

A NEW REPOSITORY WASTE FORM: GRAPHITE-CARBON HIGH-LEVEL WASTE

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A New Repository Waste Form: Graphite-Carbon High-Level Waste

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Abstract—High-temperature gas-cooled reactors (HTGRs) are currently being investigated for use in burning actinides and thus reducing the long-term waste management burden on the repository. Because not all the actinides are destroyed in the reactor during irradiation of the fuel, it is necessary to process the spent nuclear fuel (SNF) to recover the remaining actinides for recycle and ultimate actinide destruction. The SNF consists of oxide microspheres with multiple coatings (silicon carbide, multiple carbon layers) embedded in a graphite matrix. The SNF processing generates (1) dissolver residues with noble metals, silicon carbide, and particulate carbon; (2) an aqueous nitric acid fission product stream; and (3) various carbon wastes.

Because the wastes generated in processing HTGR fuel are different from those associated with traditional light-water-reactor SNF, it is appropriate to consider a new high-level waste (HLW) form based on the characteristics of the wastes: a graphite-carbon HLW. Fission products would be solidified using the carbon in various forms from the SNF assembly. Producing a waste form based on the chemical form of the raw wastes has the potential to minimize waste processing (reduced cost and risk) and minimize total waste volumes (minimal addition of waste formers). This new waste form has the potential for excellent performance.

I. INTRODUCTION

High-temperature gas-cooled reactors (HTGRs) are being investigated for the destruction of minor actinides.¹ For this application, the spent nuclear fuel (SNF) contains driver fuel (DF) and transmutation fuel (TF). The fresh DF is a mixture of plutonium and neptunium from processing light-water reactor (LWR) SNF. The spent DF, which contains plutonium, neptunium, americium, curium, and fission products, is to be processed for recovery of unburnt actinides. The fresh TF, a mixture of neptunium, high-burnup plutonium (a mixture of primarily ²⁴⁰Pu, ²⁴¹Pu, and ²⁴²Pu), americium and curium, contains (1) the actinides from processing the HTGR DF and (2) americium and curium from processing LWR SNF. The TF fuel is designed so that most of the actinides are destroyed in a single irradiation in the reactor. The reactor-irradiated TF compacts are either directly disposed of or further irradiated for actinide destruction in an accelerator.

HTGR SNF (Table 1, Fig. 1) is very different from LWR SNF. The HTGR SNF consists of oxide microspheres coated with several layers of different types of carbon and a layer of silicon carbide (SiC). The coated particles are incorporated into cylindrical fuel compacts (rods) with a carbon matrix, which are then embedded in holes in a hexagonal graphite fuel block.

Table 1. Material Balance for Materials in One Graphite-Matrix Fuel Element

Component	Mass (kg)				
	Fuel Element	Transmutation Fuel		Driver Fuel	
		Compacts (rods)	Particles	Compacts	Particles
Graphite block	90.00	0	0	0	0
Compact filler carbon ^a	13.97	3.14	0	10.83	0
Particulate coatings					
Pyrocarbon	4.58	0.72	0.72	3.86	3.86
Porous carbon	1.96	0.26	0.26	1.70	1.70
SiC	3.58	0.56	0.56	3.02	3.02
TF (TRU)	0.20	0.20	0.20	0	0
DF (Fuel + FPs)	0.80 + 1.88	0	0	0.80 + 1.88	0.80 + 1.88
TOTAL	116.97^b	4.88	1.74	22.09	11.26

^aAssumes a DF:TF ratio of compacts of 4:1.

^bWithout the graphite block, the total mass of carbon in compacts is 20.51 kg.

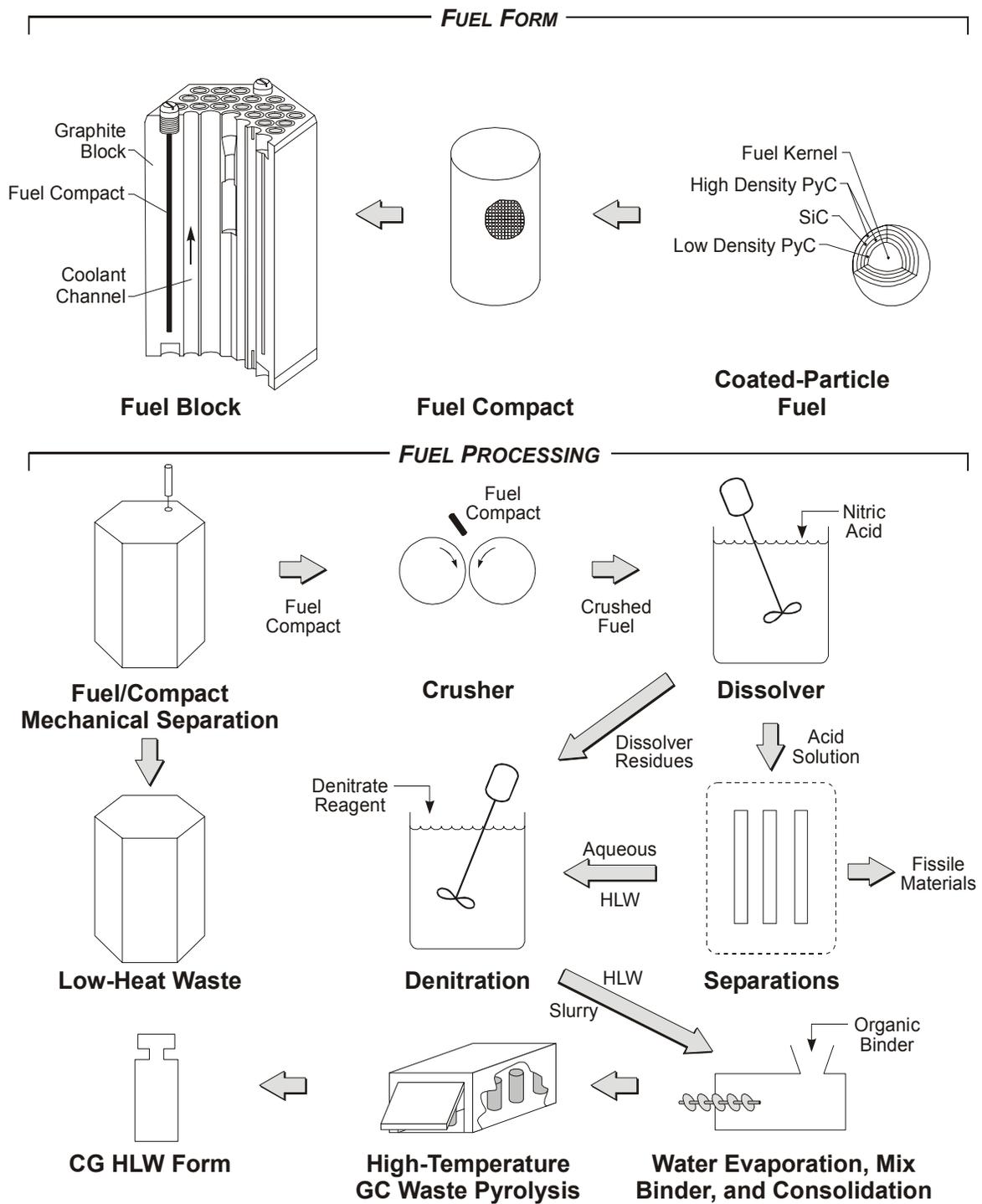


Fig. 1. Production of the graphite-carbon high-level waste (HLW) form.

Traditional approaches to processing graphite-matrix coated-particle SNF are expensive compared with those for LWR SNF because of two factors. First, only about 3% of the HTGR fuel assembly is composed of fissile, fertile, and fission product oxides, with remainder composed of graphite and SiC. In contrast, 60 to 70% of the mass of an LWR SNF assembly is composed of fissile, fertile, and fission product oxides with the remainder composed of zircaloy cladding and hardware. Larger masses of material must be processed to recover the fissile and fertile materials from HTGR SNF. Second, the graphite contains significant quantities of radioactive ^{14}C , which means the carbon must be treated as a radioactive waste.

In addition to the specific costs associated with processing graphite-matrix fuel, major costs are associated with processing any oxide fuel. The typical cost breakdown of processing LWR SNF yields the following capital cost distribution²: receiving and storage: 26%; head-end processing: 21%; separations: 17%; waste handling: 17%; and balance of plant (utilities and support facilities): 19%. If these costs are to be reduced, head-end and waste management processes must be integrated. Although limited research has been conducted on methods to integrate these operations in LWR SNF processing facilities,³ none has been performed for HTGR processing facilities.

Based on the above considerations, an evaluation¹ of new methods to process graphite-matrix coated-particle fuels was undertaken. This initiative led to a flowsheet that (1) avoided complex processing of the graphite matrix, (2) integrated front-end and waste management operations, and (3) naturally resulted in a graphite-carbon waste form.

II. PROCESS DESCRIPTION

A new HTGR SNF processing approach is proposed that yields a new HLW form (Fig. 1). The process consists of the following steps.

Carbon removal. Traditionally, the first step in processing HTGR SNF has been to burn the graphite to yield carbon dioxide (CO_2), scrub the off-gas with a calcium hydroxide ($\text{Ca}(\text{OH})_2$) solution, and produce a solid calcium carbonate (CaCO_3) waste form that contains the ^{14}C . A typical HTGR SNF assembly is 94.5 wt % carbon in different forms; thus, the largest SNF processing operations are associated with burning the carbon and recovery of the CO_2 . The equipment size is large because of large masses of materials and the very low density of the CO_2 gases compared with those of liquid solutions elsewhere in the processing plant.

An alternative front-end carbon-removal step is proposed. The fuel compacts (rods) are mechanically removed from the graphite block. The DF and TF compacts are located in different holes in the graphite block and thus can be removed separately. The mechanical technology for removal of fuel compacts from the graphite block has been demonstrated.^{4,5} The graphite block, containing ^{14}C and representing 77 wt % of the mass of the original SNF assembly, becomes a low-heat graphite waste form for direct disposal in a repository. The spent TF compacts are directly disposed of as HLW or are fabricated into new compacts that are further irradiated in an accelerator to destroy the actinides. The DF compacts are processed for actinide recovery.

If most of the graphite can be separated from the SNF, the waste volume is substantially reduced compared with that associated with processes in which the graphite is burned. The density of carbon in graphite is 2.25 g/cm³, whereas that in CaCO₃ is 0.35 g/cm³. If graphite is the final carbon waste form, its volume will be only 16% that of an equivalent CaCO₃ final waste form. This reduced volume has a significant impact on waste disposal costs and provides a large incentive to avoid changing the chemical form of the graphite.

Dissolution. The spent DF compacts (rods) are crushed and leached in nitric acid, which dissolves uranium, plutonium, higher actinides, and many fission products. The process of crushing also destroys both the compacts and the microspheres. The leach solution is then sent to a conventional processing plant (the same as that used to process LWR fuel) for recovery of the fissile and fertile materials. The leaching process leaves an insoluble residue of graphite particles, SiC hulls, and noble metal fission products. There is large-scale non-nuclear industrial experience in crushing and leaching graphite.⁶ Natural graphite is purified by grinding to a fine powder; leaching with nitric acid and sulfuric acid mixtures to remove impurities; washing; and further processing to produce high-grade graphite products such as gaskets for automobile engines.

Separations. As previously indicated, the aqueous solution with actinides and fission products is sent to a modified aqueous separations process that produces (1) the product streams containing the actinides and (2) an aqueous HLW stream consisting of nitric acid, the soluble fission products, and trace quantities of actinides.

Denitration. The aqueous HLW stream from the separations process is denitrated and mixed with the dissolver residues. The aqueous HLW stream may be thermally denitrated, with the resultant oxides mixed with the dissolver residue. Thermal denitration of HLW is the standard industrial process⁷ in existing SNF processing facilities. (In those facilities, the HLW liquid is thermally denitrated, the resultant oxides are mixed with glass frit, and the mixture is melted to produce HLW glass.)

Alternatively, the dissolver residue and the aqueous HLW stream are mixed and the solution is then denitrated. In the process of denitration, most of the fission products precipitate onto the dissolver residues. The denitration can be performed by using electrolytic processes or by addition of appropriate reagents,⁸ the requirement being denitrification without oxidation of the carbon containing the ¹⁴C. Although several chemical processes are theoretically capable of performing this task, these processes have not been demonstrated using simulated HLW or real HLW liquids. Only the thermal denitration process has been demonstrated and commercialized.

Binder addition and waste consolidation. The denitrated HLW and dissolver residue are mixed with an organic binding agent and compressed to produce a “green” compact. A wide variety of processes that can accomplish this task have been used to manufacture various carbon and graphite objects. One such option is a heated extruder. These devices have been used to solidify radioactive wastes with bitumen while simultaneously evaporating any water from the feed.

High-temperature waste pyrolysis. The solid product is heated at temperatures from 800 to 1000°C, a process that destroys the organic binder and produces the final graphite-carbon (GC) HLW. There is large-scale industrial experience with the addition of binders to graphite and the subsequent bake-out to convert the organic binders to various forms of carbon. This method is used to produce impervious graphite, which is used for the fabrication of many graphite products. In France, this option is being

investigated as a waste treatment process for irradiated graphite moderator blocks from gas-cooled reactors. The objective is to reduce the permeability of the graphite and thus reduce long-term leachability of various radionuclides that are incorporated in the graphite.⁹

The choice of organic binder and temperature determines the specific morphology of the carbon produced from the pyrolysis of the organic. For this application, bake-out temperatures will be limited by the desire to avoid vaporization of cesium compounds from the graphite waste form. The option exists to place the waste form in a graphite cylinder before bake-out to produce a waste form with a relatively clean exterior.

Each step in this flowsheet has been used in one or more industrial applications. However, in many cases (1) the materials were not radioactive, (2) the chemical compositions were not identical, and (3) the product requirements were different. Although a basis exists to conclude that the process could be successfully developed, many uncertainties remain.

III. WASTE FORM

Thermodynamic analysis indicates that most of the radionuclides in a graphite-carbon waste form will be in the similar chemical forms as those found in HLW glass. Cesium, strontium, and the rare earths will primarily remain as oxides. However, some elements, such as iron, will be reduced by the pyrolytic step to the metal state—rather than to oxides, as is found in HLW glass.

Selected radionuclides will embed themselves within the planer structure of the graphite by a process called intercalation¹⁰ and will be very resistant to being leached from the waste form under almost all potential repository environments. Other radionuclides will be embedded in the GC HLW. The waste loading is determined by the materials in the fuel compact. If higher waste loadings are viable, it may be feasible to add wastes from other processes. The matrix will consist of graphite, the carbon from the SNF compacts, and the degradation products of the organic binder.

The thermal performance of the GC HLW is expected to be superior to that of traditional HLW glass or SNF. SNF temperatures are limited to 350EC to avoid clad degradation, while HLW glass typically has a maximum storage temperature of 400EC to avoid devitrification. A carbon waste form, however, would be expected to maintain its integrity far above these temperatures. Although the thermal conductivity of the proposed GC HLW form is not known, the thermal conductivities of its components are higher than those of glass. The thermal conductivity of SiC is 20 times that of glass, while that of graphite is 50 times that of glass. Combined, these factors should allow much higher heat loads in a GC HLW than in traditional HLW forms without exceeding allowable waste form temperatures. This allows for larger HLW log sizes; reduces the number of HLW logs; and decreases the associated handling costs in storage, transport, and disposal.

Decay heat in a Yucca Mountain waste package (WP) is limited to 11 kW. This is a result of several constraints: preventing waste form damage from high centerline temperatures and limiting the thermal impacts to the repository from the decay heat. The higher-temperature capabilities of the GC HLW eliminate the first WP decay-heat constraint, while the compositional differences between this waste and traditional HLW may relax the second constraint. The two sources of decay heat are the fission products (⁹⁰Sr and ¹³⁷Cs) and the actinides. The removal of the higher actinides reduces the long-term decay heat compared with that associated with SNF and traditional HLW.¹¹ More detailed analysis will be required to determine the ultimate WP decay-heat limits for GC HLW.

The HLW WPs used in a repository are expensive because they are designed for very long lifetimes. Thus, there are incentives to minimize the volume of HLW and the number of WPs. For a given amount of reactor-produced energy (the product desired by society), the volume of the GC HLW is less than half that of LWR SNF. Irradiation and processing of this SNF decrease HLW volumes compared with those produced by the existing nuclear power system. The proposed Yucca Mountain WP is designed with an internal volume of 7.3 m³ and contains 21 pressurized-water-reactor (PWR) SNF assemblies (- 10 metric tons of initial heavy metal). The typical PWR SNF burnup is 30,000 MWd/ton. In terms of energy, the WP accepts the PWR SNF from producing 300,000 MWd of energy. For the proposed GC HLW, the same WP accepts the wastes from HTGRs that produced - 700,000 MWd of energy, assuming an average waste density of 2 g/cm³.

Preliminary assessments suggest that the GC HLW form may have a high resistance to combustion, but extensive testing will be required for confirmation. Because of the lack of volatile off-gassing upon heating and the low surface area, high-density graphite and carbon are very hard to burn.⁹ Equally important, the waste form contains large quantities of SiC—13 wt %. Under oxidizing conditions, this compound is expected to form a protective layer of nonburnable SiO₂ that prevents oxidation. The addition of SiC has been investigated as a means of preventing combustion of graphite-matrix nuclear fuels under extreme fire conditions in a reactor accident. The amounts of SiC in this waste form are greater than those proposed for fire resistance.

A GC HLW has the potential for superior long-term performance in the repository environment. The initial analysis of direct disposal of graphite-matrix SNF shows excellent performance under Yucca Mountain conditions. While carbon forms are not thermodynamically stable under oxidizing geochemical environments, measured oxidation kinetics at expected repository temperatures imply lifetimes of hundreds of millions of years.¹² At one time, a graphite WP was considered for the Yucca Mountain project. Although this type of WP had outstanding geochemical durability, it was ultimately rejected because of the brittle characteristics of graphite, which made it unsuitable as a package material to keep groundwater out. Although a single crack causes a graphite WP to fail, cracking only increases the surface area of the GC-HLW log.

IV. REPOSITORY CONSIDERATIONS

The processing of graphite-matrix coated-particle fuel results in two primary waste forms: graphite (containing ¹⁴C, radionuclides from activation of graphite impurities, and fission products that have escaped from the coated-particle microspheres) and a GC HLW form. Because of the very low decay-heat levels in the graphite waste form, a variety of low-cost geological disposal options exist. For example, the waste can be disposed of in large underground silos with dimensions of tens of meters.¹¹ The silo performs the same functions as a traditional WP in isolating the radioactivity from the environment. The GC HLW is a more traditional HLW form that will require conventional WPs and use of traditional disposal technologies.

V. CONCLUSIONS

The traditional HLW form, borosilicate glass, was chosen because the original HLW was high in sodium and silicon: the sodium, from neutralization of the nitric acid with sodium hydroxide, and the silicon, an additive in the early metallic fuels. If the SNF composition is very different and large quantities of SNF

are expected to be processed, alternative waste forms should be considered that minimize processing and final waste form volumes.

An investigation of processing options for graphite-matrix coated-particle SNF was undertaken. The potential exists to produce a GC HLW form that reduces additives and results in a high-performance final waste form. Significant experimental work will be required to (1) develop the process, (2) develop the waste form, (3) measure the performance of the GC HLW, and (4) provide the quantitative data to evaluate this alternative waste form.

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