made of conventional concrete, the external diameter is reduced by about 1 m (40 in.)—from about 3.3 m (130 in.) to 2.3 m (90 in). The total weight is reduced from about 135 Mg (135 t) to about 100 Mg (100 t). This is predicted to significantly reduce the cost of storage container loading by eliminating the need for transfer casks while simultaneously reducing occupational radiation dose.

The use of DU aggregate in high-density shielding has the potential of consuming the entire DU inventory—depending on the timing of SNF and waste receipts by the repository program. However, there are technical issues associated with this option. For DUCRETE™, issues needing further study include optimum DU aggregate formulations (e.g., preferred uranium oxide state— UO_2 , U_3O_8 , or UO_3) and optimum aggregate size(s). Various binder materials need to be investigated. Additional information is needed concerning the thermo-mechanical-chemical performance of heavy concrete. For example, the thermal conductivity, mechanical strength, and long-term stability under elevated temperatures and oxidizing conditions must be determined. More information is also needed on the fabricability of heavy concrete, with issues such as pourability and homogeneity (i.e., settling of aggregate and/or filling of interstices).

Other technologies have been proposed for making high-density DU shielding, although they are less advanced than DUCRETE™. A PYRolytic Uranium Compound (PYRUC) has been proposed, and a patent application has been submitted. The PYRUC process is best described in two articles [Murray, Mirsky, and Krill 1997 *a,b*]. Brookhaven National Laboratory has proposed DUPoly technology and has a patent pending on the concept. DUPoly is a formable material composed of DUO_3 , which is bound in a polyethylene matrix. The Idaho National Engineering and Environment Laboratory has a patent application pending to convert DUF_6 directly into dense DU_6 , in a one-step process with concurrent evolution of fluorine as a by-product.

Research activities are currently focused on acquiring samples and measuring key physical properties of DUCRETE™. If funding becomes available, the technology for fabricating large DUCRETE™ shapes and constructing and testing of full-scale storage casks will be undertaken.

4. DU STORAGE CYLINDERS

Many DUF_6 storage cylinders are in relatively good condition and capable of further use as a container. However, after being emptied and washed with water, the cylinders are still considered to be radiologically contaminated. It is generally not economical to refabricate contaminated steel such as that that would result from cylinder recycle, and current DOE policy does not allow recycle of contaminated metal into unregulated environments. However, it appears both institutionally feasible and economically attractive to reuse most of the intact cylinders as low-level waste (LLW) disposal packages by cutting a relatively small opening in the cylinder, inserting LLW, welding a cover over the opening, and transporting the package to an LLW disposal site.

Current research activities include assessing DOE regulations and waste acceptance criteria related to use of cylinders for disposal packages and conducting a cradle-to-grave demonstration of using cylinders as LLW disposal packages.

5. FLUORINE PRODUCTS

Approximately 225,000 t of elemental fluorine could be derived from the - 700,000 t of DUF_6 , which is stored at DOE enrichment sites. This fluorine is potentially recoverable as elemental fluorine, hydrofluoric acid (aqueous HF), anhydrous HF, or other fluorine-bearing compounds. These could be recycled to conserve natural resources and partially defray costs associated with conversion of DUF_6 to forms that are more acceptable for storage. The HF product can be used in many commercial activities, particularly in the nuclear industry to fluorinate natural uranium.

There is a large list of potential processes that could recover the fluorine, most with the intention of having HF as the product. However, the bulk price of HF is low, currently about \$1.50/kg. Additional processing to produce higher value compounds may generate larger net revenue. While such high-value-added fluorinated compounds are being used by the semiconductor industry, the stored inventory of DU is so large that the production of any single fluorine product would probably saturate the market and lower prices. Therefore, a flexible conversion process is sought that could, according to demand, selectively produce any of several high-value-added fluorine products. Several possible compounds are envisioned in a suite of fluorine products: BF_3 , CoF_3 , SbF_3 , SF_6 , NF_3 , SiF_4 , PF_5 , AsF_3 , ClF_3 , IF_5 , etc.

Research activities will include evaluating the chemistry and economics of producing a suite of higher value fluorine compounds that may offer greater savings to DOE. An integrated flow sheet must be defined for producing the preferred suite of compounds. This research activity has not begun due to limited funding.

6. URANIUM-BASED CATALYSTS

DOE has initiated an activity to investigate the basic chemistry of DU with a view to determining its potential usefulness in a variety of catalysis applications. The overall goal of the catalysts research is to investigate a new class of mesoporous sol-gel catalysts containing DU oxides as the active component. The initial goal is to understand how well such catalysts decompose a range of volatile organic

compounds (VOCs), including alkanes, aromatics, and chlorinated organic compounds, which would be of interest in environmental restoration. This investigation is motivated by the demonstrated high efficiency and long-term stability of uranium-oxide-based catalysts, as compared to some commercial catalysts using precious metals, (e.g., TiO_2 and Co_3O_4), [Hutchings, Heneghan, Hudson, and Taylor 1996, Pollington, et al., 1999]. Preliminary experiments have demonstrated that mesoporous uranium oxide (U_3O_8) with a surface area as high as $65.1 \text{ m}^2/\text{g}$ can be synthesized [Dai 1999]. This surface area is at least 650 times larger than that of commercial U_3O_8 ($<0.1 \text{ m}^2/\text{g}$). It is well known that heterogeneous catalytic efficiencies are proportional to catalyst surface areas. Accordingly, much higher catalytic efficiencies are expected for the mesoporous uranium oxides. Subsequent investigations will analyze the uses of catalysts in a variety of other applications. Figure 2 shows a transmission electron microscope image of uranium oxide supported by ordered mesoporous SiO_2 .

The DU Uses R&D Program is currently synthesizing mesoporous sol-gel catalysts containing uranium. When enough of these samples are available, experiments will be conducted to measure the efficiency of uranium catalysts to decompose various VOCs.

7. URANIUM SEMICONDUCTOR PROPERTIES

The electrical and semiconductive properties of uranium could potentially lead to a new generation of electronic devices. There has never been an electronic device made using uranium oxide as a semiconductor. Yet, uranium oxides have electrical and electronic properties equivalent to or much better than the properties of conventional Si, Ge, and GaAs semiconductor materials. The 1.3-eV energy band gap [Samsonov 1982] for uranium dioxide (UO_2) lies between Si and GaAs at the optimum of the band gap vs efficiency curve, indicating that one should be able to use uranium oxides to make very efficient solar cells, semiconductors, or other electronic devices. Figure 3 shows the ideal solar efficiency for various semiconductor materials. The intrinsic electrical conductivity of UO_2 is approximately the same as that of GaAs. The dielectric constant [Samsonov 1982] of UO_2 (- 22) is nearly double that for Si (11.2) and GaAs (14.1). The ceramic oxides of uranium (e.g., UO_2) can withstand much higher operating temperatures (- 2,600EK) than can Si or GaAs ($<473\text{EK}$). Thus, it appears that a new higher-performance class of semiconductors is possible: DU-based semiconductors. It is envisioned that these new semiconductors may be suitable for use in harsh environments wherein traditional semiconductors are inappropriate, such as in space applications. DU use as a semiconductor material is a worthy idea that will be aggressively pursued if additional funding becomes available.

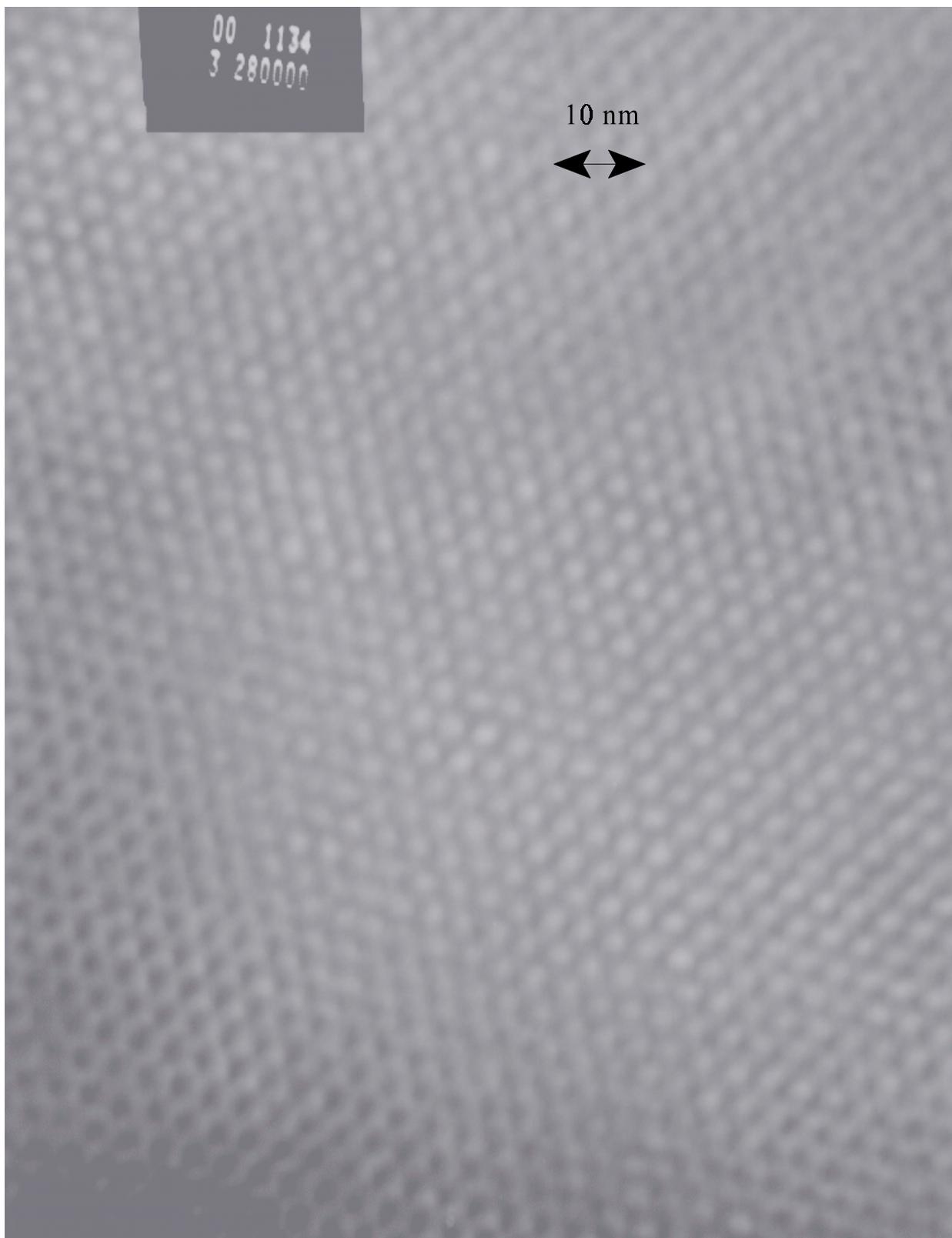


Figure 2 TEM image of ordered mesoporous SiO₂ used to support uranium oxide catalysts.

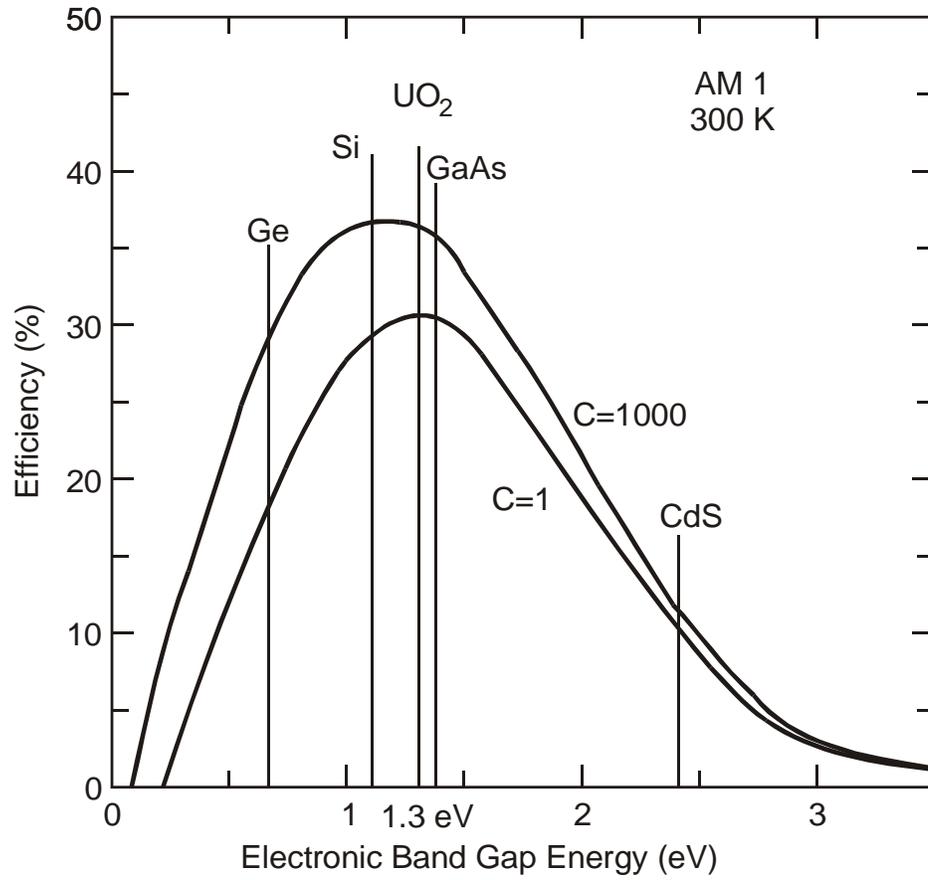


Fig. 3. Ideal Solar-Cell Efficiency at 300K for 1 Sun and for a 1000-Sun Concentration [Sze 1985].

8. SUMMARY

DOE has - 500,000 t of DU stored at sites across the country. This material is mostly DUF_6 that resulted from uranium enrichment operations. In a ROD, DOE committed to converting this DUF_6 inventory to a more chemically stable form as rapidly as is practicable. DOE has initiated a DU Uses R&D Program to explore the beneficial uses of converted DU, the fluorine associated with the DUF_6 , and the emptied carbon-steel DUF_6 storage cylinders. Research will also be carried out to ensure the direct disposal of DUF_6 to the extent that cost effective realistic beneficial uses are not found.

There are many possible applications for DU and innovative uses continue to be discovered (e.g., DU catalysts and semiconductors). DOE has focused the DU Uses R&D Program's limited resources on DU applications in repositories and DUCRETE™ shielding material. A fairly significant amount of research is being conducted on uranium-based catalysts. There are a number of other worthy ideas for DU uses, e.g. as semiconductor material, that DOE would pursue aggressively if additional funding becomes available. Significant technical and institutional issues exist that must be resolved before some of these uses can be implemented. However, the inventory of DU in the United States is seen as an asset—with the realistic potential for beneficial uses. Through the DU Uses R&D Program, DOE is working to realize the potential of this DU inventory.

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