ORNL/TM-2002/111

Radiation Shielding Using Depleted Uranium Oxide in Nonmetallic Matrices

August 2002

L. R. Dole
W. J. Quapp

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via the U.S. Department of Energy (DOE) Information Bridge:

Web site: http://www.osti.gov/bridge

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-605-6000 (1-800-553-6847)
TDD: 703-487-4639
Fax: 703-605-6900
E-mail: info@ntis.fedworld.gov
Web site: http://www.ntis.gov/support/ordernowabout.htm

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and International Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Telephone: 865-576-8401
Fax: 865-576-5728
E-mail: reports@adonis.osti.gov
Web site: http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

ORNL/TM-2002/111

RADIATION SHIELDING USING DEPLETED URANIUM OXIDE IN NONMETALLIC MATRICES

Compiled by

Leslie R. Dole, Ph.D., CM
Oak Ridge National Laboratory

William J. Quapp, PE
Teton Technologies, Inc.

Published: August 2002

Prepared by
OAK RIDGE NATIONAL LABORATORY
P.O. Box 2008
Oak Ridge, Tennessee 37831-6285
managed by
UT-Battelle, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

FIGURES AND TABLES v
ABBREVIATIONS AND ACRONYMS vii
ABSTRACT ix

1. INTRODUCTION 1
2. DUCRETE CONCRETE 3
    - 2.1 Early Development 3
    - 2.2 DUCRETE Proof-of-Concept Testing 5
    - 2.3 Development of DUAGG 7
    - 2.4 Commercial DUAGG Manufacturing 10
    - 2.5 Mechanical Properties 11
    - 2.6 Nuclear Properties 11
    - 2.7 Environmental Characteristics of DUCRETE 12
    - 2.8 Potential DUCRETE Applications 13
        - 2.8.1 Reactor Spent Fuel Storage 13
        - 2.8.2 Transportable Storage Cask 14
        - 2.8.3 Disposal Waste Package Shield 15
        - 2.8.4 High-Level Waste Canister Shielding 16
        - 2.8.5 Remotely Handled Transuranic (TRU) Waste Drum Overpack 17
    - 2.9 Current ORNL DUAGG Testing 17
    - 2.10 DUAGG and DUCRETE Development Needs 18
3. DUPOLY 19
4. PYRUC 21
5. FUTURE RESEARCH AND DEVELOPMENT NEEDS 23
6. CONCLUSIONS 25
7. REFERENCES 27

FIGURES AND TABLES

Figures

1 Comparative diameters of concrete and DUCRETE dry-storage cask or silo 1
2 Comparison of storage cask or silo wall thicknesses required to attenuate neutron and gamma doses from 24 pressurized water reactor (PWR) spend nuclear fuel assemblies to 10 mR/h 3
3 Diagram of the Sierra Nuclear VSC-24 spent fuel storage cask 4
4 Cask external dose vs DUCRETE aggregate volume fraction 4
5 Compression test results from DUCRETE and reference concrete samples (room temperature) 5
6 Compression test data following elevated-temperature exposures 6
7 Process flow diagram for DUAGG manufacturing 7
8 Backscattered electron image of a fractured surface of DUAGG 8
9 Compression test results with DUCRETE exposed to high-temperature cure (DUAGG aggregate) 9
10 Comparison of the compressive strengths between 28-day cured samples made from DUAGG and fuel pellet aggregates 10
11 DUAGG briquettes produced at Starmet 11
12 Half-value layer thickness for DUCRETE shielding compared to other traditional shielding materials at 1.25 MeV 12
13 Estimated cumulative number of SNF assemblies for PWR and BWR light-water reactors through 2020, low-case scenario 13
14 Potential cumulative use of DUO_2 in SNF storage casks through 2020 14
15 GNB CONSTOR cask for storage and transportation of RBMK spent fuel 14
16 High-level waste (HLW) canister shield developed for a multipurpose HLW canister 15
17 Cross section of Starmet/Duke DUCRETE DWPF cask for Savannah River Site HLW glass 16
18 Stainless steel–clad DUCRETE drum overpack 17
19 DUPoly samples produced at BNL containing 80 wt % depleted UO_3 19
20 DUPoly density as a function of UO_3 loading 20
21 DUPoly compressive strength as a function of UO_3 loading 20
22 PYRUC process flow diagaram 21

Tables

1 Concrete temperature limits for nuclear fuel storage tanks 6
2 DUCRETE compressive strength after elevated temperatures 9
3 Composition of DUCRETE samples and physical properties 11
4 DUCRETE density and compressive strength as a function of composition 11
5 Comparative leach test results for DU subjected to EPA TCLP testing 12
6 Estimated accumulated number of spent nuclear fuel assemblies through 2020 for the low case 13

ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing and Materials
BNL	Brookhaven National Laboratory
BWR	boiling water reactor
DOE	U.S. Department of Energy
DU	depleted uranium
DUAGG	depleted uranium aggregate
DUCRETE	depleted uranium concrete
DUPoly	depleted uranium oxide powder
EDX	X-ray spectroscopy
GNB	Gesellschaft für Nuklear-Behälter
HLW	high-level waste
IAEA	International Atomic Energy Agency
ICP	ion-coupled plasma
INEEL	Idaho National Engineering and Environmental Laboratory
LWR	light-water reactors
ORNL	Oak Ridge National Laboratory
PYRUC	pyrolytic uranium compound
RBMK	Russian graphite moderated boiling water reactor
RCRA	Resource Conservation and Recovery Act
SEM	scanning electron microscope
SNF	spent nuclear fuel
TCLP	Toxic Characteristic Leaching Procedure
tonne	metric ton
TRU	transuranic waste
UO_2	urania
UO_x	uranium oxide
XRD	X-ray diffraction

ABSTRACT

The depleted uranium (DU) inventory in the United States exceeds 500,000 metric tons (tonnes). This report reviews the status of U.S. Department of Energy (DOE) research concerning the use of its inventory of DU as neutron and gamma shielding. The focus is the use of uranium oxide (UO_x) in nonmetallic matrices, (e.g. concrete). Research on CerMets, which incorporate UO_x in metallic matrices, is discussed elsewhere.[a] This program envisions that a large portion of the U.S. inventory of DU will be used in the fabrication of nuclear shielding for the storage, transport, and disposal of spent nuclear fuels. Just in the storage of commercial U.S. spent nuclear fuel (SNF), the cumulative amount of DU oxide (DUO_2) that could be used in nonmetallic matrix dry-storage casks though 2020 is 408,455 tonnes (360,058 tones of DU).

The purpose of this U.S. research effort is to develop DU shielding technologies to the point that a demonstrated technical basis exists for deployment. In particular, a need exists to (*a*) establish the ability to manufacture DU aggregates in large, heavy concrete shapes; (*b*) optimize the design and costs; and (*c*) ensure confidence in the reliability and safety of the chemical and physical stability of the DU aggregate. In addition, the neutron-shielding characteristics of these aggregates and their binders must be enhanced. This research and development will underpin public, regulatory, and purchaser confidence.

Current concepts are to form UO_x aggregates and to combine these aggregates with binders that enhance neutron shielding. Uranium is a very effective gamma shield because of its high density and high atomic number (Z). Binders under consideration include cementitious pastes, thermoplastic polymers, and pyrolytic carbon. The use of these DU-based shielding materials will greatly reduce the size and weight of storage, transport, and disposal casks. The economic advantage gained through using smaller and lighter casks will offset the increased fabrication costs of using the DU.

In 1993, the DOE Office of Environmental Management began investigating the potential use of DU in heavy concretes. DUCRETE™, or depleted uranium concrete, was an outcome of that investigation. This material is a high-density concrete that uses depleted uranium ceramic aggregates. Researchers also developed DUPoly, which uses depleted uranium oxide powder as the filler material in a thermoplastic polyethylene binder material to produce a high-density shielding material. A third concept uses a micro-aggregate DU oxide (DUO_2) that is produced by a sol-gel precipitation of uranium into microspheres in a process developed for nuclear fuel technology in the late 1960s. These sol-gel particles are then mixed with an organic binder and pyrolyzed to make uranium carbide and/or UO_x pyrolytic-carbon matrices. This matrix is called PYRUC.

All of these materials use DU in a neutron-moderating or -absorbing binder. In a dense, compact shield, these materials have both an efficient gamma absorber and a neutron-slowing material. Therefore, they are ideal for shielding sources, such as spent nuclear fuels and vitrified high-level waste. This report provides the background for these technologies and some of the associated mechanical and nuclear performance data that have been developed.

---

[a] C. W. Forsberg, L. B. Shappert, P. Byrne, and B. Broadhead, “CerMet Transport, Storage, and Disposal Packages Using Depleted Uranium Dioxide and Steel,” in *Proceedings of the 13th International Symposium on the Packaging and Transport of Radioactive Materials for the Institute of Nuclear Materials Management,* Chicago, Ill., September 7, 2001 (Warrendale, Pa.: Materials Research Society, August 2002).

1. INTRODUCTION

One of the most obvious uses for the large U.S. inventory of depleted uranium (DU)—which exceeds 500,000 metric tons (tonnes)—is as nuclear shielding. A research program being conducted by the U.S. Department of Energy (DOE) envisions that a large portion of this DU will be used in the fabrication of nuclear shielding for the storage, transport, and disposal of spent nuclear fuel (SNF). DU metal has been used in casks as shielding because its high density provides the needed gamma attenuation for the lowest-weight and smallest casks. Studies have assessed the use of uranium metal for shielding in both spent fuel[1] and high-level waste (HLW)[2] casks. A review of DU metal production and fabrication costs showed that depleted metal was more expensive than other common shielding materials such as steel, lead, and concrete.[3] Therefore, the primary application for uranium metal shielding is for transportation casks, where the most stringent total-package size and weight limits exist and where high-cost, DU metal shielding can be justified. Also, there is an added benefit to the nuclear community if this use as shielding consumes large quantities of DU from the existing national inventory.

These findings led to the consideration of alternative uses for DU such as a DU ceramic, which is still very dense but has considerably lower production and fabrication costs than DU metal. The first alternative developed was a concrete called DUCRETE™, which was followed by DUPoly and PYRUC. DUPoly uses depleted uranium oxide powder as the filler material in a thermoplastic polyethylene binder material to produce a high-density shielding material. PYRUC uses a micro-aggregate DU oxide (DUO_2) that is produced by a sol-gel precipitation of uranium into microspheres in a process developed for nuclear fuel technology in the late 1960s. These sol-gel particles are then mixed with an organic binder and pyrolyzed to make uranium carbide and/or UO_x pyrolytic-carbon matrices.

All of these concepts have in common the use of DU in a neutron-absorbing binder. This provides a material that has characteristics of both an efficient gamma absorber (uranium) and a low–atomic number (low-Z) neutron-slowing material such as hydrogen or carbon. Figure 1 shows the effectiveness of using DUO_2, such as DUCRETE, to reduce the size and weight of a dry-storage cask or silo for spent nuclear fuel.

This report discusses the backgrounds of these technologies and some of the mechanical and nuclear performance data developed. It also identifies additional development requirements.

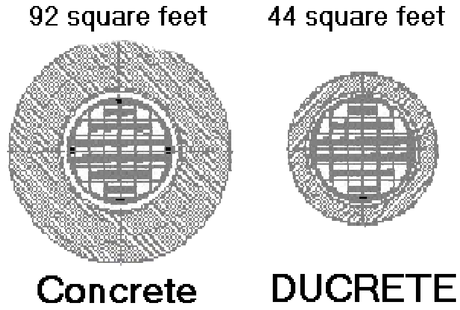


Fig. 1. Comparative diameters of concrete and DUCRETE dry-storage cask or silo. Using DUCRETE in a spent nuclear fuel cask or silo reduces the weight by 30%, the footprint by 50%, and the diameter from 132 in. (3.5 m) to 90 in. (2.3 m).

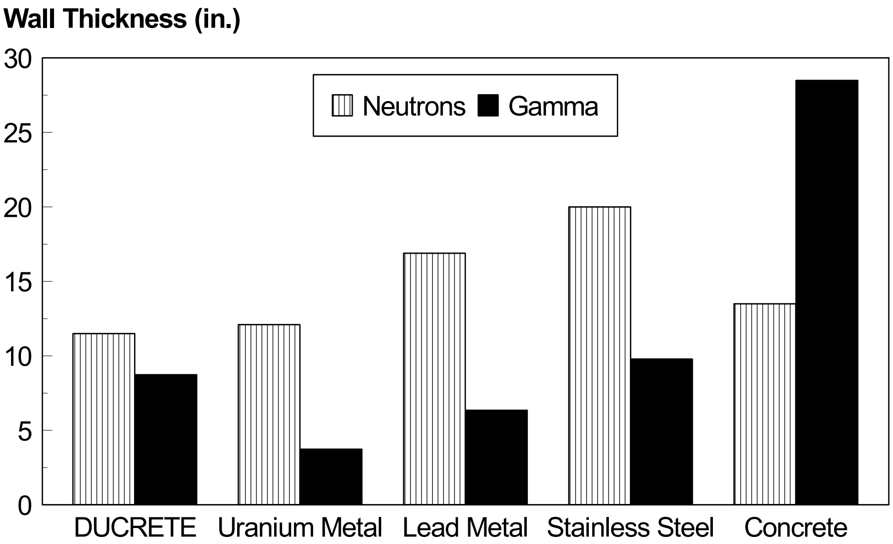
2. DUCRETE CONCRETE

DUCRETE consists of a DU ceramic that replaces the coarse aggregate used in standard concrete. The DU coarse aggregate is combined with Portland cement, sand, and water in the same volumetric ratios used for ordinary concrete. If the ceramic can be produced at a low enough cost, it would be practical to consider using DUCRETE concrete as a shielding material. The cost of concrete cask fabrication is low when compared to fabricating steel, lead, and DU metal casks.

2.1 Early Development

DUCRETE concrete was conceived at the Idaho National Engineering and Environmental Laboratory (INEEL) by W. Quapp and P. Lessing, who jointly developed the process and were awarded both U.S. and foreign patents in 1998 and 2000, respectively.[4,5] DUCRETE is formed by agglomerating DUO_2 to a dense, stable, low-cost aggregate and combining it with the normal concrete paste (cement, sand, and water). This matrix has both high-Z materials for gamma attenuation and low-Z material for neutron attenuation. Emulating nuclear fuel technology, the sintered uranium oxide (UO_x) aggregate has a very high density (>95% theoretical density). Thus, a theoretical concrete density of 7.2 g/cm^3 is possible.

Based on this conceptual work, J. Sterbentz of INEEL performed the first shielding calculations.[6] Initial shielding evaluations were made for DUCRETE shielding in a spent fuel application. Figure 2 shows the nuclear shielding effectiveness of this conceptual DUCRETE shielding material. The figure shows comparisons of the relative effectiveness for gamma and neutron attenuation of DUCRETE and that of other common shielding materials in a proposed SNF storage silo or cask.



Dr. J. Sterbentz, INEEL

Fig. 2. Comparison of storage cask or silo wall thicknesses required to attenuate neutron and gamma doses from 24 pressurized water reactor (PWR) spent nuclear fuel assemblies to 10 mR/h.

Another series of studies conducted by two firms in the U.S. private sector, Packaging Technology and Sierra Nuclear Company, provided a commercial perspective for the DUCRETE concept.[7, 8, 9, 10] Their results showed that if DUCRETE is found to be producible at relatively low cost, the concept appeared to be technically sound.

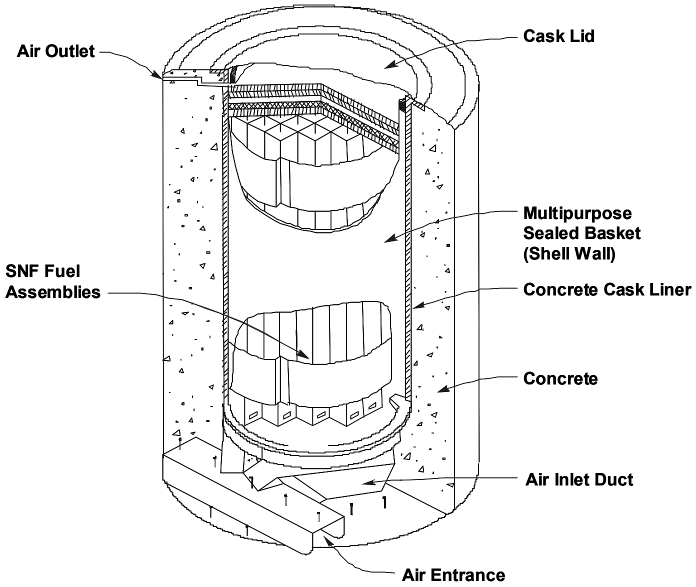


Fig. 3. Diagram of the Sierra Nuclear VSC-24 spent fuel storage cask. Substituting DUCRETE into this current design reduced the weight of the cask (24-PWR assemblies) by 30 tons and the footprint by a factor of 2 (see Fig. 1).

Sierra Nuclear Company found that spent fuel storage casks, with performance improvements and weight savings (Fig. 3), would nearly offset the greater fabrication costs through eliminating redundant handling costs. Sierra Nuclear also showed that an optimum uranium-to-binder ratio exists for a combined attenuation of gamma and neutron radiation at a given wall thickness (Fig. 4). A balance needs to be established between the attenuation of the gamma flux in the UO_x and the cement phase with water to attenuate the neutron flux. Figure 4 shows the DU aggregate-loading-to-attenuation relationships for two different types of sand added to the DUCRETE binder materials: ordinary quartz sand (SiO_2: density of 2.65 g/cm^3) and colemanite sand ($Ca_2B_6O_{11}{\cdot}H_2O$: density of 2.4 g/cm^3). With regard to neutron attenuation, the colemanite sand has the added advantage of adding boron to the shield matrix, for a small reduction in overall density. Neutron-absorbing elements like hafnium and gadolinium also may be used to enhance the shield's neutron attenuation, allowing even thinner, lighter combinations of UO_x and binders.

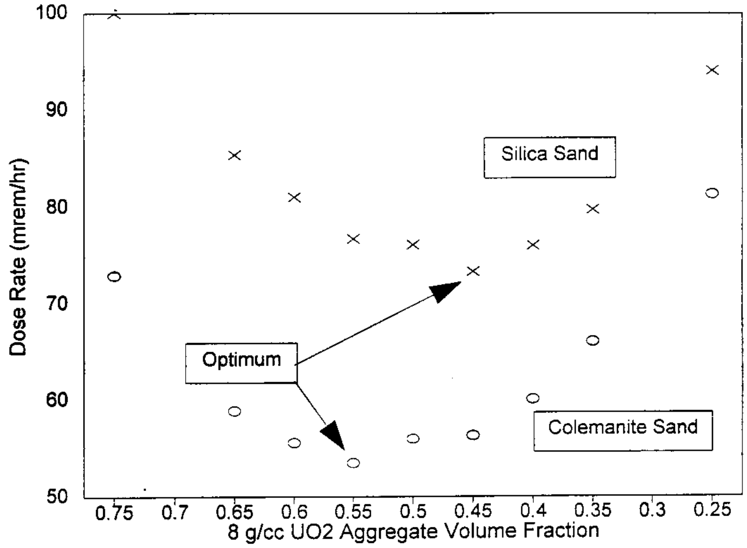


Fig. 4. Cask external dose vs DUCRETE aggregate volume fraction (Ref. 9): optimum aggregate loading.

2.2 DUCRETE Proof-of-Concept Testing

Lessing conducted proof-of-concept tests to determine whether there were deleterious chemical reactions between depleted urania (UO_2) aggregate and the concrete paste.[11] Under aqueous oxidizing conditions in the cement paste, U_3O_8 is the more thermodynamically stable form of uranium. The transition from UO_2 to U_3O_8 results in an expansion of the aggregate that could generate stresses that could crack this shield material and lower its compressive strength. However, U_3O_8 DUCRETE is less dense than UO_2 DUCRETE.

Initial tests used DU sintered fuel pellets as simulated coarse aggregates. These fuel pellets were right circular cylinders 0.25 in. (0.635 cm) in diameter by 0.5 in. (1.25 cm) long, with smooth surfaces. DUCRETE concrete samples were made with these fuel pellets, and blank concrete samples were made using ordinary gravel. The volume densities of all these samples were varied to determine the maximum loading while still retaining acceptable mixing characteristics and the compressive strength of the concrete. A series of DUCRETE and normal concrete control samples were prepared and cured for 7, 28, and 90 days and compression-tested to get reference data. The results are shown in Fig. 5. A sample size of 2 in. (5 cm) in diameter by 4 in. (10 cm) long was selected to minimize the use of the uranium ceramic per sample. These small specimen sizes are responsible for the large spread in the data for both materials. For the size of aggregate used, the cylinders should be at least 3 in. (7.6 cm) in diameter by 6 in. (15.2 cm) long. The normal effects of cure time on the compressive strength are masked by the data spread. Nevertheless, it can be seen that the compressive strength of DUCRETE and normal concrete are comparable.

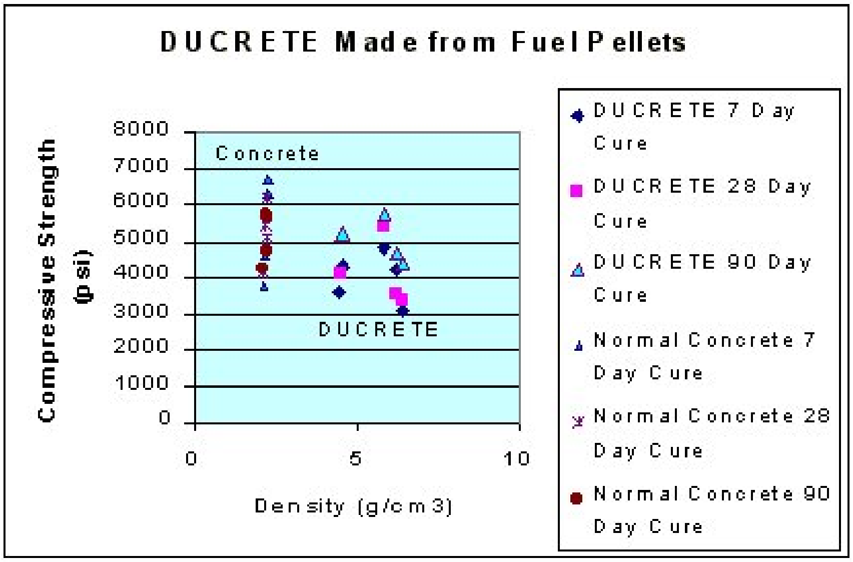


Fig. 5. Compression test results from DUCRETE and reference concrete samples (room temperature).

To evaluate the potential for any chemical interaction between the UO_x ceramic and the cement phase, additional samples were prepared and cured for 7, 14, and 28 days at temperatures ranging from room temperature to 250°C. After the appropriate curing period, the DUCRETE samples were compression-tested to compare their strengths with that of ordinary concrete with the same volume fraction of coarse aggregate. These tests assessed the effects of elevated temperature on the samples' compressive strengths. The data from this test are shown in Fig. 6. Lessing found no discernable difference in the strength for samples cured at temperatures below 150°C as compared to samples cured at room temperature, within the statistical uncertainty of the data.[12] For the samples cured at elevated temperatures (250°C), damage occurred to both normal and DUCRETE samples. However, some DUCRETE samples had crumbled at the end of 14 days, implying a different damage mechanism than for the normal concrete.

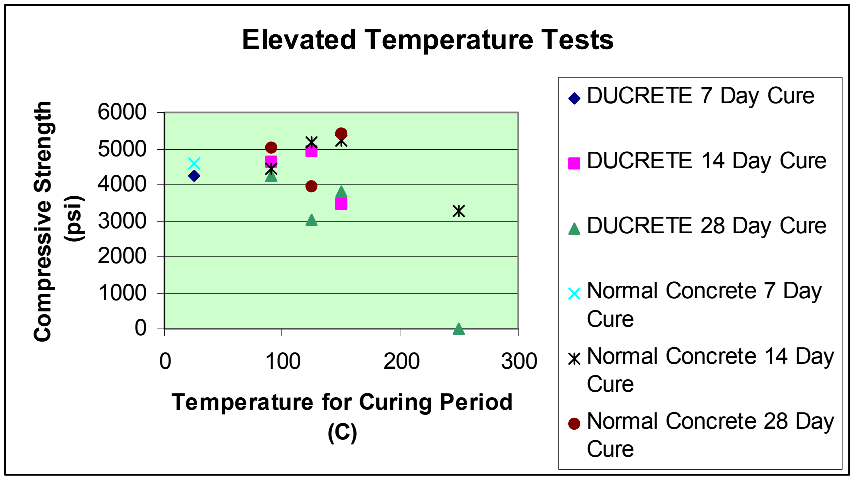


Fig. 6. Compression test data following elevated-temperature exposures.

Lessing investigated the damage mechanism.[12] He concluded that while there did not appear to be any chemical reaction between the concrete materials and the fuel pellets, some oxidation of the UO_x pellets occurred during the high-temperature exposure tests. The oxidation, although invisible to the unaided eye, was apparently sufficient when combined with the concrete dehydration at the test conditions to cause dramatic failure of the DUCRETE samples due to volume increase of the coarse aggregate during the transition from UO_2 to U_3O_8.

While UO_2 was expected to behave as a reactive coarse aggregate, the temperature threshold at which reactions occur and the reaction rates are still not known. Under dry conditions at elevated temperature, concrete can dehydrate. For most storage and disposal casks and conditions, the bulk-concrete shield temperature is limited to 66°C. But localized temperatures at the inner walls of the shielding casks can be up to 149°C. During a short-term accident, some parts of the shield could reach temperatures of up to 343°C. Table 1 shows the specifications from several cask vendors.[12, 13] The performance limits shown in the table are derived from the American Concrete Institute standards.

Table 1. Concrete temperature limits for nuclear fuel storage casks

Source	References cited	Normal "bulk" temp.	"Local" long-term temp.	Short-term (accident) temp.
Depleted Uranium Concrete Container Feasibility Study	ACI-349 Appendix A and NRC Guidance	66°C (150°F)	93–149°C (200–300°F)	177–343°C (350–650°F)
Pacific Nuclear "NUHOMS" System[a]	ACI-349 Appendix A	66°C (150°F)	93°C (200°F)	177°C (surface) to 343°C (local) (350–650°F)
Sierra Nuclear "VSC" Systems[b]	ACI-349 Appendix A and NRC Guidance	66°C (150°F)	149°C (local) (300°F)	—
Babcock & Wilcox Fuel Company[c]	—	—	121°C (250°F)	

[a] R. T. Haelsig, *Depleted Uranium Concrete Container Feasibility Study,* EGG/MS-11400 (Washington, D.C.: Packaging Technology Inc., 1994).

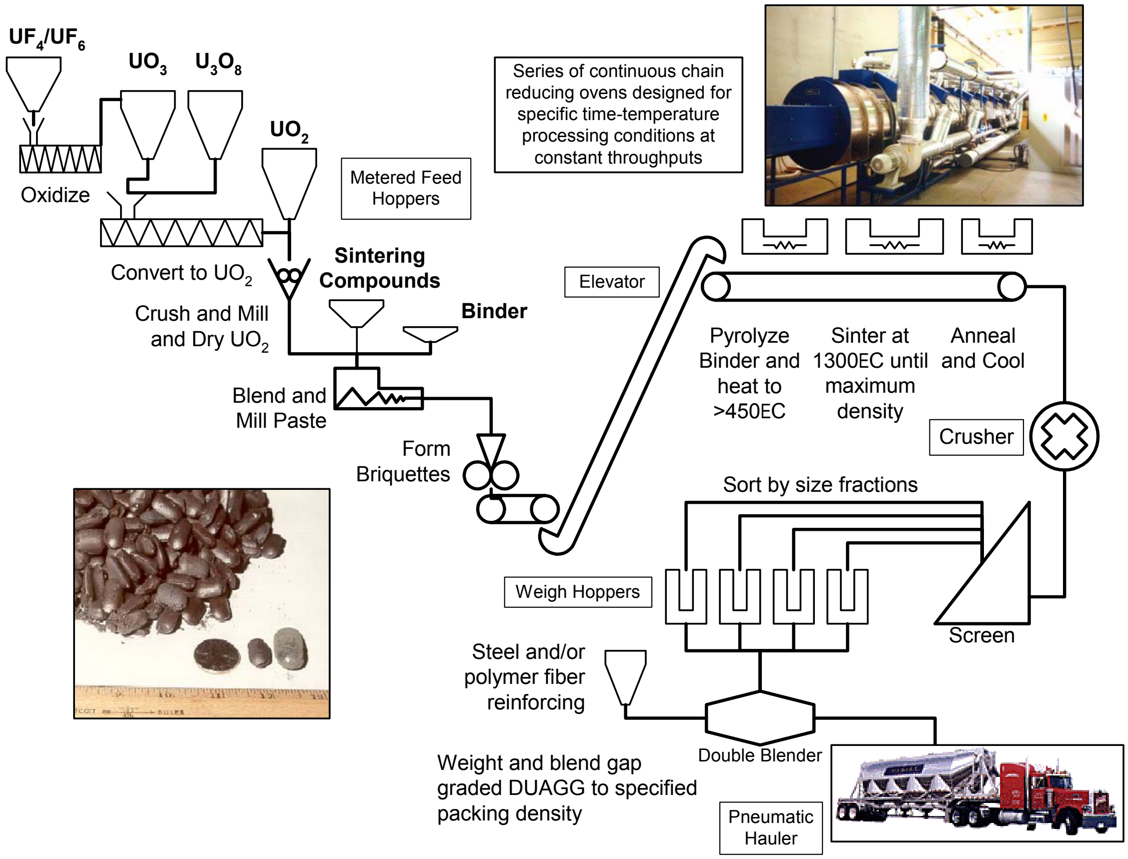
[b] Pacific Sierra Nuclear Associates, *Safety Analysis Report for the Ventilated Storage Cask System*, PSN-91-001 Rev. 0 (Scotts Valley, Calif., October 1991).

[c] Babcock & Wilcox Company, *BR-100 Shipping Cask Preliminary Design Report*, 51-1177082-01 (Lynchburg, Va., n.d.), p. II-3-11.

At the higher temperatures, the oxidation of the fuel pellets may have been accelerated, but the dehydration of the concrete paste could also have contributed to the disintegration. The dominant mechanism is not yet known. Nevertheless, it was concluded that if the UO_x aggregate could be rendered less reactive with water and oxygen at elevated temperatures, DUCRETE should be more suitable for cask applications.

2.3 Development of DUAGG

"Depleted uranium aggregate" (DUAGG) is the term applied to the stabilized, depleted UO_x aggregate that was developed to reduce the rates of UO_2 oxidation previously described. In the formation of DUAGG, a coating covers the surfaces of sintered urania particles and fills between the grains. This coating is an oxygen barrier. The sintering temperature normally associated with UO_x sintering (~1700˚C) is also reduced to below 1300˚C, an added benefit from a manufacturing perspective. Other work at INEEL led Lessing to consider a basalt-based binder because of its demonstrated resistance to corrosion in hot, aqueous environments. Therefore, DUAGG was formulated with inorganic binder materials consisting of clays, boria, iron oxide, and other materials similar in composition to basalt. Basalt is a dense crystalline rock of volcanic origin, composed largely of plagioclase feldspars ($[Na, Ca]\ Al\ [Si, Al]Si_2O_8$) and dark minerals such as pyroxene ($\sim n[Si_2O_6]\sim$) and olivine ($[Mg, Fe_2]\ SiO_4$). A process flow diagram for the INEEL manufacturing process is shown in Fig. 7.



UF4/UF6
UO3
U3O8
UO2
Oxidize
Convert to UO2
Crush and Mill and Dry UO2
Metered Feed Hoppers
Sintering Compounds
Binder
Blend and Mill Paste
Form Briquettes
Series of continuous chain reducing ovens designed for specific time-temperature processing conditions at constant throughputs
Elevator
Pyrolyze Binder and heat to >450EC
Sinter at 1300EC until maximum density
Anneal and Cool
Crusher
Sort by size fractions
Screen
Weigh Hoppers
Steel and/or polymer fiber reinforcing
Double Blender
Weight and blend gap graded DUAGG to specified packing density
Pneumatic Hauler

Fig. 7. Process flow diagram for DUAGG manufacturing.

Lessing designed the mixture so that the aggregate could be made using liquid-phase sintering at reduced temperatures. Sintering temperatures of 1250 to 1300°C produced an aggregate exceeding 95% of theoretical density. Since the mixture was about 7 wt % of lower-density oxides and only 93% UO_2, the resultant theoretical density was reduced to about 8.9 g/cm^3, compared to 10.4 g/cm^3 for 95% dense urania. Based on the work of Hopf,[8] this density loss results in only a slight increase in the wall thickness for the same attenuation and external dose. Research on the optimization of the time-temperature processing conditions, as well as on the introduction of neutron poisons into the DUAGG matrices, is continuing.

The challenge in this process is to obtain the proper sintering cycle to both reduce the UO_3 or U_3O_8 to UO_2 and come close to achieving the theoretical density. This requires a two-step sintering process: (1) achieving a hold period at 900°C for about 2 hours in a reducing atmosphere, followed by (2) completion of sintering at 1250 to 1300°C.

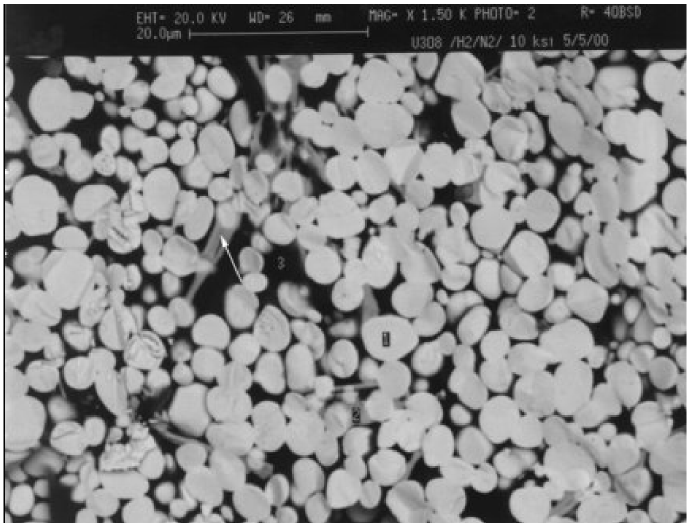

EHT= 20.0 KV WD= 26 mm MAG= X 1.50 K PHOTO= 2 R= 40BSD
20.0μm
U3O8 /H2/N2/ 10 ksi 5/5/00
3
1
2

Fig. 8. Backscattered electron image of a fractured surface of DUAGG. The arrow highlights the U-Ti-oxide phase. The light, rounded particles are UO_2, while the black area surrounding the UO_2 is the silicate phase, which is molten during sintering.

Based on optical examination of DUAGG, the liquid-phase binder seemed to coat all urania particles. A scanning electron microscope (SEM) photograph of a DUAGG sample is shown in Fig. 8. This figure shows the results from the liquid-phase sintering process. The spherical UO_x grains are nearly completely surrounded by the silicate-based phase (the liquid phase at the sintering temperature). This coating gives corrosion and leach resistance to DUAGG.

The UO_x phase was determined by X-ray diffraction to be predominantly UO_2. The UO_2 appears in all specimens analyzed as rounded particles measuring ~1–5 µm. The silicate phase wets the UO_x phase and fills space between the UO_x particles, demonstrating the success of the liquid-phase sintering. The silicate phase contains a mixture of Si, Al, Ca, Ti, K, Na, Zr, Fe, and Mg. Microchemical analysis by energy-dispersive X-ray spectroscopy (EDX) in the SEM revealed similar composition from point to point both within and between samples. This indicates that a homogeneous silicate phase exists. X-ray diffraction (XRD) showed the silicate phase to be predominantly crystalline.

Lessing repeated most of the previously described compression tests using DUCRETE made with DUAGG, focusing on the elevated temperature performance. These data are shown in Fig. 9. Again these tests have a large data spread because of the use of small compression-test cylinders relative to the size of the coarse aggregate. In general, the compressive strength at low temperatures was similar to that obtained in prior test results. However, at the higher temperatures, the behavior of the DUAGG generally improved. Still at 250°C, the compressive strengths are reduced compared to the baseline data for both DUCRETE and normal concrete. Because of the scatter in the data, however, the difference between the performance of ordinary concrete and DUCRETE was not statistically significant.

Both types of concrete seem to be affected by dehydration at 250°C.[14] However, microscopic examination revealed no discernable effect by oxidation on the DUAGG aggregate surfaces. Apparently, the liquid-phase sintering materials coat the UO_2 grains and improve the durability of the DUAGG, when compared to durability achieved using sintered UO_2 pellet aggregates, as in the first tests (Fig. 6).

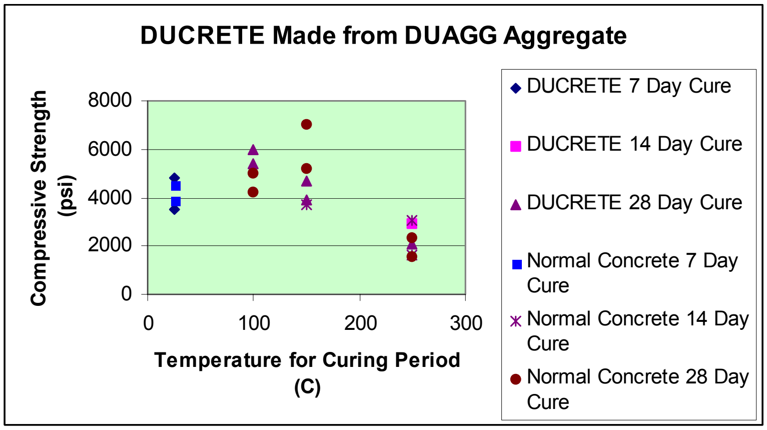


Fig. 9. Compression test results with DUCRETE exposed to high-temperature cure (DUAGG aggregate).

The compression test data in Fig. 9 is tabulated in Table 2. To compare the effect of DUAGG versus fuel pellets on compressive strength, the compressive strength data were plotted against the 28-day temperature data (Fig. 10). The DUCRETE samples made from DUAGG aggregate appear to have better strength at all curing temperatures. This could be caused by the poor statistical quality of the results or could be explained by the differing physical shape of the two aggregates. As previously noted, the fuel pellets were smooth right circular cylinders (0.25 in. diam by 0.5 in. long), whereas the DUAGG aggregate, beginning with sintered discs of 0.75 in. in diameter by 0.375 in. thick, was crushed and screened to sizes between 0.187 and 0.5 in. with rough surfaces. The INEEL work concluded at this point, and Starmet Corporation in South Carolina performed subsequent development.

Table 2. DUCRETE compressive strength after elevated temperatures

Sample ID	Aggregate type	Aging temperature (°C)	Time (days)	Compressive strength (psi)	Average strength (psi)
OST-1	Gravel	Baseline	Baseline	3899	
OST-2	Gravel	Baseline	Baseline	4535	4217
ORT-1	DUAGG	Baseline	Baseline	3500	
ORT-2	DUAGG	Baseline	Baseline	4790	4145
OST-3	Gravel	100	28	5033	
OST-4	Gravel	100	28	4239	4636
ORT-3	DUAGG	100	28	6007	
ORT-4	DUAGG	100	28	5399	5703
OST-5	Gravel	150	14	3700	3700
OST-6	Gravel	150	28	5193	
OST-7	Gravel	150	28	6998	6096
ORT-5	DUAGG	150	28	4659	
ORT-6	DUAGG	150	28	3883	4271
OST-9	Gravel	250	14	1655	
OST-10	Gravel	250	14	3026	2341
ORT-8	DUAGG	250	14	2911	2911
OST-11	Gravel	250	28	2349	

Table 2. DUCRETE compressive strength after elevated temperatures

Sample ID	Aggregate type	Aging temperature (°C)	Time (days)	Compressive strength (psi)	Average strength (psi)
OST-12	Gravel	250	28	1545	1947
ORT-9	DUAGG	250	28	2084	2084

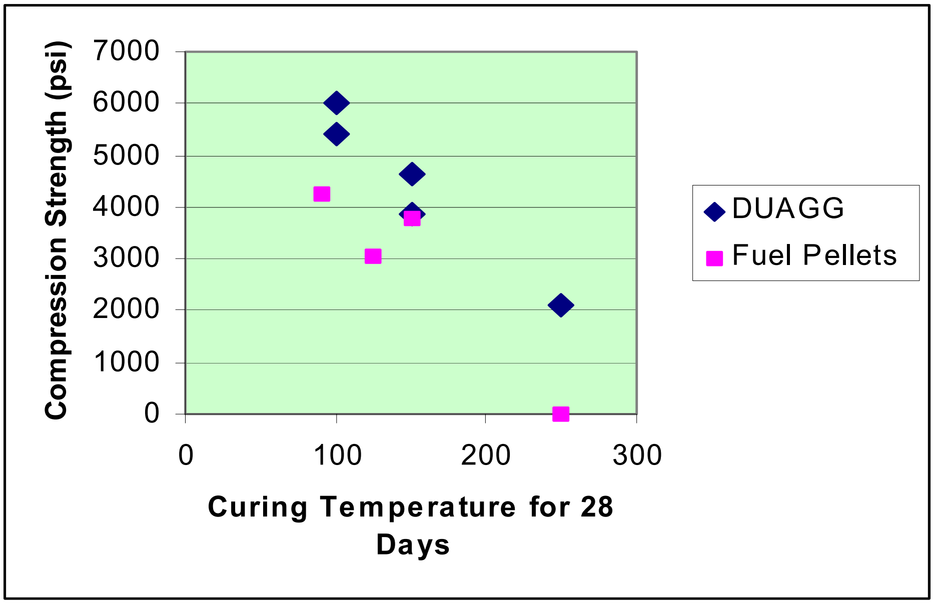


Fig. 10. Comparison of the compressive strengths between 28-day cured samples made from DUAGG and fuel pellet aggregates.

2.4 Commercial DUAGG Manufacturing

Starmet Corporation envisioned that the DUCRETE process could be commercialized if the production and fabrication costs that were predicted in the previous studies could be achieved. The UO_3, stored at the Savannah River DOE site adjacent to the Starmet facility could be used in DUCRETE casks for HLW storage needs at that site. Therefore, Starmet established a pilot-scale manufacturing facility in 1997 to demonstrate the manufacturing process developed by Lessing. Starmet used UO_3 as a starting oxide because it was the most abundant DU oxide material in the DOE inventory.

The Starmet process was originally designed to produce about 1000 lb of DUAGG per day. The only significant difference between the Starmet and Lessing processes (besides capacity) was Starmet's use of a rotary briquetting press (see Fig. 11) instead of the uniaxial laboratory press used at INEEL.

The first briquettes that Starmet produced were not of the proper density because of the limitations of the furnace. The furnace's two-zone temperature control did not allow the proper combination of time and temperature for the respective reduction and sintering steps. Consequently, the process steps were adjusted to achieve a satisfactory briquette density. Finally, the sintering was successfully completed using the furnace in two separate passes in which the reduction and sintering steps were accomplished independently. The briquettes shown in Fig. 11 have a density of 8.1 g/cm^3. Because of the furnace's limitations, Starmet was never able to accomplish the target production capacity for DUAGG.

Production was limited to about 100 lb/day. Nevertheless, it is still believed that a furnace with the appropriate temperature-zone control could achieve effective production of DUAGG of 1000 lb/day.

2.5 Mechanical Properties

Using different DUCRETE batch mixtures, Starmet performed further testing. Selected composition data are provided in Table 3, and the results of compression tests are presented in Table 4. Again, as with Lessing's data, the compression-testing results for these samples show a lot of variability. These tests used the same small (2 × 4 in.) cylinders used previously.

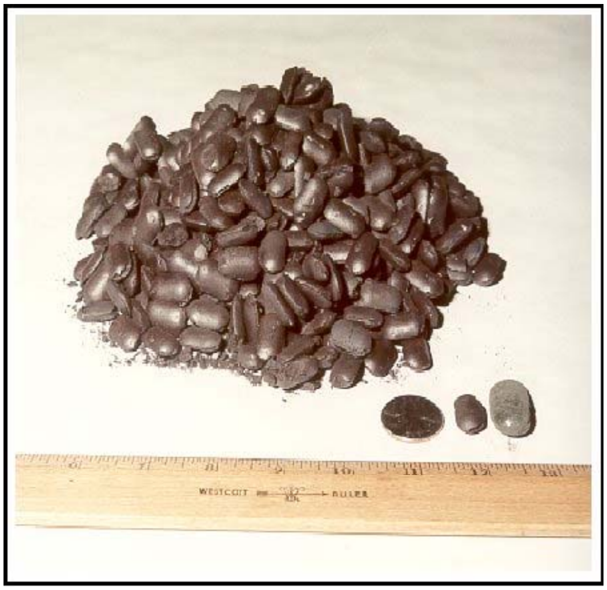


Fig. 11. DUAGG briquettes produced at Starmet.

Table 4 shows the effect on the density with samples made from lower-density DUAGG (8.1 vs 7 g/cm^3). For comparison, normal concrete has a density of about 2.26 g/cm.[3] Thus, even the "low-density" DUAGG formulation of DUCRETE results in much higher-density concretes than normal. A revised manufacturing process developed by Starmet produced an aggregate of 8.8 g/cm^3, which makes concrete of about 6.3 g/cm^3.

Table 3. Composition of DUCRETE samples and physical properties

Major ingredient[a]	Sample 7 ratios	Sample 8 ratios
Cement	1	1
DUAGG	9.6	8.18
Fly ash	0.2	—
Water	0.32	0.29
Cured density (g/cm^3)	5.72	5.87

[a] Both samples contained small quantities of thin metal steel fibers and superplastizer.

Table 4. DUCRETE density and compressive strength as a function of composition

Sample no.	Measured density (lb/ft^3)	Strength, (psi)	DUAGG density[a] (g/cm^3)	Small fines
6	5.66	5101	8.1	Fly ash
7	5.72	4310	8.1[b]	Fly ash
8	5.87	4430	8.1[b]	None
13	4.81	3880	7	Micro silica
14	4.73	4390	7	Micro silica

[a] DUAGG briquettes are crushed and screened to yield American Concrete Institute no. 8 size fraction.
[b] Sample contained about 0.36 wt % metal fibers to increase DUCRETE flexural strength.

2.6 Nuclear Properties

Most of the initial nuclear work done on DUCRETE has used attenuation calculations that assume various cask designs.[6–9, 13, 14] Experimental data were taken on two samples at the University of Missouri by Professor William Miller to determine the gamma attenuation. Figure 12 depicts the measured half-value thickness plotted against density for DUCRETE along with the textbook values for other materials.[15] The two lower DUCRETE densities are measured values, while the third and highest density is a predicted value based on aggregate density. The DUCRETE data were taken using ^{60}Co as the radiation source.[16]

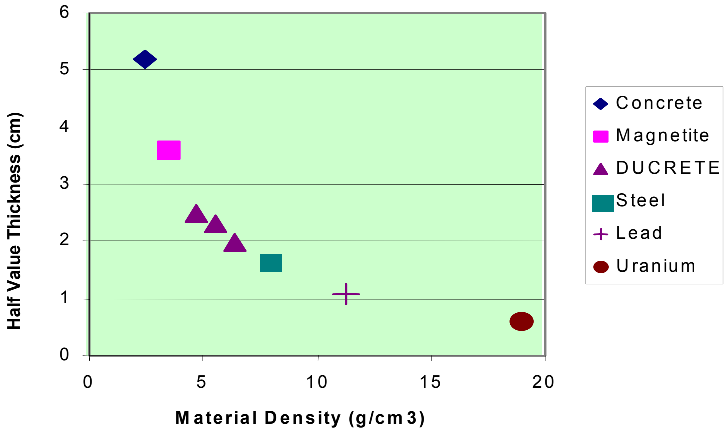


Fig. 12. Half-value layer thickness for DUCRETE shielding compared to other traditional shielding materials at 1.25 MeV.

Neutron attenuation is a function of the hydrogen content in the material, which in this case is the water bound in the cement paste and its pores. Holtec International Company made an independent neutron attenuation measurement of a sample in March 2000 using a graphite-moderated reactor neutron source. Transmission measurements on a 2-in.-thick slab confirmed the expected attenuation.

2.7 Environmental Characteristics of DUCRETE

Table 5. Comparative leach test results for DU subjected to EPA TCLP testing

Uranium form[a]	U concentration in leachate (mg-U/L)
DUCRETE	0.42
DUAGG	4
UO_2	172
U_3O_8	420
UF_4	7367
UO_3	6900

[a] The DUAGG and U_3O_8 were manufactured at Starmet CMI from SRS UO_3. The UF_4 was converted from UF_6 at Starmet. The UO_3 is from the DOE Savannah River Site and was recovered from reprocessing.

Potential leaching of DU into the environment is a consideration whether uranium forms the material for spent fuel storage casks, is used for other shielding applications, or is disposed of. Table 5 presents the results of leaching tests conducted by Starmet on several common forms of DU, DUAGG, and DUCRETE. The leach test used was the EPA Toxic Characteristic Leaching Procedure (TCLP), which is used to assess heavy metal risks to the environment. Although uranium is not regulated as a toxic heavy metal under the Resource Conservation and Recovery Act (RCRA), it is a toxic metal. The potential effects on groundwater should be considered in the case of any exposure to the environment in a shielding product or in a disposal cell. The data in Table 5 show that the conversion of UO_3 into DUAGG reduces the leaching by 1700- fold, from 6900 mg-U/L to 4 mg-U/L. These results also compare DUAGG and DUCRETE to other solid forms of uranium. Encapsulating DUAGG into cement further reduces the leaching results by another order of magnitude to 0.42 mg-U/L, which is still above the 0.03 mg-U/L drinking water limit in 40 CFR 141–142 within the repository horizon.

2.8 Potential DUCRETE Applications

The effectiveness of DU in nuclear shielding for spent fuel and HLW is apparent. While uranium metal may be cost-prohibitive for many shielding applications, INEEL cost estimates show DUCRETE shielding to be cost-effective.[10]

Table 6. Estimated accumulated number of spent nuclear fuel assemblies through 2020 for the low case

Year	PWR assemblies	BWR assemblies	Total
2002	69,900	89,700	159,600
2003	72,900	93,000	165,900
2004	75,700	96,800	172,500
2005	79,200	100,000	179,200
2006	81,900	104,700	186,600
2007	84,900	108,700	193,600
2008	88,400	111,600	200,000
2009	90,700	116,300	207,000
2010	93,800	120,400	214,200
2011	96,500	123,800	220,300
2012	98,800	129,500	228,300
2013	102,900	132,800	235,700
2014	105,800	139,400	245,200
2015	107,300	140,800	248,100
2016	109,900	144,200	254,100
2017	111,700	145,500	257,200
2018	113,300	147,900	261,200
2019	114,900	149,400	264,300
2020	116,400	151,600	268,000

2.8.1 Reactor Spent Fuel Storage

Sierra Nuclear developed a conceptual model of its VSC-24 storage casks with DUCRETE. This dry-storage cask will store 24 pressurized water reactor (PWR) or 61 boiling water reactor (BWR) fuel assemblies. Through a series of calculations, Sierra Nuclear showed that such a storage cask is about 30% lighter than one made of ordinary concrete and has a much smaller footprint on the storage pad (see Fig. 1). The DUCRETE storage cask had a diameter of 89 in. (226 cm), compared with 132 in. (335 cm) for standard heavy concrete. The DOE Integrated Data Base Report for 1994[17] estimates the potential cumulative number of SNF assemblies expected from PWRs and BWRs through the year 2020. The projected numbers of SNFs from both of these light-water reactors (LWRs) are presented in Table 6, and these data are presented graphically in Fig. 13.

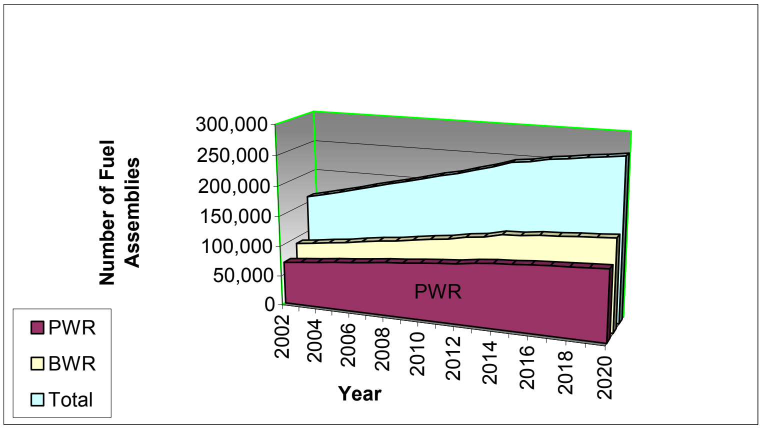


Fig. 13. Estimated cumulative number of SNF assemblies for PWR and BWR light-water reactors through 2020, low-case scenario.

These data show that in the conservative, low case as many as 268,000 total LWR SNF assemblies will be released. These assemblies require dry storage in some type of interim storage facility. These dry-storage facilities will be at the reactor sites and perhaps at the geological disposal site as well. Many current interim dry-storage facilities use concrete casks or silos to hold their SNF. Because of the events of September 11, 2001, there will be a strong push to accelerate the removal of the current large backlog of LWR SNF assemblies from their current storage in at-the-reactor wet-storage pools.

Studies of the use of DUCRETE in these silos showed that as much as 55.68 tonnes of DUO_2 would be used in the DUAGG for each dry-storage cask or silo. This is the equivalent of 49.09 tonnes of DU, or 72.59 tonnes of DUF_6, for each cask or silo. Given the conservative assumptions of 24 PWR and 61 BWR assemblies per cask or silo, the cumulative amount of DUO_2 that could be used in these dry-storage casks though 2020 is 408,455 tonnes. This translates into 360,058 tones of DU or 532,473 tonnes of UF_6 to be used in the shielding of SNF assemblies in dry-storage casks or silos. Figure 14 illustrates the potential cumulative use of 408,455 tonnes DUO_2 in these SNF storage casks.

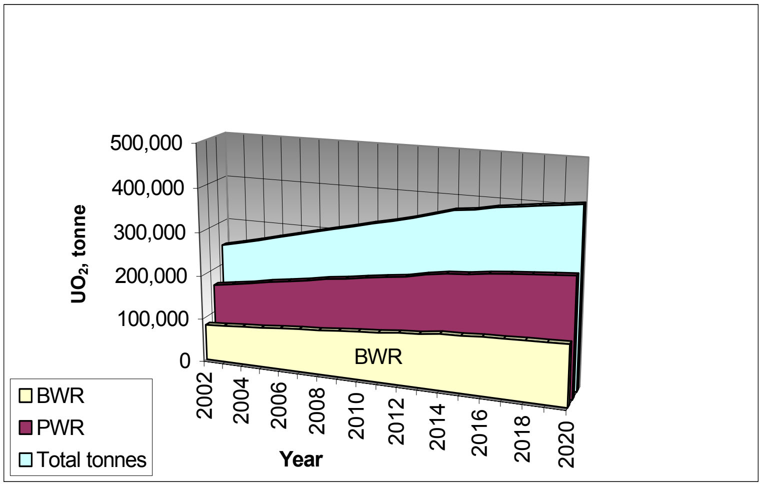


Fig. 14. Potential cumulative use of DUO_2 in SNF storage casks through 2020. Twenty-four PWR and 61 BWR assemblies per storage silo are considered.

2.8.2 Transportable Storage Cask

Current concrete storage systems are too large to transport by rail. With the reduced diameter possible with a DU shield, a concept for a transportable cask evolved. The normal unrestricted rail transportation limit in the United States is 128 in. (325 cm). A DUCRETE cask could be used advantageously at the reactor site until an interim spent fuel storage site becomes available—at DOE's deep, geological repository or elsewhere. From a DUCRETE storage cask used at the reactor site, the spent fuel could be loaded into a licensed transportation cask and shipped to its destination. Then, the DUCRETE storage cask could be shipped empty to that destination on a rail car and be used to store the spent fuel again. This would avoid the need for duplicate storage capacity at the interim storage site or lag storage at the DOE disposal site.

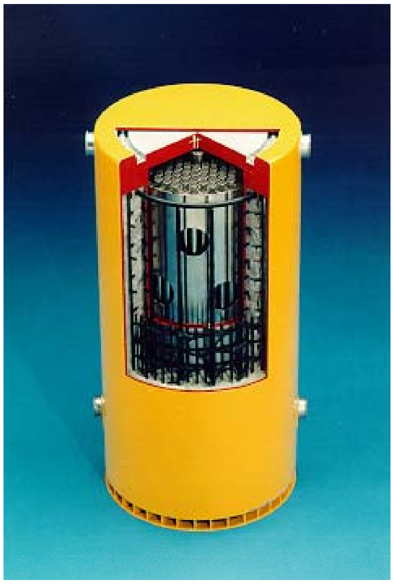


Fig. 15. GNB CONSTOR cask for storage and transportation of RBMK spent fuel.

Gesellschaft für Nuklear-Behälter (GNB) manufactures a cask, the CONSTOR, which uses reinforced heavy concrete between two 4-cm-thick steel shells.[18] A schematic of this cask is shown in Fig. 15. The cask has been developed, tested, and licensed according to International Atomic Energy Agency (IAEA) criteria for storage and transportation for the SNF from Russian graphite-moderated boiling water (RBMK) and pressurized water (VVER) reactors.

The barium sulfate in current heavy concrete casks requires a concrete-wall thickness of 17.4 cm (with a density of 4.1 gm/cm^3). DUCRETE concrete with a density of 6.0 g/cm^3 provides the same shielding effectiveness (gamma attenuation) with a wall thickness of only about 11.5 cm. Assuming that the other structural features of the CONSTOR were not compromised by the reduction in wall thickness, this cask might be redesigned to hold more fuel while maintaining the same external diameter. Furthermore, the thinner and denser DUCRETE walls can conduct more heat and reduce the inner wall temperatures of the casks, facilitating the storage and transport of “fresher” SNF bundles.

A capacity increase is a major factor in reducing the overall storage and transport cost to utility companies. Alternatively, if the capacity increase is not needed, the diameter reduction (about 6 cm, or 35%) will reduce the costs of materials and fabrication as well as the overall system weight. The thinner DUCRETE shell would also allow higher heat loadings in these casks. Based on a very simple model, the estimated weight reduction for the CONSTOR cask with DUCRETE would be about 10 tonnes.

2.8.3 Disposal Waste Package Shield

Currently, the DOE geological repository project bans the use of concrete in the repository. This is based on the perception that cement can affect the pH of the groundwater and therefore increase the mobility of nuclides and the corrosion of repository disposal packages. It is our experience that pozzolanic-based cements buffer the pH and greatly decrease the mobility of nuclides, including uranium and long-lived actinides. Furthermore, pozzolanic concretes with excess silica (see Table 4), such as those proposed for DUCRETE, can be formulated to promote the formation of passivating films to protect the metals from corrosion.

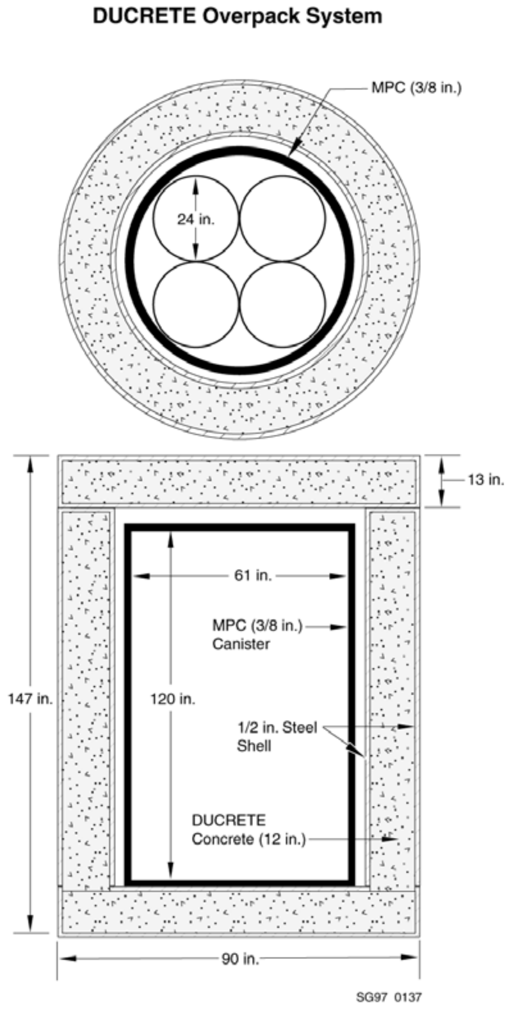


Fig. 16. High-level waste (HLW) canister shield developed for a multipurpose HLW canister.

Therefore, DUCRETE casks could be used at the geological repository for shielding the waste package, provided special pozzolanic cements are used (Fig. 16). Such special concretes have been developed for other geological disposal applications. In the repository concepts, the waste disposal package is a key engineered feature needed to ensure that the repository meets its long-term performance criteria. The waste package is the container into which the spent fuel will be loaded at the repository. For repository use, this package must be fabricated from materials that are designed to last 10,000 years.

For some repositories, design specifications for waste packages have allowed an increase in the external dose specification from about 100 R/h to over 1000 R/h. In these cases, gamma and neutron shielding is not an issue. However, a DUCRETE cask could be fabricated that would integrate the waste package and required shielding capabilities needed at a repository. Calculations by J. Tang showed that DUCRETE shielding factors are 20 times better than those of other materials evaluated.[19] Such a multiple-purpose cask would allow the repository to be designed for unrestricted human access for fuel emplacement, inspections, and underground facility maintenance. A paper by Quapp describes this concept, its benefits, and its costs.[20] Overall, the use of DUCRETE shielding for utility storage, as well as for shielding waste packages, would simplify operation of the repository and provide an answer to the long-term disposition of the huge inventory of DU.

There are a number of benefits from using a pozzolanic-based DUCRETE in the repository:

- The material provides a physical barrier to rock falls and drift convergence.
- Pozzolanic additives passivate steel and nickel surfaces and reduce corrosion rates.
- DUCRETE provides high chloride and sulfate resistance with impermeable hydroaluminosilicate phases.
- A pozzolanic-based DUCRETE buffers geochemistry to a mild alkaline pH range.
- A mild steel fiber and rebar reinforcement buffers Eh to a reducing environment that stabilizes insoluble UO_x's.
- DUO_2 and pozzolans significantly reduce the solubility and transport of uranium, fission products, and transuranics.

2.8.4 High-Level Waste Canister Shielding

The current U.S. practice for shielding vitrified HLW is to store canisters in a shielded storage building. These canister are 24 in. (61 cm) in diameter and about 10 ft (305 cm) long. The cost of the storage building for these canisters in 1990 was about $100 million. A variety of studies[21] have shown that DUCRETE casks may provide a more cost-effective solution for future storage requirements. The existing glass waste storage buildings have sufficient capacity for about 40% of the projected production of canisters. A capacity equivalent to 1.5 times the present building size is needed for the projected canister production.

As part of a proposal to the Savannah River Site, Starmet and Duke Engineering and Services evaluated the feasibility of using DUCRETE concrete material for HLW storage casks.[22] This cask concept is shown in Fig. 17. Use of DUCRETE allows the wall thickness to be kept to about 10 in. and results in an external radiation field of 10 milliroentgen/h at a 2-m distance from five HLW canisters. The cask uses a stainless steel glass canister as containment and natural convection cooling to remove the thermal energy. This cask was intended to be a storage-only cask for use at the Savannah River Site as an

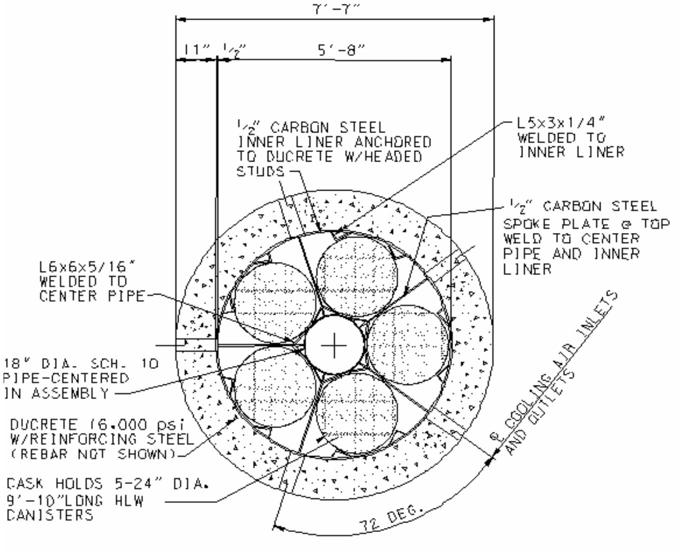

7′-7″
11″
½″
5′-8″
½″ CARBON STEEL INNER LINER ANCHORED TO DUCRETE W/HEADED STUDS
L5x3x1/4″ WELDED TO INNER LINER
½″ CARBON STEEL SPOKE PLATE @ TOP WELD TO CENTER PIPE AND INNER LINER
L6x6x5/16″ WELDED TO CENTER PIPE
18″ DIA. SCH. 10 PIPE-CENTERED IN ASSEMBLY
DUCRETE (6,000 psi W/REINFORCING STEEL (REBAR NOT SHOWN)
CASK HOLDS 5-24″ DIA. 9′-10″LONG HLW CANISTERS
℄ COOLING AIR INLETS AND OUTLETS
72 DEG.

Fig. 17. Cross section of Starmet/Duke DUCRETE Defense Waste Processing Facility cask for Savannah River Site HLW glass.

alternative to a second glass waste storage building. Cost estimates indicate that for an equivalent storage facility, including pad and handling facilities, the DUCRETE cask storage system would be less expensive than a new glass waste storage building. In addition, the casks would use most of the 55 million pounds of unneeded UO_3 on the Savannah River Site, thus saving more than $80M in disposal costs.

At the end of these casks' storage lives, they could be transported separately from the HLW and used for SNF shielding at a repository. Since DUCRETE is an excellent waste form, another alternative would involve disposing of the silos into shallow land burial and even using them as waste burial vaults.

2.8.5 Remotely Handled Transuranic (TRU) Waste Drum Overpack

In 1997, INEEL identified a need for a large number of shielded drum overpacks. Starmet designed and built DUCRETE drum overpacks as part of its internally funded product development (Fig. 18). These overpacks use a stainless steel shell (14-gage) with DUCRETE poured between the walls and within the lid.

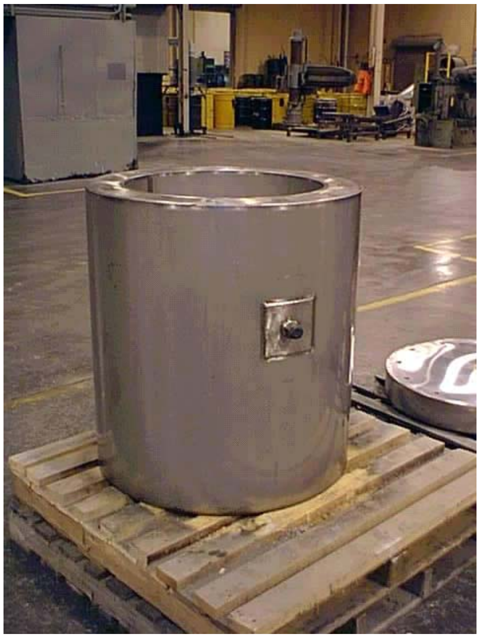


Fig. 18. Stainless steel–clad DUCRETE drum overpack.

2.9 Current ORNL DUAGG Testing

Current testing at ORNL measures the extent and rates of surface reactions of DUAGG under the expected service temperatures and the simulated chemical environments of cement pastes. The DUO_2/basalt aggregates in DUAGG samples from Starmet are cleaned in an ultrasonic bath with distilled water to remove surface residuals. These DUAGG samples are then tested for aggregate reactivity using the American Society for Testing and Materials (ASTM) C289-94 method[23] to measure interactions with pore liquids that are anticipated in concrete pastes. The almond-shaped DUAGG aggregates are 1.59 cm long, 0.95 cm wide, and 0.64 cm thick. The surface area is estimated by assuming a prolate spheroid shape of 3.5 cm^2 or 2.8 cm^2 using a parallelepiped model. Measurements on 17 DUAGG pellets arrived at an average surface area of 5.77 ± 0.01 cm^2.

At a consistent surface-to-liquid ratio of 1:10, the sintered DUAGG samples are exposed to distilled water, to a 1N sodium hydroxide standard solution, and to an extract of high-alkali cement water. The exposure temperatures are 25, 66, and 150ºC for six time intervals of 30, 60, 90, 180, 240, and 360 days. At the end of each exposure period, the vessels in which the samples are immersed are opened and the liquid phase is separated and filtered for analysis of silica, uranium, alkalies, and other elements measurable by ion coupled plasma (ICP) mass spectrometry. The elemental quantities leached are compared to determine the degree of erosion of the aggregate surfaces.

The surfaces of the exposed aggregates are compared, according to the guidelines of ASTM C295-98,[24] using SEM and energy-dispersive X-ray fluorescence (EDX) analyses. The extent of surface alteration and formation of secondary minerals are used to indicate the potential for aggregate paste interactions in DUCRETE.

For 25 pellets with an estimated density of approximately 8.5 g/cm^3, the average weight was calculated to be 6.39 ± 0.01 g, while the average volume was found to be 0.784 ± 0.002 cm^3. The measured density of a DUAGG pellet is 8.15 g/cm^3 and the surface area is 5.8 cm^2. For a leachate volume/ surface ratio of 10, the volume of liquid used in the vessels for two aggregate pellets is approximately 58 mL. The vessels are rated for 250 psig, and the maximum pressure for a vessel kept at 150ºC is less than 160 psig. The vessels are enveloped in aluminum foil in a secondary container prior to being placed in the oven to prevent leakage in case of a failed rupture disk or vessel gasket. These measurements at ORNL began in September 2001. The ICP analyses for the 30- and 60-day tests are completed, and the microscopic examinations are under way.

2.10 DUAGG and DUCRETE Development Needs

A detailed development proposal was developed in 1998[25] and updated in 2001. The DUAGG and DUCRETE development needs are as follows:

- Develop testing protocols for comparing the interactions between DU aggregate and the cement paste in the heavy concrete.
- Acquire DUAGG samples needed for tests.
- Provide a basis for economic evaluation and component design optimization by measurement of key physical properties of DUAGG matrices, such as thermal conductivity and expansion, shielding parameters, density, and strength.
- Initiate a long-term test program to evaluate the stability of DU aggregate in various matrices under elevated and cyclic temperatures between 20 and ~1400ºF. This demonstration of the stability of the DU aggregate within an oxidizing matrix is needed to provide confidence that DUAGG casks will be functional for the decades of their required service lives. Limited-duration tests have shown instability within 30 days, but at temperatures above the expected operating temperature of the DUAGG matrices. These activities are critical because a long period of time is required for each exposure test.
- Evaluate the technology for making large DUAGG matrix shapes that have adequate homogeneous aggregate distribution and compressive strength and density. This evaluation is needed to demonstrate that large, thick DUAGG matrix shapes have a consistent and uniform mixture of binder and aggregate throughout the shielding and that they can be manufactured to the required performance specifications.
- Establish the use of microfiber reinforcement to increase energy-absorption capacity to better survive assault scenarios.
- Assess alternative disposal options for heavy concrete. This will ensure that heavy DUAGG shapes have a feasible and cost-effective disposal path at the end of their useful lives as shields.
- In collaboration with a potential vendor, construct and test a full-scale DUAGG matrix storage cask.
- Assess the regulatory and econometric market for DUCRETE storage casks.

3. DUPoly

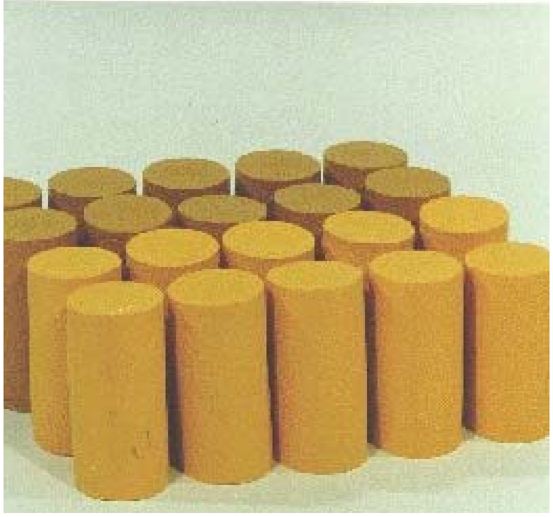


Fig. 19. DUPoly samples produced at BNL containing 80 wt % depleted UO_3.

Brookhaven National Laboratory (BNL) has completed preliminary work to investigate the feasibility of encapsulating DU in low-density polyethylene to form a stable, dense product known as DUPoly.[26, 27] DU loadings as high as 90 wt % were achieved using DU aggregate in a technique known as micro- or macro-encapsulation (Fig. 19).

BNL has used polyethylene encapsulation through the coextrusion of a mixture of polyethylene and waste materials such as salts and contaminated soils for many years.[28, 29,30] Encapsulating DU oxide or UF_4 in the polyethylene matrix was an extension of their experience.

Therefore, the treatment of DU materials by polyethylene encapsulation is technology with a proven record in processing powder and granular materials. In addition, the process is very flexible. Polyethylene products can be heated and reworked if future needs change. DU can also be retrieved from DUPoly by thermal processing if needed as a resource in the future. Recycled plastics from industrial or post-consumer sources can be used in place of virgin materials to reduce costs and produce valuable products entirely from recycled materials. BNL has extensively developed, tested, and demonstrated the polyethylene encapsulation processes for low-level radioactive, hazardous, and mixed wastes. During processing, waste materials are mechanically mixed into the molten polyethylene binder, producing a workable homogeneous product. The process is not susceptible to chemical interactions between the waste and binder, enabling a wide range of acceptable waste types, high waste loadings, and technically simple processing under heterogeneous waste conditions. The process has evolved from proof of principle, through bench-scale development and testing, to full-scale technology demonstration.

A prototype DUPoly transportation and disposal cask has recently been fabricated to facilitate the disposal of a highly radioactive radium-beryllium source being stored at BNL. DUPoly is ideally suited for reducing both gamma and neutron radiation from the source. The prototype DUPoly transportation and disposal cask will allow a one-time transfer of the source into the shielded cask, shipment to the Hanford disposal site in compliance with U.S. Department of Transportation standards, and burial—all without having to remove the source or handle it again. The DUPoly cask is constructed from recycled materials, so it is inexpensive and can be economically used for disposal.

BNL recently published a patent that gives performance data on the material.[4] A plot of density versus uranium loading is shown in Fig. 20. The maximum product density of 4.2 g/cm^3 was achieved using UO_3, but use of UO_2 would increase density to an estimated 6.1 g/cm^3. Use of DU aggregate through micro- or macro-encapsulation would provide additional density improvements of up to about 7.2 g/cm^3.[31]

BNL also conducted compression tests of the DUPoly using 2 × 4 in. cylinders. The compression test data from the patent is shown in Fig. 21.

The melting point of polyethylene is 140°C, and its maximum long-term service temperature is 100°C. If used, DUPoly must be encased in a design that mechanically meets the service criteria without a physical contribution from the shield materials. Also, UO_3 is a mild oxidizer that can release oxygen when heated in a reducing environment. Therefore, fine particles and high temperatures must be avoided.

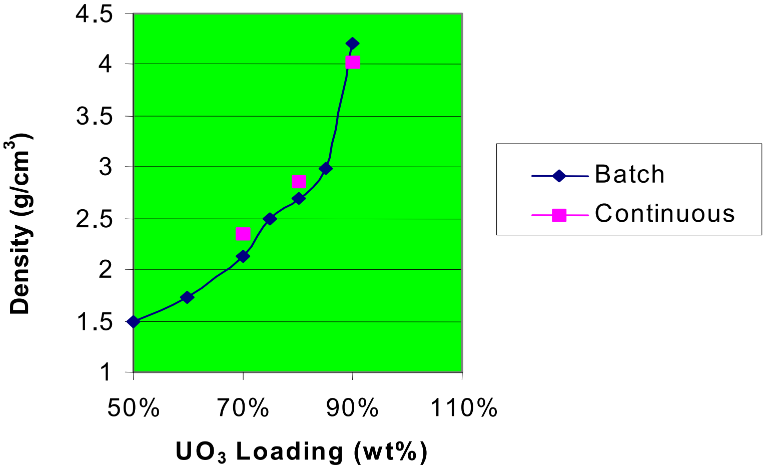


Fig. 20. DUPoly density (in g/cm^3) as a function of UO_3 loading. "Batch" and "continuous" refer to two types of UO_3 production processes. The processing rate was about 16 lb/h.

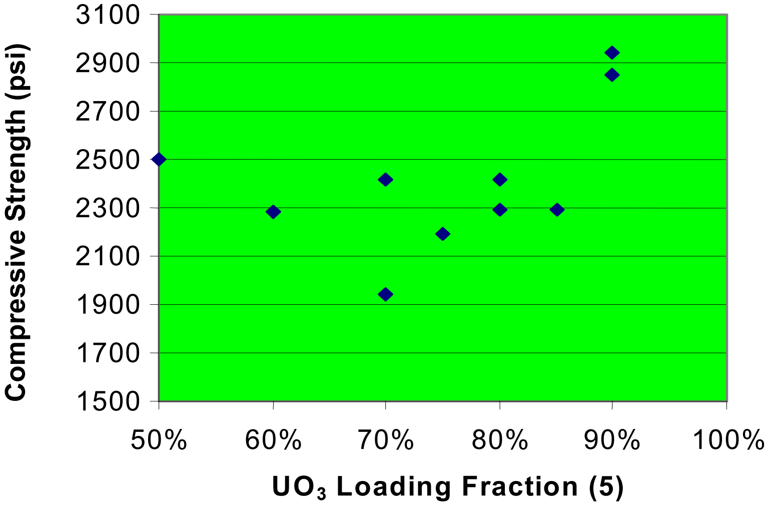


Fig. 21. DUPoly compressive strength (psi) as a function of UO_3 loading.

4. PYRUC

Pyrolytic uranium compound (PYRUC) is a shielding material consisting of DU (UO_2 or UC) in either pellet or microsphere form, coated or uncoated, and combined with a solid matrix binding material. Microspherical products have been formed by treating uranyl nitrate by gelation methods.[32, 33, 34] A number of binding materials are possible (e.g., tar or pitch precursor and high-temperature resins). Murray and his colleagues also considered cement as a binder material.

The production of coated UO_x microspheres is an established technique that was developed in the mid- to late 1960s as a potential alternative method for fabricating nuclear fuel for reactors. Figure 22 illustrates the production and shielding concepts. Thus, mixing microspheres with binders will clearly produce a matrix with both high-Z and low-Z materials for shielding against both gamma and neutron radiation.

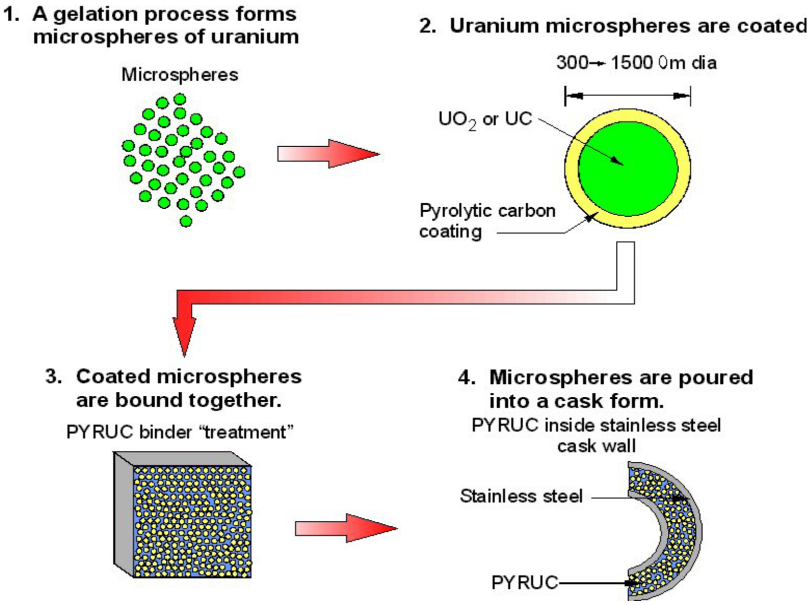

1. A gelation process forms microspheres of uranium
Microspheres
2. Uranium microspheres are coated
300→ 1500 0m dia
UO2 or UC
Pyrolytic carbon coating
3. Coated microspheres are bound together.
PYRUC binder "treatment"
4. Microspheres are poured into a cask form.
PYRUC inside stainless steel cask wall
Stainless steel
PYRUC

Fig. 22. PYRUC process flow diagram.

This initial proposal suggested using the sol-gel process for producing the carbon particles. There are much less costly routes to producing carbon particles. However, because of limited funding, only conceptual studies of PYRUC have been performed. No materials have been fabricated, and thus, no performance data are available. For systems using tar or pitch, the density would be expected to be comparable to that of DUPoly.

5. FUTURE RESEARCH AND DEVELOPMENT NEEDS

Future development efforts should be selected on the basis of the potential uses in storage, transport, and disposal casks. Both DUCRETE and DUPoly have undergone sufficient development to allow reasonable estimates of performance attributes for spent fuel and high-level waste shielding applications. Further radiation attenuation measurements should be made using the gamma and neutron spectrums expected from SNF and HLW. Additional analytical studies should be conducted to determine the optimum shielding performance for various loadings of DU in particular binders. The effectiveness of adding additional neutron attenuation elements to the aggregate-binder mixture needs to be evaluated, particularly in the case of materials with fast neutrons.

Demonstrations of the large-scale manufacture of aggregates and tests of prototype casks are needed to establish the technical feasibility of using these materials and to convince cask manufacturers that these new materials are worth their efforts. Finally, the efficacy and benefits of these technologies need to be demonstrated to the potential customers and users of these casks.

6. CONCLUSIONS

Shielding materials containing DU provide beneficial uses for a large portion of the DU inventory. Two of these materials, DUCRETE and DUPoly, have been successfully tested with small quantities. The third, PYRUC, is a hybrid of both that uses the sol-gel production process for the DU aggregate.

DUCRETE, DUPoly, and PYRUC provide shield matrices with high–atomic number (high-Z) and low-Z shielding attributes when optimized. Their properties allow a reduction in the size and weight of storage, transport, and disposal casks. However, further development will be required if structural strength is needed in a cask design.

Research on these materials is needed to complete the optimization of gamma and neutron absorbers and to qualify them for licensed nuclear applications. Lower-cost production processes also need to be developed. It is still possible to qualify these materials for use in final geological disposal. Experimental work needs to be completed to demonstrate that these materials can meet disposal sites' shielding and durability requirements.

DU materials can provide a large performance advantage over existing shielding materials. Commercial cask firms interested in proposing technologies have not done so because the fabrication technologies are not yet mature. Their biggest concerns are related to manufacturing costs and regulatory acceptance.

7. REFERENCES

1 T. J. Hertzler and D. D. Nishimoto, *Depleted Uranium Management Alternatives,* EGG/MS-11416 (Washington, D.C., August 1994).

2 H. R. Yoshimura et al., *Use of Depleted Uranium Metal as Cask Shielding in High-Level Waste Storage, Transport, and Disposal Systems*, Sand94-0826/TTC-1311 (Livermore, Calif.: Sandia National Laboratories, 1994).

3 F. E. Kosinski, "Review of Commercial Uranium Processing Capability," Letter Report to C. R. Cooley, U.S. DOE, EM50, TDC-100, Rev. 1, Technics Development Corporation, October 29, 1993.

4 W. J. Quapp and P. A. Lessing, U.S. Patent No. 5,786,611, "Radiation Shielding Composition," July 28, 1998.

5 W. J. Quapp and P. A. Lessing, U.S. Patent No. 6,166,390, "Radiation Shielding Composition," Dec. 26, 2000.

6 J. W. Sterbentz, *Shielding Evaluation of a Depleted Uranium Heavy Aggregate Concrete for Spent Fuel Storage Casks*, INEL-94/0092 (Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory, October 1994).

7 R. T. Haelsig, *Depleted Uranium Concrete Container Feasibility Study*, EGG/MS-11400 (Washington, D.C.: Packaging Technology Inc., 1994).

8 J. E. Hopf, *Conceptual Design Report for the DUCRETE™ Spent Fuel Storage Cask System*, INEL-95/0030 (Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory, February 1995).

9 J. E. Hopf, *Conceptual Design Report for a Transportable DUCRETE™ Spent Fuel Storage Cask System*, INEL-95/0167 (Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory, April 1995).

10 F. P. Powell, *Comparative Economics for DUCRETE™ Spent Fuel Storage Cask Handling, Transportation, and Capital Requirements*, INEL-95/0166 (Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory, March 1995).

11 P. A. Lessing, *Development of "DUCRETE™,"* INEL-94/0029 (Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory, March 1995).

12 Pacific Sierra Nuclear Associates, *Safety Analysis Report for the Ventilated Storage Cask System,* PSN-91-001, Rev. 0 (Scotts Valley, Calif., October 1991).

13 Babcock & Wilcox Company, *BR-100 Shipping Cask Preliminary Design Report,* 51-1177082-01 (Lynchburg, Va., n.d.), p. II-3-11.

14 P. A. Lessing, "High Temperature Oxidation Tests of DUCRETE™," unpublished paper, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho, October 1997.

15 J. K. Schultis and R. E. Faw, *Radiation Shielding* (LaGrange Park, Ill.: American Nuclear Society, 2000).

16 W. J. Quapp et al., “DUCRETE™: A Cost Effective Radiation Shielding Material,” Spectrum 2000.

17 U.S. Department of Energy, *Integrated Data Base Report —1994: U.S. Spent Nuclear Fuel and Radioactive Waste Inventories, Projections and Characteristics,* DOE/RW-0006, Rev 11 (Washington, D.C.: September 1995), p. 36.

18 R. Diersch and A. Jack, *The CONSTOR Steel-Concrete Cask for Transport and Storage of Spent Nuclear Fuel from RBMK, INMM* (Washington, D.C.: Gesellschaft für Nuklear-Behälter [GNB] January 1998).

19 J. Tang, *Shielding Characteristics of Various Materials on PWR Waste Packages*, BBAC00000-001717-0210-00008, Rev. 00 (Yucca Mountain Project Office, February 1998).

20 W. J. Quapp, “DUCRETE™ Shielding Applications in the Yucca Mountain Repository,” paper presented at Waste Management 1999, Tucson, Ariz., March 1999.

21 W. J. Quapp, “An Advanced Solution for the Storage, Transportation and Disposal of Spent Fuel and Vitrified High Level Waste,” paper presented at Global ’99, Jackson, Wyo., August 29–September 2, 1999.

22 N. Seagle, Duke Engineering Services, “DUCRETE HLW Storage System Feasibility,” unpublished report, February 1998.

23 ASTM C 289–94, “Standard Test Method for Potential Alkali-Silica Reactivity of Aggregate” (Chemical Method).

24 ASTM C 295–98, “Standard Guide for Petrographic Examination of Aggregates for Concrete.”

25 W. J. Quapp, “Unsolicited Proposal for DUCRETE™ Concrete Material Property Measurements and Fabrication Studies,” Letter to Charles Bradley, DOE, Nuclear Energy, June 15, 1998.

26 P. Kalb et al., “DUPOLY Process for the Treatment of Depleted Uranium and the Production of Beneficial End Products,” U.S. Patent, No. 6,030,549, February 29, 2000.

27 J. W. Adams, P. R. Lageraan, P. D. Kalb, and S. P. Rutenkroger, *Feasibility Study of DUPoly to Recycle Depleted Uranium,* BNL-52597 (Upton, N.Y.: Brookhaven National Laboratory, February 1998).

28 J. W. Adams and P. D. Kalb, “Thermoplastic Stabilization of Chloride, Sulfate, and Nitrate Salts Mixed Waste Surrogate,” paper presented at the I&EC Special Symposium, American Chemical Society, September 1994.

29 P. D. Kalb and P. R. Lageraaen, “Full-Scale Technology Demonstration of a Polyethylene Encapsulation Process for Radioactive, Hazardous, and Mixed Wastes,” *Journal of Environmental Science and Health* A31, no. 7 (1996).

30 R. P. Bhavesh, P. R. Lageraaen, and P. D. Kalb, *Review of Potential Processing Techniques for the Encapsulation of Wastes in Thermoplastic Polymers,* BNL-62200 (Upton, N.Y.: Brookhaven National Laboratory, August 19950.

31 J. W. Adams, P. R. Lageraaen, P. D. Kalb, and B. R. Patel, *Polyethylene Encapsulation of Depleted Uranium Trioxide*, ed D. W. Tedder and F. G. Pohland (New York: Plenum Press, 2000).

32 A. P. Murray, S. M. Mirsky, and S. J. Krill, “Pertinent Attributes of Depleted Uranium Shielding and its Manufacture,” paper presented at the Third International Hexafluoride Handling Conference, Paducah, Ky., December 1995.

33 A. P. Murray, S. M. Mirsky, P. Hogroian, and S. J. Krill, “Gelatin Conversion of Depleted Uranium Hexafluoride into Dense Uranium Dioxide Microspheres,” paper presented at the Third International Hexaflouride Handling Conference, Paducah, Ky., December 1995.

34 A. P. Murray, S. M. Mirsky, and S. J. Krill. “Production of Dense Uranium Dioxide on a Large Scale,” paper presented at the American Institute of Chemical Engineers Meeting, Houston, Texas, March 9–13, 1997.

INTERNAL DISTRIBUTION

1. J. M. Begovich
2. A. G. Croff
3–8. L. R. Dole
9–14. M. J. Haire
15. J. R. Hightower
16. D. J. Hill
17. G. E. Michaels
18. D. L. Williams
19. Office of Technical Information and Classification

EXTERNAL DISTRIBUTION

20–22. Howard Huie, ME-222/Germantown Building, U.S. Department of Energy, EM-32, 1000 Independence Ave. SW, Washington, DC 20585-1290
23–28. W. J. Quapp, Teton Technologies, Inc., 860 W. Riverview Drive, Idaho Falls, ID 83401-5691
29. Office of Assistant Manger of Energy Research and Development, P.O. Box 2008, DOE-ORO, Oak Ridge, TN 37381-6269