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ORNL/TM-2002/156

TRISO-Coated Fuel Processing to Support High-Temperature Gas-Cooled Reactors

September 2002

Prepared by

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ORNL-27 (4-00)

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SUPPORT HIGH-TEMPERATURE GAS-COOLED REACTORS**

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Date Published: September 2002

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P.O. Box 2008
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managed by
UT-Battelle, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

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ACRONYMS

BISO	designation for particle fuel coating consisting of layers of two types: a porous carbon layer and a pyrolytic carbon layer
DOE	U.S. Department of Energy
DF	driver fuel
DU	depleted uranium
FP	fission product
FR	fast reactor
GA	General Atomics
GC	graphite-carbon
GT-MHR	gas turbine–modular helium-cooled reactor
HLW	high-level radioactive waste
HTGR	high-temperature gas-cooled reactor
LLW	low-level radioactive waste
LWR	light-water reactor
MHA-bT	modular helium-cooled accelerator–based transmutation
MHR	modular helium-cooled reactor
MHR-bT	modular helium-cooled reactor–based transmutation
MHTGR	modular high-temperature gas-cooled reactor
MOX	mixed oxide
NCS	nuclear criticality safety
NRC	U.S. Nuclear Regulatory Commission
ORNL	<i>Oak Ridge National Laboratory</i>
PWR	pressurized-water reactor
SNF	spent nuclear fuel
SRS	Savannah River Site
TF	transmutation fuel
TRISO	designation for particle fuel coating consisting of layers of three types: a porous carbon layer, a pyrolytic carbon layer, and a silicon carbide layer
TRU	transuranium
YM	Yucca Mountain

EXECUTIVE SUMMARY

The initial objective of the work described in this report was to identify potential methods and technologies needed to disassemble and dissolve graphite-encapsulated, ceramic-coated gas-cooled reactor spent fuels so that the oxide fuel components can be separated by means of chemical processing. The purpose of this processing is to recover (1) unburned fuel, including off-specification or defective fuel, for recycle; (2) long-lived actinides and fission products for transmutation; and (3) other fission products for disposal in acceptable waste forms. Follow-on objectives were to identify and select the most promising candidate flow sheets for experimental evaluation and demonstration and to address the need to reduce technical risks of the selected technologies.

High-temperature gas-cooled reactors (HTGRs) may be deployed in the next ~20 years to (1) enable the use of highly efficient gas turbines for producing electricity and (2) provide high-temperature process heat for use in chemical processes, for example the production of hydrogen for use as clean-burning transportation fuel. Also, HTGR fuels are capable of significantly higher burn-up than light-water-reactor (LWR) fuels or fast-reactor fuels; thus, the HTGR fuels can be used efficiently for transmutation of fissile materials and long-lived actinides and fission products, thereby reducing the inventory of such hazardous and proliferation-prone materials. The “deep-burn” concept, described in this report, is an example of this capability.

Processing of spent graphite-encapsulated, ceramic-coated fuels presents challenges different from those of processing spent LWR fuels. LWR fuels are processed commercially in Europe and Japan; however, similar infrastructure is not available for processing of the HTGR fuels. Laboratory studies on the processing of HTGR fuels were performed in the United States in the 1960s and 1970s, but no engineering-scale processes were demonstrated. Regulations developed since that time concerning emissions will impact the technologies used in processing the fuel.

Results of a material balance on one graphite fuel block (fuel element) are summarized in Table ES.1. The mass of recoverable fissionable metal oxides is only 0.8 kg in a fuel element having a total mass of ~117 kg. Removal of both driver fuel (DF) and transmutation fuel (TF) compacts from the graphite block, which account for 90 kg of carbon, reduces significantly the amount of material to process (~8% reduction). The DF compacts themselves contain all 0.8 kg of fissionable metal oxide but constitute a total mass of only ~22.1 kg.

Previous processing of TRISO-coated fuel was based on crushing the graphite fuel blocks and separating the coated fuel particles from the graphite. Oxidation was then used to remove the filler carbon and the outer carbon layer, followed by crushing of the SiC shells and additional burning of the inner carbon layer. The remnant ashes were leached using nitric acid and the resulting solution interfaced with a conventional solvent extraction process. This technology was demonstrated for fuels in which the fissile components were either carbides or oxides. For both types of fuels, the bulk of the graphite was removed by mechanical means, followed by the previously mentioned process of burning, crushing, and leaching. Burning was especially important to processing carbide fuels because hydrolysis of the metal carbides in the dissolution step resulted in soluble organic acids that were deleterious to the solvent extraction process. Studies were also performed in which the entire fuel block was burned, a technique to reduce the number of processing steps.

Burning of graphite fuels results in large quantities of carbon dioxide. Current regulations prohibit disposal of this carbon dioxide to the atmosphere because of the ^{14}C produced in irradiated fuels. Expensive off-gas treatment systems are required to sequester the carbon dioxide, usually by reaction with calcium hydroxide. Such sequestration techniques greatly increase the mass and volume of the waste as compared with that of the original elemental carbon. This encourages identification of alternative processing techniques.

Table ES.1 Materials in one fuel element^a

Component	Mass (kg)				
	Complete	TF		DF	
	Fuel element	Compacts	Particles	Compacts	Particles
Graphite	90.00	0	0	0	0
Filler carbon	13.97	3.14	0	10.83	0
Pyro carbon	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 the compacts is 20.5 1 kg.

Our present analysis has identified two very attractive and promising processing options that, if developed, will greatly simplify the recovery of fissile species from spent TRISO-coated fuels. Simple processing steps, waste minimization, economy of reagents, and the utilization of existing industrial-scale processes and equipment were very important considerations in the design and selection of both processing options. To achieve economy of scale, both options can be directly interfaced with LWR fuel processing plants. Selection of one of the options depends on the type of LWR fuel processing plant that will be deployed.

Conceptually, the process involves removing the fuel compacts from the graphite fuel element, grinding the compacts to expose the fuel kernel, separating the lighter carbon particles from the heavier fuel particles, and leaching or dissolving the fuel components from the remaining carbon fines. The leaching/dissolution alternatives include the use of nitric acid and carbochlorination. The nitric acid leaching can be directly interfaced with conventional aqueous solvent extraction processes. The carbochlorination process will produce a chloride salt that can be further processed by pyrochemical methods. The finely divided carbon waste may be reformed into a compact and durable waste form. The exact details need to be developed and demonstrated.

It is recommended that methods for processing TRISO-coated fuels focus initially on the processing steps needed to place the fissile materials in aqueous solution. This permits the aqueous nitrate product from a custom head-end to be fed to the tri-*n*-butyl phosphate (TBP)-based solvent extraction systems of an LWR spent fuel processing plant. Mechanical separation and nitric acid dissolution do not convert the carbon to other forms, thus keeping the carbon in the most compact form. Mechanical separation is judged desirable for all processing schemes to reduce the production of carbon compounds having greater mass and volume than the original carbon. The mechanical head-end should therefore support either aqueous processing or pyroprocessing techniques. Nitric acid dissolution is expected to effectively dissolve the fuel and fission products (except the noble metals) and permit separation from the carbon fines. Should dissolution become problematic, a fallback position is to resort to oxidation of the carbon, but only as small a quantity as is practical. In either case, a significant quantity of elemental carbon remains from the processing of the fuel. It is further recommended that graphite-carbon HLW forms be explored as a means not only to disposition the excess carbon but also to immobilize the fission product wastes arising from the processing of the spent fuel. The primary processes that require development and careful attention to detail include (1) crushing and milling, (2) carbon-kernel separation, (3) multistage dissolution and leaching of oxide particles from a matrix of carbon and silicon carbide fines, (4) solid-liquid separation, and (5) carbon waste consolidation.

Testing and development of the key processes will be done using a phased approach. Initial tests will be conducted using cold surrogates to simulate the properties of the actual fuel compacts that are important to the particular step to be developed. For example, processing characteristics related to grinding and milling will be initially tested using compacts made from quartz, glass, or alumina spheres in place of actual TRISO particles. Further tests will be done using compacts having surrogate TRISO-coated particles (e.g., kernels made with ZrO_2 , HfO_2 , or UO_2). Solid-solid and solid-liquid separation and dissolution will be initially tested using appropriate mixtures of carbon, pyrocarbon, porous carbon, SiC, and metal oxides of the expected particle sizes and composition. As development progresses and TRISO-fuel compacts become available, final testing will be done using actual fuel compacts.

To test and develop the proposed processing options in the most efficient and economical way, it is proposed that a collaboration be established with relevant industrial partners to adapt existing industrial-scale processes and equipment and to fully utilize the experience gained during previous studies.

The path with the generation of the least amount of waste and the one having the fewest number of process steps includes coring to remove the fuel compacts, grinding and milling of the fuel compacts, solid-solid separation to remove a fraction of the carbon from the fuel oxides, dissolution to produce actinide and fission product nitrates, and liquid-solid separation with washing to remove the carbon, SiC fragments, and undissolved noble metals from the nitrate solution. Solid-liquid separation may be combined with the dissolution process. Waste consolidation to produce a compact graphite-carbon high-level waste form is included as part of the overall process.



1. INTRODUCTION

The initial objective of the work described herein was to identify potential methods and technologies needed to disassemble and dissolve graphite-encapsulated, ceramic-coated gas-cooled-reactor spent fuels so that the oxide fuel components can be separated by means of chemical processing. The purpose of this processing is to recover (1) unburned fuel for recycle, (2) long-lived actinides and fission products for transmutation, and (3) other fission products for disposal in acceptable waste forms. Follow-on objectives were to identify and select the most promising candidate flow sheets for experimental evaluation and demonstration and to address the needs to reduce technical risks of the selected technologies.

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Processing of spent graphite-encapsulated, ceramic-coated fuels presents challenges different from those of processing spent LWR fuels. LWR fuels are processed commercially in Europe and Japan; however, similar infrastructure is not available for processing of the HTGR fuels. Laboratory studies on the processing of HTGR fuels were performed in the United States in the 1960s and 1970s, but no engineering-scale processes were demonstrated. Currently, new regulations concerning emissions will impact the technologies used in processing the fuel.

Potential processing methods will be identified both by a review of the literature regarding the processing of similar fuels and by a reliance on the experience and innovation of the authors. The objective is not to generate an exhaustive list of options but rather to identify a number of potentially practical processing options. These options necessarily take into consideration the chemical characteristics of the entire fuel element and its component parts.

Once the practical options are identified, a qualitative assessment of the technical merit and maturity, relative costs, and relative quantity of waste generation will be used to rank the various options. Through this form of analysis, a base-case flow sheet will be identified for further study and development. A fallback flow sheet will also be selected to reduce the overall technical risk of the development plan.

To support the base-case flow sheet, a technical development plan will be used to identify the key issues for the highest-rated option(s). In this effort the technical uncertainties will be more fully articulated, and research and development activities will be recommended to reduce the technical risks.

2. BACKGROUND

2.1 HTGRs AND TRISO-COATED FUEL

Effective destruction of plutonium with few recycle loops requires a very high burn-up of the fuel. High burn-up requires an exceptionally sturdy fuel form, and efficient waste disposition requires durable encapsulation. An existing reactor technology and fuel type are being developed to meet these needs: the modular helium-cooled reactor (MHR), which uses ceramic-coated-particle fuels (Venneri et al., 2001). The *MHR* is similar to the HTGR that was developed in the 1960s and uses a similar coated-particle fuel. One such reactor was deployed, the Fort Saint Vrain reactor, which used a TRISO-coated highly enriched uranium fuel. High enrichments permit long burn times and reduce the time between refuelings. Use of HTGRs or *MHRs* for reactor-based transmutation to destroy fissionable plutonium is a logical extension of developed technology.

HTGRs and MHRs use ceramic-coated fuel particles that are strong and highly resistant to irradiation. Both use a fixed graphite moderator and neutronically transparent coolant (helium). The fuel particles and the graphite block in which they are imbedded can withstand very high temperatures (up to -1600°C). In addition, the coated particles and graphite block are impervious to moisture for very long periods of time. These attributes make the spent fuel elements a waste form that is more durable than the metallic containers typically used for final waste disposition.

The makeup of TRISO-coated fuel particles is illustrated in Fig. 2.1. The basic construction begins with a spherical fuel particle, or kernel, of UO_2 and/or PuO_x prepared by the internal gelation method (Lerch and Norman, 1984). The kernel is then coated with a porous carbon layer that provides space for gaseous fission products. A second layer of pyrolytic, high-density carbon is deposited over the porous carbon to provide structural strength and to prevent chlorine, used during deposition of the silicon carbide (SiC) layer, from reacting with the kernel. The SiC layer is deposited on the carbon-coated kernel via a chemical vapor deposition method. This layer is very strong and very resistant to chemical attack and provides containment for both gaseous and metallic fission products. A final outer layer of pyrolytic carbon is deposited to further support the SiC layer and to act as a containment barrier should the SiC layer be defective. This final carbon layer also provides a bonding surface for making fuel compacts.

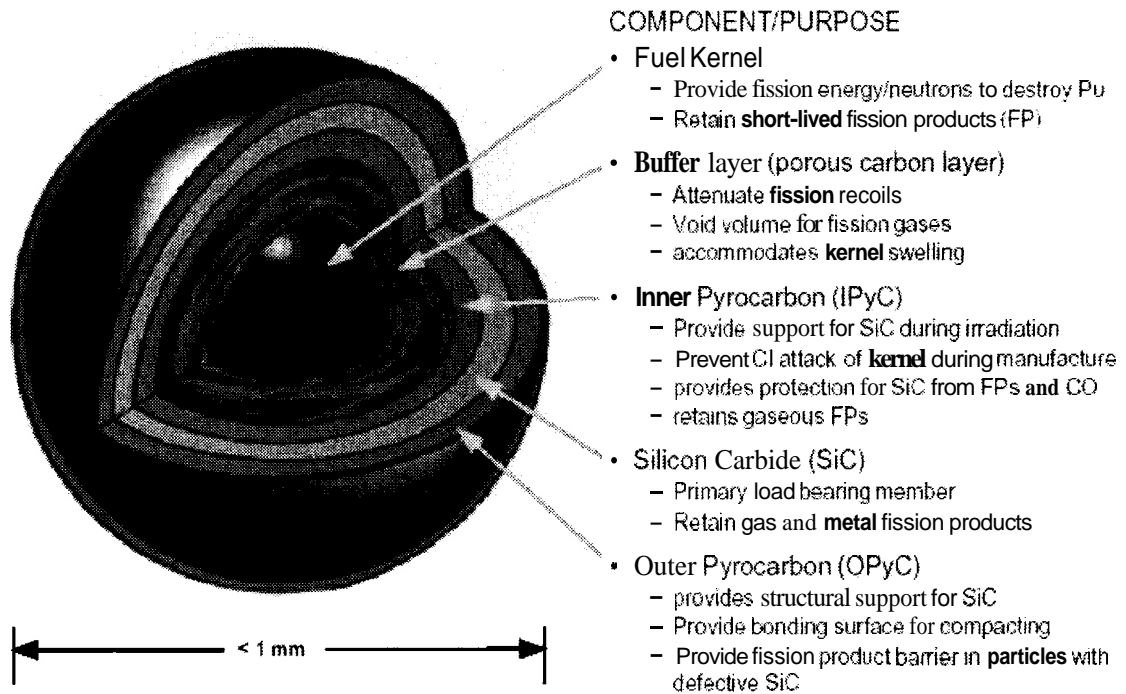


Fig. 2.1. Description of TRISO-coated fuel particle.
(Source: Reprinted with permission from General Atomics.)

A large number of fuel particles are mixed with a carbon-based mastic (tar) to make fuel compacts. The mixture is pressed into the shape of a short right-circular cylinder and sintered at a high temperature to drive off all the volatile components. These compacts are similar in function to fuel rods. The compacts are then loaded into predrilled holes in a machined graphite block to make the fuel element. The fuel elements are hexagonal in shape and contain additional holes to accept control rods and provide a path for flowing coolant. Figure 2.2 illustrates the components of the HTGR fuel elements. Detailed data concerning specific dimensions are given in Sect. 2.3.

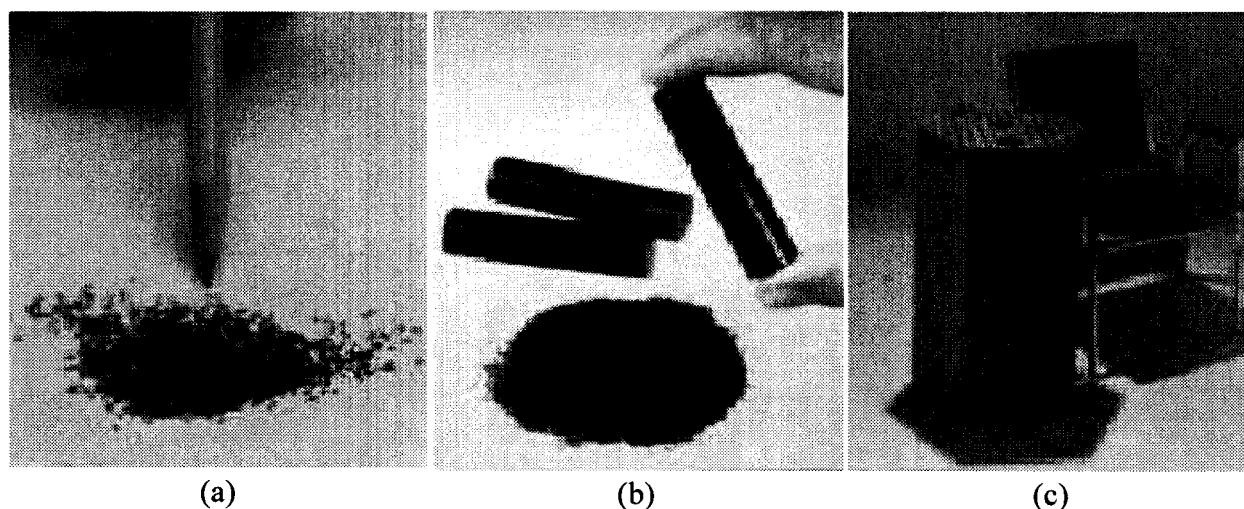
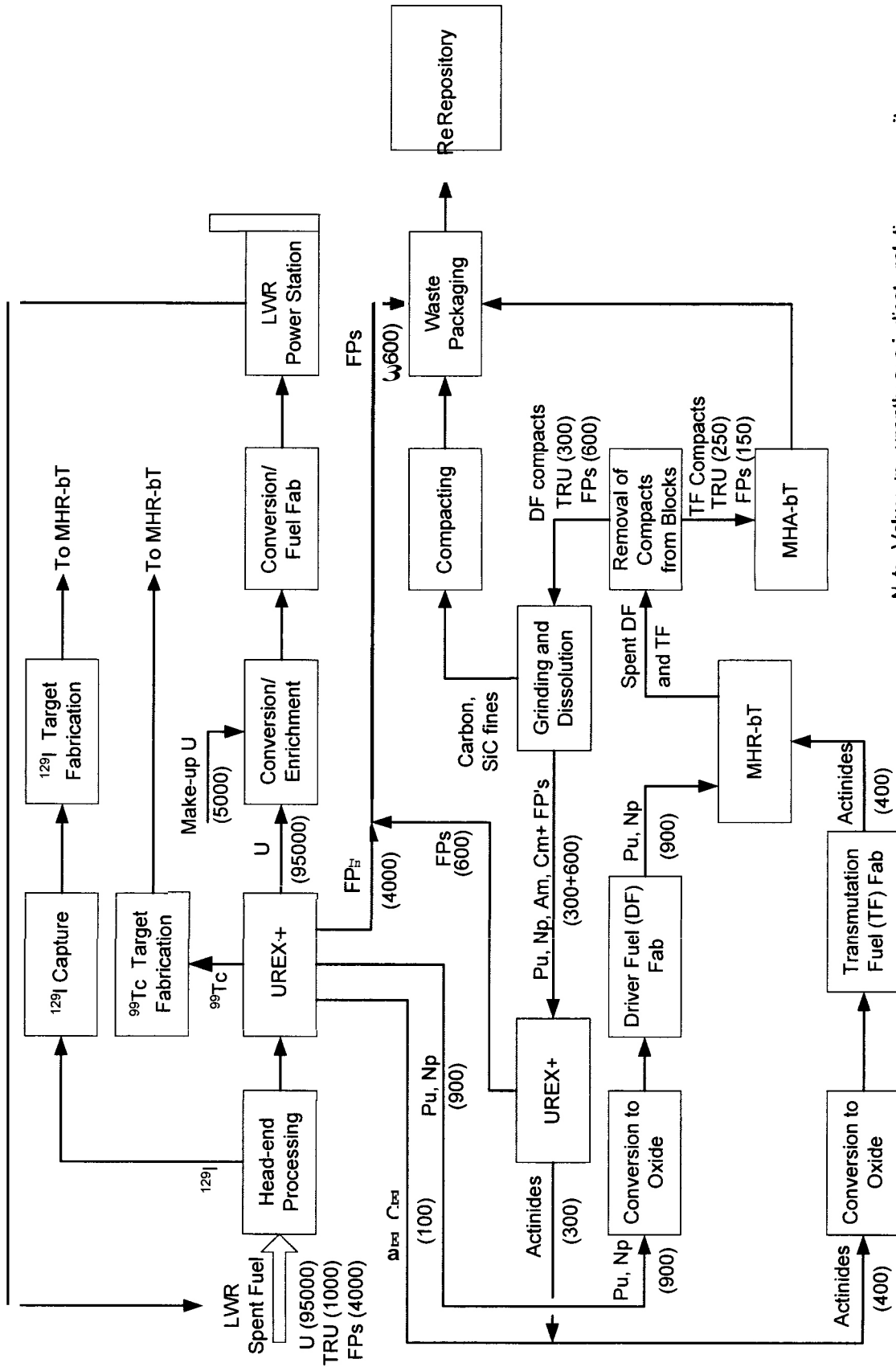


Fig. 2.2. Aggregation of (a) fuel particles into (b) compacts which fit into (c) fuel elements.
 (Source: Reprinted with permission from General Atomics.)

2.2 DEEP-BURN STRATEGY AND ACTINIDE DESTRUCTION

The deep-burn strategy seeks very high burn-up of plutonium-bearing nuclear fuel to effectively destroy the fissionable plutonium isotopes with only two or three cycles through the reactor (Venneri et al., 2001). Either surplus weapons-grade plutonium or reactor-grade plutonium may be destroyed (primarily fissioned) in a transmutation reactor, while at the same time producing electrical power for public consumption. The greatest supply of plutonium originates with the commercial power-production reactors, which are predominantly LWRs fueled with low-enriched uranium dioxide. The deep-burn strategy is illustrated in Fig. 2.3. Essentially, spent LWR fuel is processed to recover the uranium, using a process that does not separate purified plutonium. The remaining transuranium and fission product elements are further separated to produce three streams: (1) a combined plutonium-neptunium fraction (0.9% of the spent fuel mass), (2) a fraction containing all other transuranium (or actinide) elements (0.1% of the spent fuel mass), and (3) a fraction containing the fission products (4.0% of the spent fuel mass).

The plutonium-neptunium fraction is rendered undesirable as a weapons material because of an undesirable isotopic mix, particularly ^{238}Pu , which is formed during the first transmutation cycle. This fraction is fabricated into transmutation reactor driver fuel (DF), which provides the fissionable material to produce neutrons for transmutation of higher actinides in the transmutation fuel (TF) and to produce energy to make electricity. The DF is burned for about 3 years in the transmutation reactor. This step is referred to as modular helium-cooled reactor-based transmutation (MHR-bT). After the burn cycle, the DF is processed to separate the fission products from the actinides. The plutonium and neptunium are recycled to produce DF, and the fission products (FPs) are packaged for disposal.



Note: Values in parentheses indicate relative mass units.

Fig. 2.3. Flow diagram of deep-burn concept.

The remaining actinides, primarily americium and curium mixed with small amounts of neptunium and the higher isotopes of plutonium, are recovered from the spent DF to make TF. Reactor-based transmutation of this fuel destroys most of the remaining fissile isotopes over a 3-year period. Another 4 years in a transmutation accelerator promotes most of the remaining heavy isotopes of plutonium to americium and curium, a step referred to as modular helium-cooled accelerator-based transmutation (MHA-bT). Figure 2.4 shows a material balance for the actinides.

Fission products remaining from the processing of LWR fuel are wastes. Most of the radioactive species have a short half-life (e.g., ^{90}Sr and ^{137}Cs , which have half-lives of 29.0 and 30.2 years, respectively). Some long-lived fission products could be separated and irradiated to transmute them into either stable isotopes or short-lived isotopes. As shown in Fig. 2.4, ^{99}Tc (half-life of 213,000 years) may be separated and used as a burnable neutron poison, resulting in transmutation to stable $^{100-102}\text{Ru}$.

2.3 DIMENSIONS AND CONSTITUENTS OF MHR FUEL ELEMENTS

The objective of this section is to give the specific dimensions and content of fuel elements without giving a complete isotopic breakdown of the fission products.

Data on the composition and dimensions of fresh DF and TF fuel particles are shown in Table 2.1. These data indicate that the outside diameter of DF particles is $820\ \mu\text{m}$ (0.82 mm) and the outside diameter of TF particles is a minimum of $620\ \mu\text{m}$ (0.62 mm). Present assumptions are that only the DF will be processed while the TF will either remain in the hexagonal graphite fuel block destined for disposal or be removed and placed in an accelerator assembly for further transmutation and later disposal.

Table 2.1 Characteristics of driver and transmutation fuel particles

		Driver fuel	Transmutation fuel
Kernel			
Composition (metal atom %) ^a		Pu-Np ^b (95-5)	Pu-Np-Am-Cm (65-5-25-5)
Diameter (μm)		300	200
Density (g/cm^3)		>10	>10
Oxygen:metal ^c		<1.7	TBD
Coating	Density (g/cm^3)	Thickness (μm)	Thickness (μm)
Buffer layer	1.0	-150	>100
IPyC	1.85	35	35
SiC	3.2	35	35
OPyC	1.85	40	40

^aThe values in parentheses give the atom percent in the same order as the isotope is listed.

^bThe metals are in the form of oxides, PuO_2 , and NpO_2 , for the DF.

^cThis refers to the ratio of atomic oxygen to atomic metal, which is substoichiometric to accommodate valence changes upon fission.

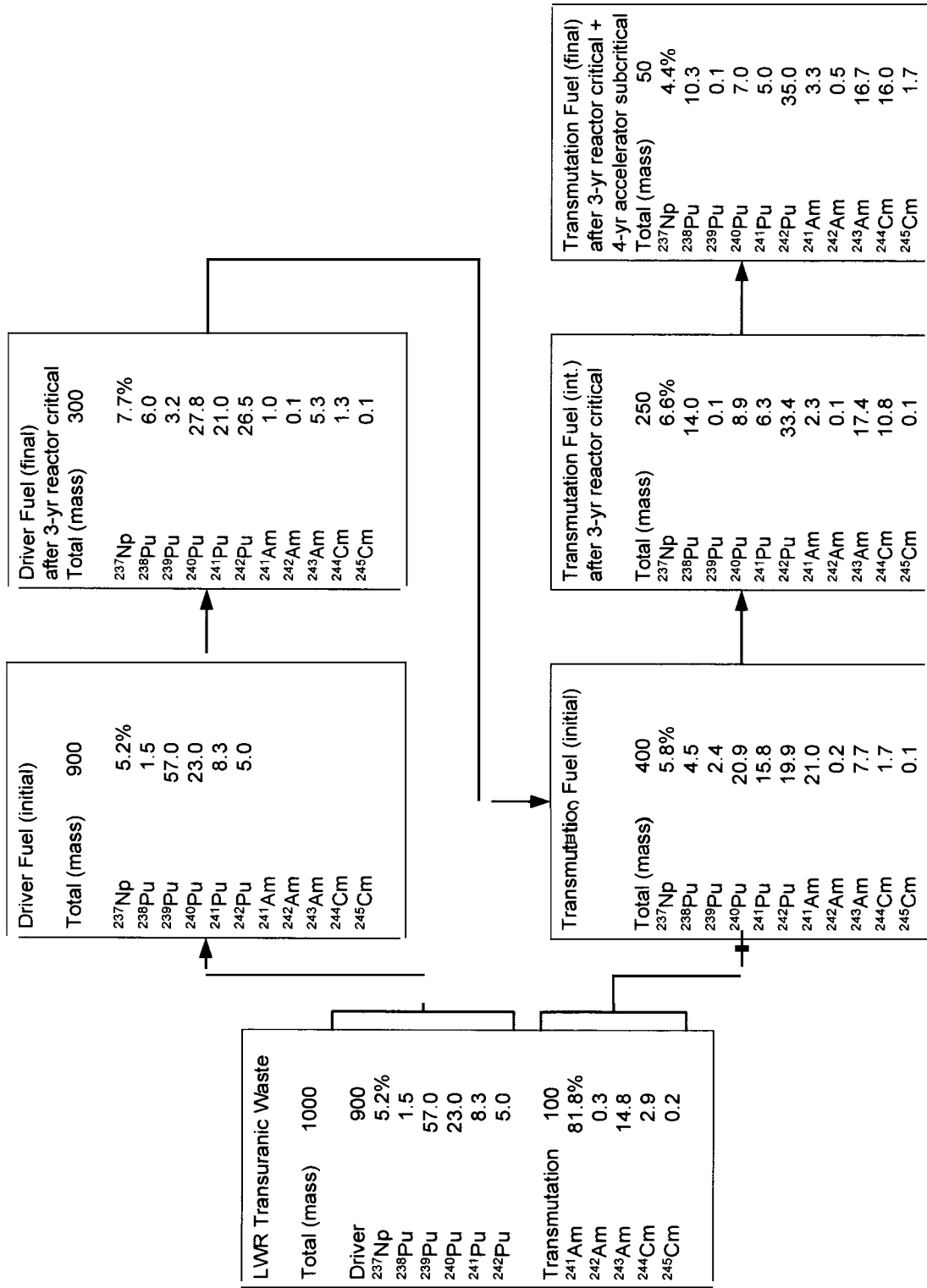


Fig. 2.4. Actinide mass balance for the deep-burn concept.

Fuel compacts are formed from ~7160 fuel particles held together in a carbon matrix. The particles constitute 15 to 30% of the mass of the compact by weight; the remainder is filler carbon. Each compact is a right-circular cylinder 0.5-in. diam by 1.94 in. long (12.7-mm diam by 49.3 mm long). A compact is shown in Fig. 2.5.

Fuel elements are hexagonal prisms machined from graphite. Longitudinal holes are bored through the graphite to form channels for the fuel compacts and for coolant flow. Each fuel element contains 3010 fuel compacts. Compacts include both DF and TF fuel types with a ratio of DF:TF ranging from 2:1 to 5:1, depending on the desired transmutation agenda. An entire reactor core contains 1020 of these hexagonal fuel elements. With a 3-year burn time, it is anticipated that one-third of the core (i.e., 340 fuel elements) will be replaced each year. Figure 2.6 illustrates a cross section of a fuel element, and Table 2.2 lists some design parameters.

2.4 BALANCE ON FUEL MATERIALS

The amount of each type of material in a graphite fuel block has a strong influence on the economic processing strategies that may be selected. Based on the data provided in the previous section on the physical characteristics of the fuel element, the mass of the various materials in a fuel block may be calculated. Because some of the specific details are as yet undetermined, the following assumptions were made.

1. The buffer layer over the TF fuel kernels is the same thickness as the buffer layer used for DF kernels (i.e. $150\mu\text{m}$). Although the thicknesses of the coatings are assumed to be identical, the smaller size of the TF kernel results in fuel particles smaller in size than the DF particles.
2. The same number of heavy metal fuel particles are contained in a TF fuel compact as are in a DF fuel compact (i.e., ~7160, to obtain the total shown in Table 2.2). Because the TF particles are smaller than the DF particles, the extra space in the TF compacts is necessarily occupied with filler carbon.
3. The ratio of fuel compacts (DF:TF) is 4:1. Without specifications on the waste transmutation schedule and performance requirements, this ratio was selected simply because it falls roughly in the middle of the expected range.

Results of a material balance on one graphite fuel block (fuel element) are summarized in Table 2.3. The mass of recoverable fissionable metal oxides is only **0.8 kg** in a fuel element having a total mass of ~117 kg. Removal of both types of compacts eliminates the graphite block, which accounts for 90 kg of carbon. The DF compacts themselves contain all **0.8 kg** of fissionable metal oxide but constitute a total mass of only ~22.1 kg. Removal of the DF compacts from the graphite block therefore increases the concentration of material to be recovered from 0.0068 kg/kg to 0.036 kg/kg, (i.e., a 5.3-fold increase). Thus, removing the fuel block reduces the mass of material to be processed by ~81%. If the fuel particles were removed from the carbon matrix of the compact, the concentration of material to be recovered would further rise to 0.071 kg/kg, or the equivalent of a 90% overall reduction in the mass of material to be processed. The DF particles themselves contain a combined fraction of carbon and SiC of 76%, the remainder being the recoverable fissionable material and waste fission products.

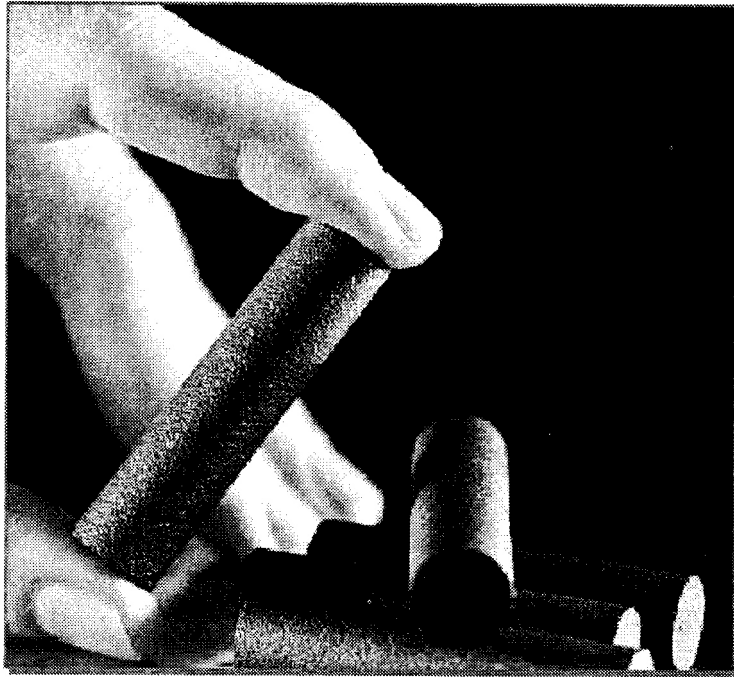


Fig. 2.5. Fuel compact. (Source: Reprinted with permission from General Atomics.)

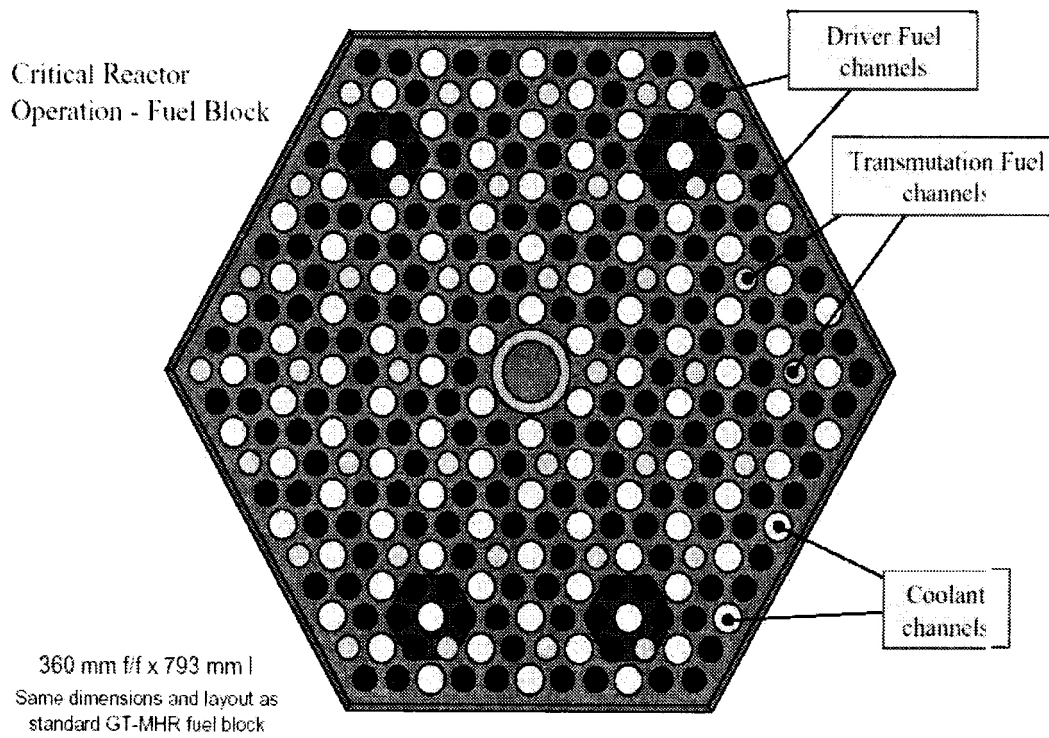


Fig. 2.6. Layout of hexagonal graphite fuel element. (Source: Reprinted with permission from General Atomics.)

Table 2.2. Some design characteristics of an MHR fuel element"

Characteristic	Value
Dimensions	
Length	31.2 in. (794mm)
Across flats	14.2 in. (360mm)
Graphite, type	Nuclear Grade H-451
Fuel holes	
Number	202
Diameter	0.5 in. (12.7mm)
Coolant holes	
Number	108
Diameter	102 at 0.625 in. (15.9mm) 6 at 0.5 in (12.7mm)
Pitch of coolant/fuel hole array	0.74 in. (18.8mm)
Compacts per element	3010
Fuel particles per element	2.155×10^7
Mass carbon in graphite	90.0kg
Mass carbon in compacts	20.5kg
Number fuel elements in MHR core	1020

^aReference: Richards and Ketchen, 1994(GA/DOE-164-94).

Table 2.3 Materials in one spent HTGR fuel element"

Component	Mass (kg)				
	Fuel element	TF		DF	
		Compacts	Particles	Compacts	Particles
Graphite	90.00	0	0	0	0
Filler carbon	13.97	3.14	0	10.83	0
Pyro carbon	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

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

^b Without the graphite block, the total mass of carbon in the compacts is 20.51 kg.

2.5 CARBON DISPOSAL ISSUES

The preceding discussion illustrates that a very large fraction of the HTGR fuel element is simply carbon, in the form of either graphite or pyrolytic carbon. Disposal of the carbon (for example, the graphite block) to the environment is not acceptable for several reasons.

First, ^{14}C is dispersed throughout the particle fuel, graphite filler, and graphite block. The fission process produces some ^{14}C as a by-product, most of which would be retained in the fuel particle if the SiC coating were to remain completely intact. However, there is a fraction, albeit small, of fuel particles that possess SiC coatings that are defective or may have broken. Neutron activation of impurities, or of the naturally occurring ^{13}C , in the graphite or carbon can lead to further radioactive contamination. Nitrogen is a commonly occurring impurity in graphite. Interaction of ^{14}N with neutrons produces ^{14}C , which will be dispersed throughout the fuel block. Absorption of a neutron by ^{13}C also results in production of ^{14}C , which will be found throughout the fuel block.

Second, fission products produced within a fuel particle may escape the protective coating either because of diffusion or because of failed particle coatings. Failure of the coating leads to migration of gaseous fission products that include I_2 , Xe, and Kr, as well as some semivolatile fission products that include Cs (Sawa et al., 1996). Some of these isotopes escape during reactor operations, and others may become imbedded in the graphite matrix. Rates of diffusion of materials through the coatings are very low but cannot be ignored. Detailed models of diffusion have been developed (Prados and Scott, 1963). A few noble metal fission products (e.g., palladium and silver) and rare earth fission products are known to diffuse at low rates through the SiC shell (Pearson et al., 1982). Again, fission products that diffuse from the fuel particles contaminate the surrounding carbon matrix.

Generally, the quantities of radioactive materials in the graphite of spent fuel elements are low. There are no reports of a significant heat generation rate in the graphite block caused by these contaminants. Operations such as simple burning can be used to remove the carbon and graphite surrounding the fuel kernels, and the noncarbon impurities can be removed from the resulting CO_2 stream. However, no simple and inexpensive process exists to selectively sequester only the $^{14}\text{CO}_2$. Therefore, all the carbon dioxide must be sequestered and disposed of to prevent release of ^{14}C to the environment. This encourages identification of alternative processing techniques.

2.6 SCALE AND PROCESSING REQUIREMENTS

Any rationale for selecting the scale of a pilot plant or demonstration-scale TRISO-coated fuel reprocessing plant is nebulous at this early stage of development of the deep-burn transmutation concept. No reactors are presently operating with the type of fuel mixture proposed, although the Fort Saint Vrain reactor has operated with fuel having similar physical characteristics. Three potential bases for selecting a pilot or demonstration scale are discussed.

2.6.1 Basis of Full Deployment

In the current concept, the transuranium (TRU) wastes produced by five large LWRs will be destroyed using a cluster of four MHRs [300 MW(e) each] and one accelerator [100 MW(e)]. There are 103 LWRs currently operating in the United States, which discharge 2500 tonnes/year of spent fuel (initial heavy metal basis). More reactors are presumed to come on-line over the next few decades, which complicates the analysis. However, based on the current fleet of reactors, 20 clusters of deep-burn reactors would be required to destroy the waste at the same rate as it is being generated. The TRU wastes are ~1% of the mass of the spent fuel, implying a production rate of 250 tonnes/year. This amount of material could be processed in a single production plant. Pilot plants are often ~1/10 full-scale production plants. On such a basis, a pilot plant should be capable of processing the spent DF from two clusters of deep-burn reactors (i.e., eight MHRs), or ~25 tonnes/year.

A pilot plant of this scale is unwarranted at this time. No decision has been made to fully implement the deep-burn strategy. If it were made, it would take years or decades to construct the fleet of deep-burn reactors. It may also be desirable to associate *MHR* spent fuel processing with LWR spent fuel processing. It would require two or three large processing plants to handle the spent fuel discharge rate from the current LWR fleet. In concept, the aqueous separation processes in LWR reprocessing plants could be used to handle dissolved *MHR* fuel, so only the mechanical head-end for processing TRISO-coated fuel would be different. Whether all the TRISO-coated fuel should be processed at one plant or at multiple locations is a question yet to be addressed. Generally, it will be advantageous to minimize transportation of TRU materials between plants, which may be separated by large distances. Should a TRISO-coated fuel processing capability be added to each LWR fuel processing plant, full-scale operations would be only one-half to one-third of that mentioned above and the pilot-scale facility would be correspondingly reduced.

2.6.2 Basis of One Cluster of MHRs

A very large and dedicated effort could result in the construction of one cluster of MHRs to act as both a power production and TRU destruction prototype. In such a case, a processing facility scaled to process the spent fuel from the entire cluster would be a reasonable basis to select. The processing basis would be more logically measured in the number of spent fuel elements to be processed per year. Each *MHR* contains **1020** fuel elements, which are subjected to a nominal 3-year burn time (Table 2.2). About one-third of the core of each reactor is replaced each year; thus, with **4** reactors, 1360 fuel elements would become available for reprocessing each year. Assuming that the reprocessing rate matches the discharge rate and that the pilot reprocessing plant has a 200 day/year availability, the plant would need to process 6.8 fuel elements per day.

2.6.3 Basis of One MHR Demonstration Reactor

One *MHR* could be built to demonstrate the deep-burn/transmutation concept and provide operational information both to feed the design of subsequent reactors and to provide licensing data. Again, the core contains **1020** graphite block fuel elements, and a 3-year burn time results in an average discharge rate of one-third of the core (or 340 fuel elements) per year. Assuming that the reprocessing rate matches the discharge rate and that the pilot reprocessing plant has a **200** day/year availability, the plant would need to process **1.7** fuel elements per day.

Alternatively, existing reactors could be used to irradiate test fuels at approximately the same rate of throughput.

2.6.4 Selected Demonstration-Scale Basis

Full deployment of MHRs as the exclusive means to destroy TRU waste is, at best, many decades away. Even if full agreement concerning the methodology and the economics could be attained, the construction and licensing schedule would dominate the deployment schedule. It is also unlikely that a cluster of four reactors and an accelerator will be deployed in the near future. Until proof-of-principle experiments are performed (which will take from **5** to **10** years to complete), the same delay is also anticipated for the construction of one demonstration reactor. As a basis for a demonstration-scale or pilot-scale TRISO-coated fuel treatment plant, it is reasonable to select a throughput of one to two fuel elements per day. Such a scale is meaningful in terms of (1) demonstrating all the necessary unit operations, (2) obtaining operating data for scale-up, and (3) providing sufficient feed for demonstration of accelerator-based transmutation (i.e., MHA-bt fuel).

3. PROCESSING STRATEGIES

3.1 PREVIOUS EXPERIENCES REPORTED IN THE LITERATURE

Previous processing of TRISO fuel was based on crushing the graphite fuel blocks and separating the coated fuel particles from the graphite. Oxidation was then used to remove the filler carbon and the outer carbon layer, followed by crushing of the SiC shells and additional burning of the inner carbon layer. The remnant ashes were leached using nitric acid and the resulting solution interfaced with conventional solvent extraction (Flanary et al., 1964; Vaughn et al., 1970; Colby et al., 1971). This technology was demonstrated for fuels in which the fissile components were either carbides or oxides. For both types of fuels, the bulk of the graphite was removed by mechanical means followed by the previously mentioned process of burning, crushing, and leaching. Burning was especially important to processing carbide fuels because hydrolysis of the metal carbides in the dissolution step resulted in soluble organic acids that were deleterious to the solvent extraction process. Studies were also performed in which the entire fuel block was burned, a technique to reduce the number of processing steps (Bamert-Wiemer, 1974).

Burning of graphite fuels results in large quantities of carbon dioxide. Current regulations prohibit disposal of this carbon dioxide to the atmosphere because of the ^{14}C produced in irradiated fuels. Expensive off-gas treatment systems are required to sequester the carbon dioxide, usually by reaction with calcium hydroxide (Lotts et al., 1992). Such sequestration techniques greatly increase the mass and volume of the waste as compared with that of the original carbon.

Another variation in HTGR fuels included mixing fertile fuel particles with fissile-laden fuel particles. Fertile fuel contained thorium, usually in the form of thorium dioxide (ThO_2) with UO_2 , coated with only the buffer carbon and pyrolytic carbon layers (called BISO-coated fuel). Processing of these fuels could be performed with a variation of the crush-burn-leach method (Benedict et al., 1981). The basic steps involved crushing the graphite blocks together with the fuel compacts and then burning the carbon. For the fissile particles, the carbon would burn away, leaving the TRISO-coated particles; the fertile particles would burn down to the heavy metal kernel. The larger, lighter TFUSO-coated particles could then be separated from the denser thorium kernels by elutriation with carbon dioxide gas. The thorium particles would be processed in a THOREX process. In parallel, the TRISO-coated particles would be crushed to break the SiC shell, subjected to burning (or voloxidation) to remove the inner carbon layers and then processed through a PUREX process. Figure 3.1 shows the general flow sheet for the crush-burn-leach processes.

3.2 GENERIC PROCESSING STEPS

Previously reported methods to process graphite-block fuel elements can be organized into five general steps that precede solvent extraction separation of the actinides from the fission products. These steps are (1) mechanical preparation; (2) removal of the carbon external to the SiC shell; (3) removal or breaching of the SiC shell; (4) removal of the internal carbon layers between the SiC shell and the heavy metal kernel; and (5) dissolution of the heavy metal kernel or, more generally, preparation for solvent extraction. The solvent extraction process and other processes downstream of solvent extraction are very similar to those used for spent LWR fuels. There are variations in the partitioning chemistry, but the processing methods and equipment to implement the separations have changed little since the 1970s.

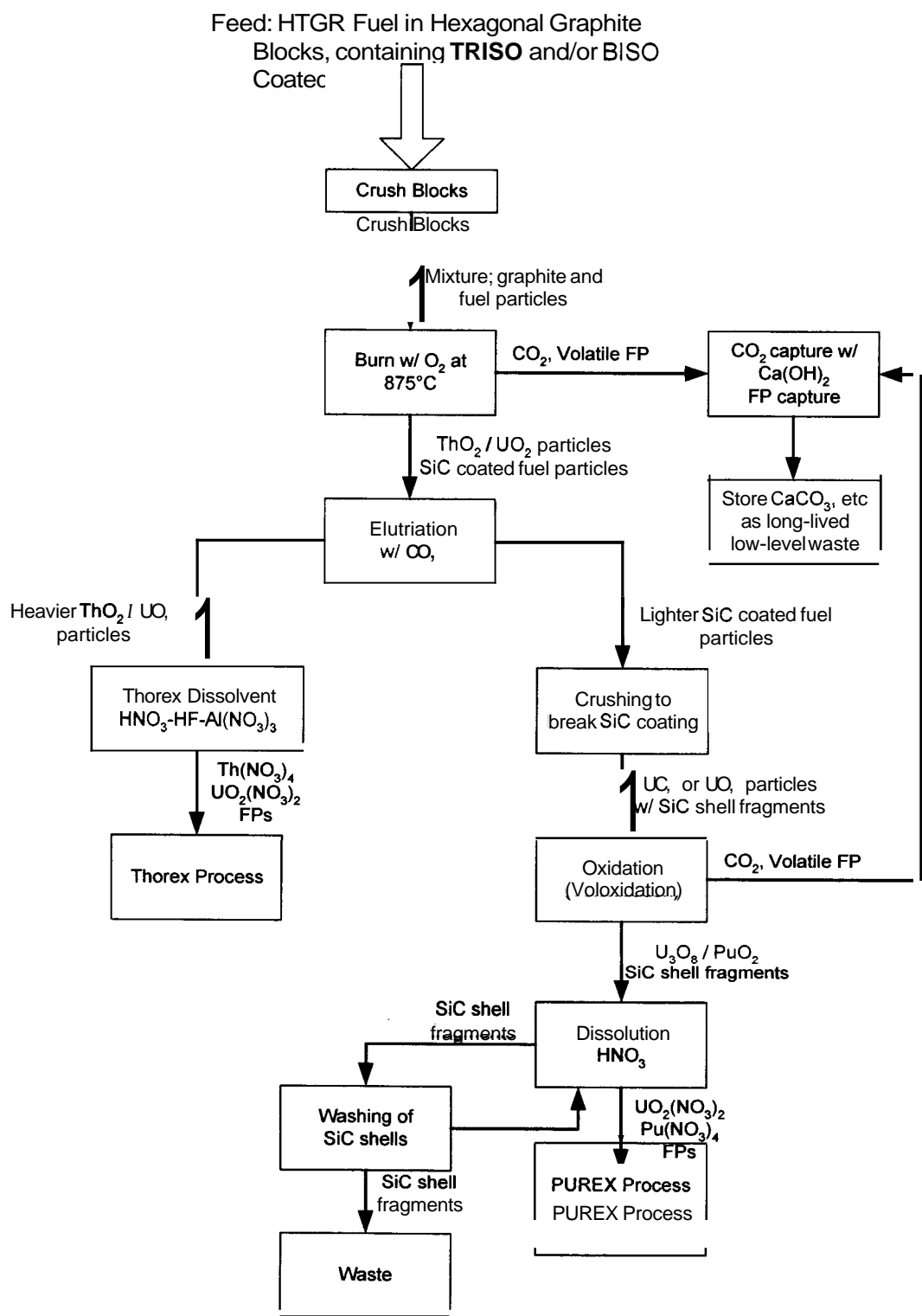


Fig. 3.1. HTGR fuel reprocessing flow sheet, ca. 1970.

3.2.1 Mechanical Preparation

Mechanical preparation usually involves some type of disassembly of the graphite fuel element. Crushing the fuel block produces fragments of all carbon (graphite) and fragments with the SiC-coated fuel particles. Separation processes based on differences in the size and density of the fragments may be used to recover the heavy metal-bearing fraction, while the carbon may be packaged as low-level waste. The primary problem with this method is that some of the SiC shells may be broken, prematurely releasing gaseous fission products or releasing heavy metal fines that require more-elaborate separation methods. Mechanical separations following crushing are not 100% efficient, so some loss of heavy metal must be accepted.

Removal of the fuel compacts from the graphite by a type of coring operation can eliminate the bulk of the carbon-graphite without damaging the particle fuel coatings. Although all the carbon within the fuel compact continues to the next step with the heavy metal, there should be 100% recovery of the heavy metals by this method. In addition, coring should be cleaner and easier to control.

Mechanical preparation can, in effect, be achieved by methods such as whole-block burning, which results in a product that is similar to that produced by a combination of mechanical preparation and removal of the external carbon layers.

3.2.2 External Carbon Removal

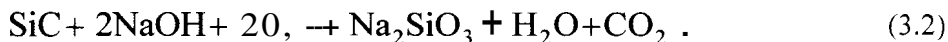
Depending on the method of mechanical preparation selected, varying amounts of carbon external to the SiC shell of the fuel particle will be associated with the fuel. Crushing will result in carbon composed of fragments of the outer carbon shell that encloses the SiC shell, fragments of the graphite, and fragments of the fuel compact binder carbon, all of which may or may not be adherent to the fuel kernel.

One approach is to convert the external carbon to a gas without harming the SiC layer. Burning the carbon in air or oxygen is the conventional method. This process produces a carbon dioxide by-product that must be sequestered. Any fission products associated with the outer carbon either report to the gas phase and require a gas-cleaning method or report the solid phase as an oxide that follows the SiC-coated particles to the next processing step. The outer carbon may also be gasified by reaction with steam, producing carbon monoxide and hydrogen:



The CO and H₂ may be used as fuel, but the presence of fission products and ¹⁴C continues to require gas cleanup prior to release to the atmosphere. Generally, the fate of the fission products is similar to that produced by air oxidation.

Another approach is to destroy the outer carbon in an environment that also attacks the SiC shell. The fuel particles can be treated in a molten salt, such as NaOH. For oxidation in molten NaOH, the expected gaseous products are CO, and the volatile fission products. In addition, the molten salt reacts with the SiC to produce sodium silicate:



Gasification of the carbon with steam in molten NaOH may also be accomplished along with destruction of the SiC shell:



Again, the CO and H₂ could be used for their fuel value. These methods combine the removal of the outer carbon, SiC, and inner carbon in one step. The resulting slag oxides containing the actinides and fission products as oxides may be mechanically separated and fed to the dissolution step.

3.2.3 Silicon Carbide Shell Removal

Treatment methods, such as burning, generally leave the spherical SiC coating intact. The inner carbon layers and fuel kernel are consequently unharmed. The SiC coating may be breached by grinding to expose the inner carbon and fuel kernel. Further treatment methods may then recover the fuel while leaving the empty SiC shell fragments as a waste. Grinding and milling can be followed by a solid-solid separation as an option prior to aqueous dissolution, or dissolution may follow directly.

Once the carbon layer has been removed, chemical methods to remove the SiC layer may also be implemented. Dry fluorination in which the processing time is adjusted to a period sufficiently long to permit removal of the SiC coating but short enough to prevent attack of the heavy metal kernel has been studied (Maeda and Yagi, 1977). Both silicon and some carbon, from the inner layers, are volatilized as by-products:



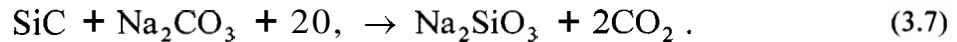
and



The SiC layer can also be removed in a mixture of molten NaNO_3 and Na_2CO_3 ; the reactions are



and

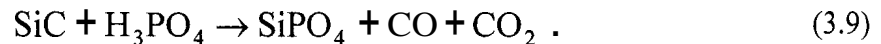


In the absence of oxygen, the carbon layers are largely unaffected by this solvent and reaction (3.7) is eliminated.

Aqueous methods are also available for removing the SiC layer. A strong caustic solution sparged with oxygen will cause oxidation of the SiC,



The noble gas fission products, Xe and Kr, will escape the aqueous solution while the halides (e.g., I_2) will be absorbed by the caustic. The silicon dioxide is largely inert in subsequent processing steps such as dissolution. Another aqueous method involves digesting the SiC with phosphoric acid:



The dissolution rate is slow and parallel reactions producing both H_2 and CH_4 are reported (Schroder, 1986). Both aqueous methods require a liquid-solid separation to recover the oxide fuel kernels from the solution. If the inner carbon layers are to be burned, then drying of the solids is also indicated.

3.2.4 Removal of Internal Carbon Layers

The remaining internal carbon layers contain a relatively small fraction of the carbon in the original fuel block. This carbon can be burned or gasified as described in Sect. 3.2.2. Grinding is also an option at this juncture but probably not practical since this could have been done without removing the SiC shell as a separate step.

3.2.5 Preparation for Separation Processes

Preparation for separation by solvent extraction requires that the remaining heavy metal oxide kernel be dissolved in aqueous nitric acid. The process will liberate NO_x gases and the noble gas fission products, Xe and Kr. Some gaseous fission products (e.g., I, and ^3H) will be retained in the aqueous solution.

A liquid-solid separation is required prior to routing the aqueous nitrate-bearing solution containing the actinides and fission products to solvent extraction. Depending on the preceding steps, the solid residue may include one or more of the following: undissolved noble metals, SiC shell fragments, carbon, silicon dioxide, and sodium silicate. Solids containing SiO_2 or Na_2SiO_3 could be problematic for the dissolution process because of the possibility of forming silicic acid, a gel-forming compound that can adversely affect the liquid-solid separation or solvent extraction processes.

3.3 VARIANTS FOR TRISO-COATED DRIVER FUEL

Oxide-based fuel kernels are planned for the MHR TRISO-coated fuel. Metal oxides may be dissolved with nitric acid in the presence of carbon with little or no effect on the carbon (i.e., it is essentially inert). Recent industrial improvements in the processing, washing, and fabrication of nuclear-grade carbodgraphite products may be adapted to separation of the fuel components from the carbon. The conceptual process involves removing the fuel compacts from the graphite fuel element, grinding the compacts to expose the fuel kernel, separating the lighter carbon particles from the heavier fuel particles, and leaching or dissolving the fuel components from the remaining carbon fines. The leaching/dissolution alternatives include the use of HNO_3 or carbochlorination. The nitric acid leaching can be directly interfaced with conventional aqueous solvent extraction processes. The carbochlorination process will produce a chloride salt that can be further processed by pyrochemical methods. The finely divided waste carbon may be reformed into a compact and durable waste form. The exact details need to be developed and demonstrated.

3.4 SUMMARY OF AQUEOUS-BASED OPTIONS

Some of the more practical processing steps are shown diagrammatically in Fig. 3.2. In this figure, the small circles connecting the lines of material flow represent decision points at which one may select from more than one option for the next process step. Therefore, this diagram represents many possible flow sheets and helps show which choices lead to an expansion of additional or difficult processing steps. The path with the generation of the least waste and one of the fewest process steps includes coring to remove the fuel compacts, grinding and milling of the fuel compacts, solid-solid separation to remove a fraction of the carbon from the fuel oxides, dissolution to produce actinide and fission product oxides, and liquid-solid separation with washing to remove the carbon, SiC fragments, and undissolved noble metals from the nitrate solution.

3.5 OTHER OPTIONS

There are methods other than aqueous dissolution and solvent extraction to separate the actinides and fission products. Some of the options already discussed may be used to expose the oxide kernel. The kernel can then be dissolved in an appropriate molten salt and the actinides separated by electrorefining methods (basically plating on a metal electrode). These pyroprocessing methods have been developed at laboratory scale but not yet deployed at a commercial scale.

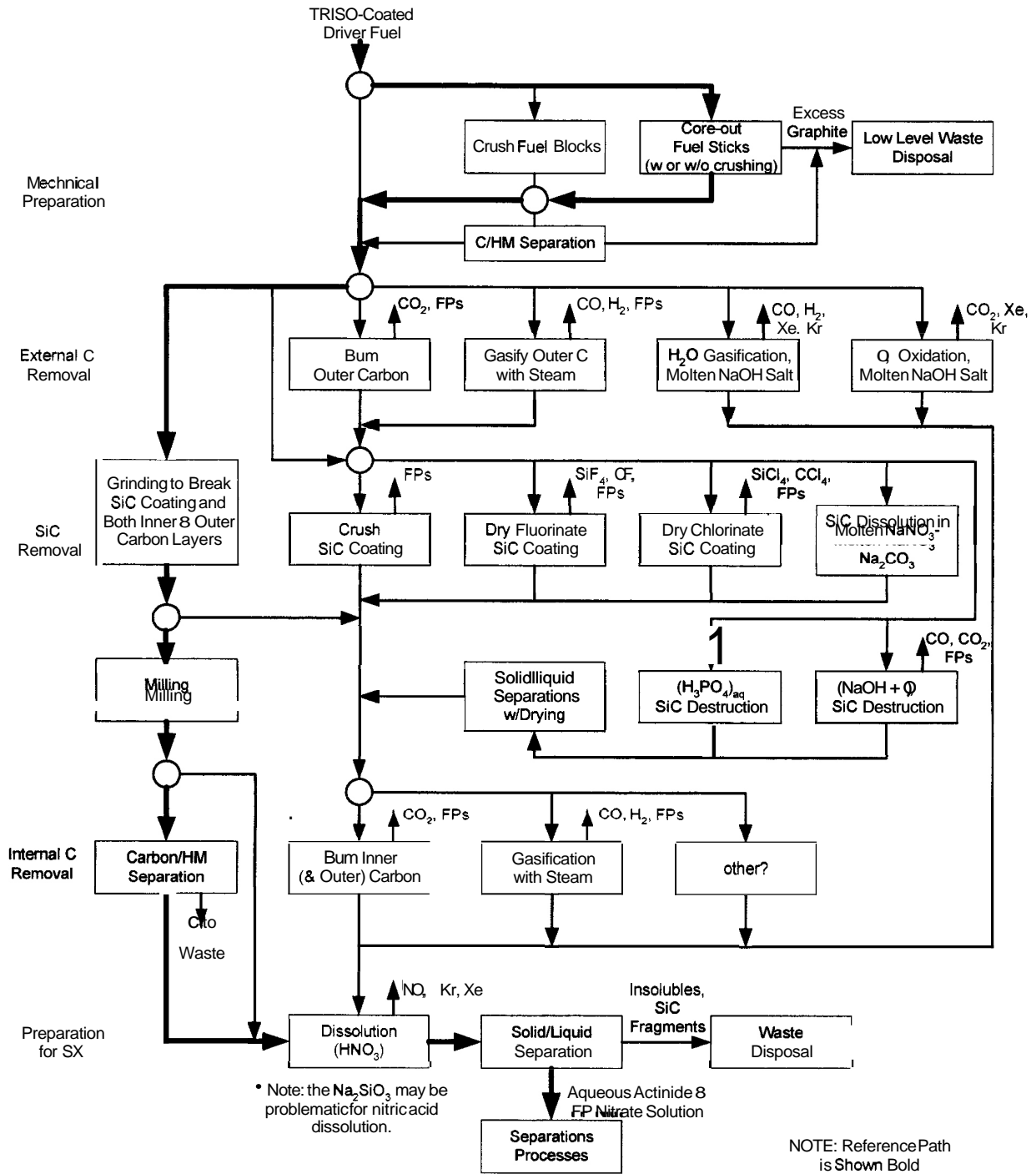


Fig. 3.2 TRISO-coated-fuel preparation options.

Another dry process involves fluorination. In these processes, exposing the spent fuel kernel by any of the methods discussed in Sect. 3.3 is optional. Although more difficult to fluorinate than uranium, both neptunium and plutonium do fluorinate. The product gases can be captured by chemisorption processes or with cold traps and then fed to a conversion process to make an oxide product. Without prior separation of the fuel kernel from the carbon and SiC, a significant quantity of CF₄ and SiF₄ will be generated as a waste and require expensive treatment prior to disposal.

3.6 PROCESSING TECHNOLOGY DEMONSTRATION NEEDS

The head-end processes must be developed, qualified by demonstration, and scaled up to ensure efficient recovery of fuel components (within specifications to be determined) and to qualify the waste form(s). Critical operations include leaching of the fuel/fission product oxides from a large excess of carbon, separating as much carbon from the fuel/fission product oxides as practical to improve the leaching step, and transforming the waste carbon fines (including SiC fragments) into a suitable waste form.

Coring of the fuel compacts from the fuel element greatly reduces the carbon associated with the fuel kernels. Still, the fuel represents a minor fraction of the mass of the compact. Mechanical separation of the fuel components from the carbon needs to be investigated. Data are needed to quantify the effectiveness of this separation as a function of particle size. Surrogates can be prepared by mixing carbon, SiC, and non-rad metal oxides; by using compacts made from silica spheres of comparable diameter to the TRISO particles; and by using compacts made of actual TFUSO particles (HfO₂ and UO₂) when they became available.

Leaching or dissolution studies can be performed using prepared mixtures of milled graphite/pyrolytic carbon and milled surrogate oxides. Initial tests will provide data on the ability to recover the metal oxides as a nitrate solution and to wash the nitrates from the major volume fraction of carbon. Various reagents and operating parameters for optimal dissolution and recovery need to be assessed, such as the need for electrochemically assisted dissolution and optimal conditions. Data are also needed on the number of stages required to achieve a specified separation and recovery of the fissile material components.

High-temperature irradiation of fuel particles may disperse actinides throughout the neighboring carbon layers, which ultimately may affect the efficacy of the dissolution process, even in finely ground particles. Data are needed to evaluate the retention of actinides by these particles. Surrogates can be prepared with finely divided carbon, metal oxides, and SiC fragments that are pressed and sintered at high temperature. Data are needed on the milling and dissolution of this material to ascertain the effects of particle size on recovery and to demonstrate that the burning processes may be omitted.

Binding agents need to be identified to re-form the waste carbon and SiC fines into monolithic waste forms. The parameters of the waste production process, such as the additive-to-waste ratio and the pressing temperature, need to be determined. Data are needed to qualify the waste form, including measurements on leaching rates, combustion potential, and mechanical strength.

The fate of the hexagonal fuel blocks made of nuclear-grade graphite emptied of fuel by coring needs to be analyzed. After irradiation the graphite will become radioactive, as a result of the nuclear activation of the impurities present in the graphite by neutron capture. Additionally, diffusion of species from the fuel particles into the graphite block needs to be evaluated. It may not be feasible to recover the spent graphite and refabricate the hexagonal fuel blocks. If this is the case, then the graphite blocks could be used to hold the consolidated carbon waste shaped as compacts.

4. FUEL TREATMENT OPTIONS

4.1 INTRODUCTION

In addition to the actual fuel processing options that will be discussed in the following sections, two global fuel cycle strategies need to be considered. The first includes the removal and reprocessing of the spent DF with the higher actinides being transformed into TF, and the removal of the spent TF for further treatment in an accelerator-driven transmutation system.

In the second option, the spent DF is also removed, recovered, and reprocessed to separate the higher actinides and produce fresh TF but the spent TF is sent to waste. In this case, the TF compacts can either be removed and repackaged or be **left** untouched in the graphite blocks.

The selection of either “fuel cycle” strategy has some impact on the handling and processing of the spent fuel and in the waste management strategy. These considerations are taken into account in the following discussion and in Sect. 6.

For the following analysis, it is assumed that operations start with the spent fuel element already inside the processing cell. The movement and transportation of the fuel elements from the reactor site to the processing site are not part of this report. Accordingly, the first task, common to all processing options, is to remove the fuel compacts from the hexagonal graphite block.

Previous experience by General Atomics (1983) on a fuel element irradiated at the Fort Saint Vrain reactor shows that the removal of the fuel compacts from the hexagonal graphitic block in a hot cell is a relatively simple process. To expose the fuel channels, the bottom surface of the fuel element was drilled and a slice was cut from the top. Subsequently, the stacks of fuel compacts were pushed **from** their cylinders using a metal rod while exerting moderate force. None of the stacks offered any significant resistance. The push-out force averaged 10.7 lb and ranged from 1.5 to 33.0 lb. The higher values were reportedly due to minor fuel-block interaction and pushrod-hole misalignment. Reportedly, the removal of the fuel compacts was a simple and clean operation with little debris collected. **On** this basis, it is proposed that the removal of the fuel stacks be a common step in all processing options.

As mentioned, the global strategy is to recover and process only the spent DF compacts. The spent TF may be recovered for further burning in an accelerator-driven system or be sent to waste. If the spent TF is sent to waste, it may be removed and repackaged or may be left untouched inside the graphite block.

To facilitate and optimize the removal and recovery of the spent DF compacts and the optional removal of the TF, a small modification of the fuel design is proposed. Since the design of the driver and transmutation fuel elements is still under development, a minor modification could greatly simplify the independent removal of the spent driver and transmutation fuel and ensure that the fuel compacts remain intact. It is proposed that the channels for the DF be about $\frac{1}{4}$ to $\frac{1}{2}$ in. longer at the top and at the bottom compared with those for the TF. Graphite spacers would be located at the top and at the bottom of all fuel channels. The graphite spacers for the TF channels will be a little bit longer than those for the DF channels so that the height of the stacked fuel compacts, including spacers, is the same for both types of fuel. In addition, the spacers could be in two parts so that the spacer next to the compacts could be loosely press-fit into the channel while the outer spacer would be sealed or sintered in place to ensure support. Figure 4.1 illustrates the concept. Under this configuration, it would be possible to first cleanly slice the top and bottom of the graphite block, between the internal and external DF spacers, exposing only the DF channels while keeping the TF channels unexposed and intact. The fuel elements could be sliced by using a cutting wheel, an operation that is fast and avoids the generation of dust. The stacks of DF and inner spacers could then be easily removed using a pushing rod, as was done in the past. If the TF compacts are to be removed, then the graphite block would be sliced again at the level between the inner and outer TF spacers.

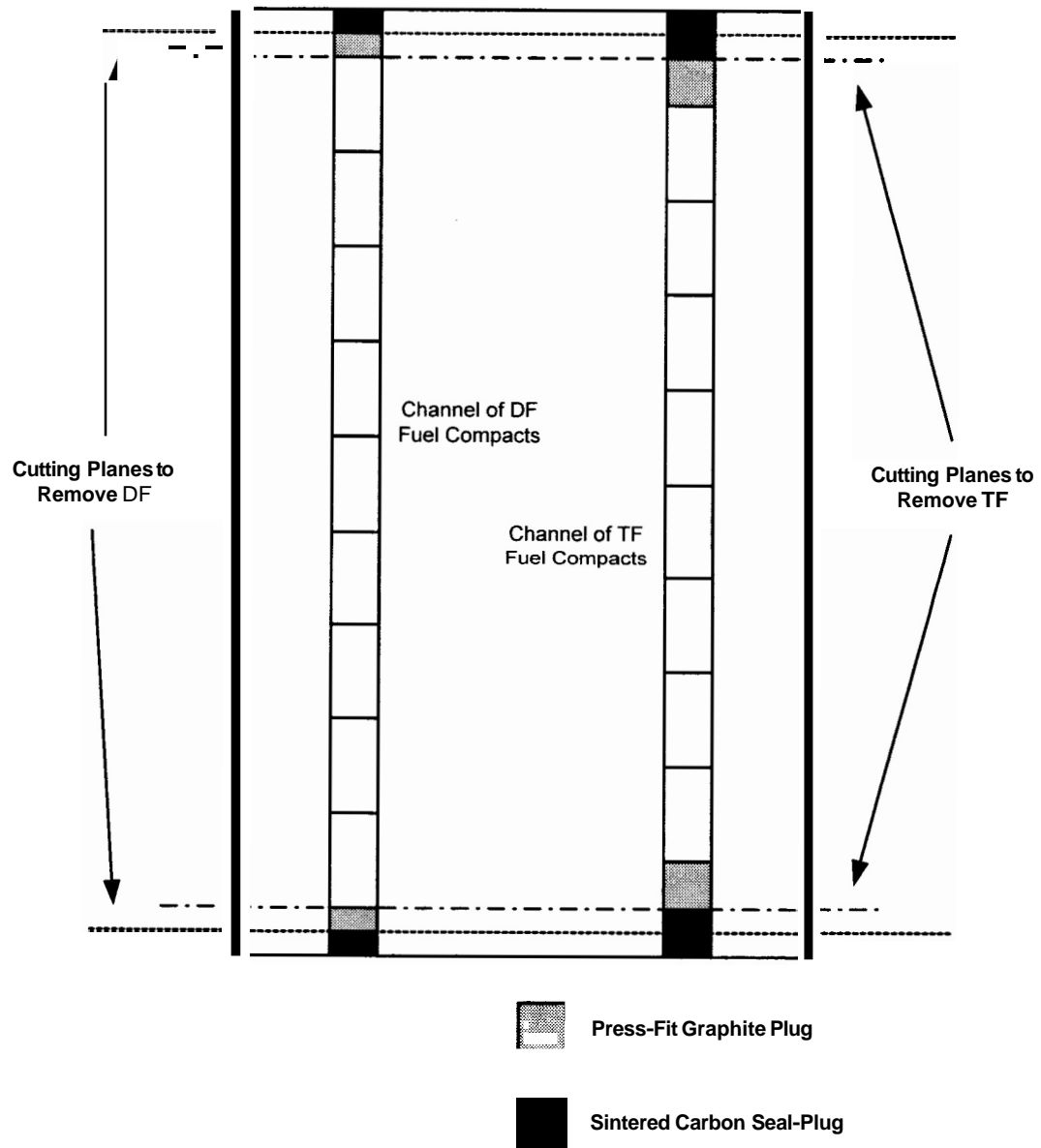


Fig. 4.1. Different channel lengths to facilitate separate removal of the DF and TF.

4.2 DESCRIPTION OF MAIN OPTIONS

A number of options have been identified for evaluation. To support a particular selection, some guidelines are presented in the next section.

Once the stacks of DF are removed from the graphite block as described in the previous section, the following step is designed to expose by physical or chemical means the inner kernel that contains the valuable residual fissile material to be recovered.

4.2.1 Key Elements of TRISO Reprocessing

One key aspect of the recovery of the fissile content from the TRISO fuel elements is the disaggregation of the fuel compacts and the removal of the different external layers to expose the innermost kernel that contains the valuable residual fissile material. It must be noted that when the coating layers are broken, gaseous fission products will be released. Consequently, the trapping, processing, and disposal of these volatile species are also key considerations to any processing option. The bulk of the fuel compacts is made of carbon and SiC. The inner kernel represents a very small fraction of the total mass. Accordingly, one very important factor to determine the most attractive options is the minimization of the overall processing and disposal cost for the bulky carbon and SiC fractions.

The processing method used to expose, treat, and recover the inner kernel must be compatible with the subsequent separative process. In the foreseeable future, the volume of TRISO fuel to be processed is expected to be very small compared with the volume of standard LWR fuel to be processed. For reasons of economy of scale, it becomes apparent that the actual separation of the fissile material from TRISO fuel should be done as a substream of an existing LWR fuel processing plant. Accordingly, the head-end processing of the TRISO fuel should be designed to produce a product that could be easily introduced into an existing LWR separative scheme. At present, the only industrial-scale process for LWR processing is the PUREX technique, which is based on extraction of actinides from a nitric acid solution using an organic solvent. However, pyroprocessing methods based on molten chloride or fluoride salts are under active development for eventual industrial deployment. Accordingly, the processing options to be considered should preferably generate either a nitric acid solution for aqueous processing, or a halide salt (chloride or fluoride) for pyroprocessing.

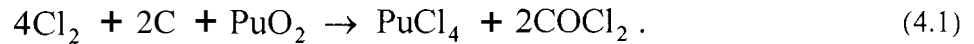
4.2.2 Description of Candidate Options and Down-Select

As mentioned in Sect. 3, previous processing of TRISO fuel was based on the burning of the outer carbon layer, followed by crushing of the SiC and burning of the inner carbon layer. The remnant ashes were leached using nitric acid and the resulting solution interfaced with conventional solvent extraction. Alternatively, the fuel compacts can be crushed and milled to a finer particle size, allowing the burning of outer and inner carbon in just one stage. Burning of the carbon results in large quantities of carbon dioxide. Current regulations prohibit disposal of this carbon dioxide to the atmosphere because of the ^{14}C produced in irradiated fuels. Expensive off-gas treatment systems must be used to sequester the carbon dioxide, usually by reaction with calcium hydroxide (Lotts et al., 1992) or by injection into deep wells. Such sequestration techniques greatly increase the mass and volume of the waste as compared with that of the original carbon. For example, burning 12 g of carbon would produce 100 g of CaCO_3 . One processing option that avoids the production of gaseous CO_2 and subsequent sequestration by chemical addition includes the crushing and milling of the fuel compacts into a very fine particle size followed by nitric acid leaching.

Using fluorine on the fuel compacts would allow for the removal of all carbon and SiC, forming the gaseous species CF_4 and SiF_4 . Also, the F_2 burning could be done on the fuel compacts without any pretreatment. However, this approach has some disadvantages, including the higher cost of F_2 versus air and the larger amount of wastes generated. (For example, 12 g of carbon would produce 100 g of CaCO_3 and 156 g of CaF_2 .) Another potentially serious problem would be the accidental formation of solid C_xF_y

(where $1 \leq x \leq 4$) fluorinated carbon species that are potentially explosive. To avoid the formation of lower carbon fluorides and ensure that CF_x is the only species formed, the temperature must be kept above 500°C throughout the processing equipment where F_2 and C could come in contact. During the fluorine burning, volatile species from the spent fuel components would also form (e.g., UF_6 , NpF_6 , PuF_6 , TcO_3F , RuF_6 , and NbF_5). Thus, fluoride volatility could be used as part of the separative scheme. Alternatively, the fluoride burning could be performed using a molten salt bed that would act as a thermal buffer and a very effective scrubbing and trapping media for most of the metallic volatile fluoride species while permitting the movement of CF_x and SiF_4 toward the off-gas treatment system.

Alternatively, chlorination can be used to transform the spent fuel kernel into a chloride salt for pyroprocessing. Chlorination has some advantages compared with the fluorination process. First, there are no concerns of forming equivalent unstable species such as the C_xF_x ; second, only a small fraction of the carbon would be consumed ($\sim 5\%$) because chlorine does not react directly with carbon except in the presence of metal oxides, for example,



Finally, chlorine will react with the SiC layer to form volatile SiCl₄ and carbon. (The compound CCl₄ forms only at very high temperatures.) The chlorination of the spent fuel kernel could be effectively accomplished in a molten chloride salt medium (e.g., LiCl/KCl or the denser CsCl/KCl). One of the key aspects to be resolved is the handling of the solids; that is, introduction of the fuel compacts into the molten *salt*, the clean removal of the excess carbon waste, **and** the transfer of clean molten salt to the separation process equipment.

Of the main options just considered, two options appear as the most promising: (1) crushing and milling of the fuel compacts into a very fine particle size followed by nitric acid leaching and (2) crushing and milling of the fuel compacts into a fine particle size followed by chlorination in a molten-chlorinated-salt medium. The first option is suited for interfacing with an aqueous separation process, while the second is suited for interfacing with a pyroprocessing plant based on chloride salts. In the first option, all carbon and SiC should remain intact and could be converted into a carbon/graphite waste form (Sect. 6); in the second option, about 95% of the carbon should remain intact. In either option, it would be highly advantageous to separate as much carbon and/or SiC as possible from the metal oxide particles during the crushing and milling operations. However, the requirement for a very high recovery of the fissile material implies a nearly 100% efficient solid-solid separation, which may or may not be achievable under practical conditions.

5. RECOMMENDED FLOW SHEET AND MATERIAL BALANCES

Because the present strategy is to recover and process only the spent DF compacts, only these compacts will be removed from the graphite fuel blocks. As envisioned, the channels for the DF will be about $\frac{1}{4}$ to $\frac{1}{2}$ in. longer than those for the TF. Spacers at the top and bottom of the fuel channels will be used so that the DF and TF compacts can be independently removed from the fuel block. To allow for the removal of the DF compacts, the top and bottom of the graphite block are sliced off, using a cutting wheel at the level of the spacers. This operation exposes only the DF channels and maintains all the fuel compacts intact. A set of pushing rods is then used to remove the stacks of DF compacts from the graphite blocks.

5.1 DESCRIPTION OF MOST-PROMISING FLOW SHEETS

The two most-promising options, acid leaching and carbochlorination, include a common mechanical head-end that starts with the previously described removal of the DF from the graphite blocks. Both processing options require crushing and milling of the fuel compacts in order to generate very fine particles, ensuring that the oxide kernels are exposed to either nitric acid or to carbon and chlorine. Most of the TRISO fuel particles will be broken during the milling operation. However, some may be broken during the initial crushing of the compacts. In either case, an off-gas system will be required to accommodate the release of volatile species from the broken fuel particles (Kr, Xe, Rn, I, ^3H , etc.).

5.2 COMMON MECHANICAL HEAD-END

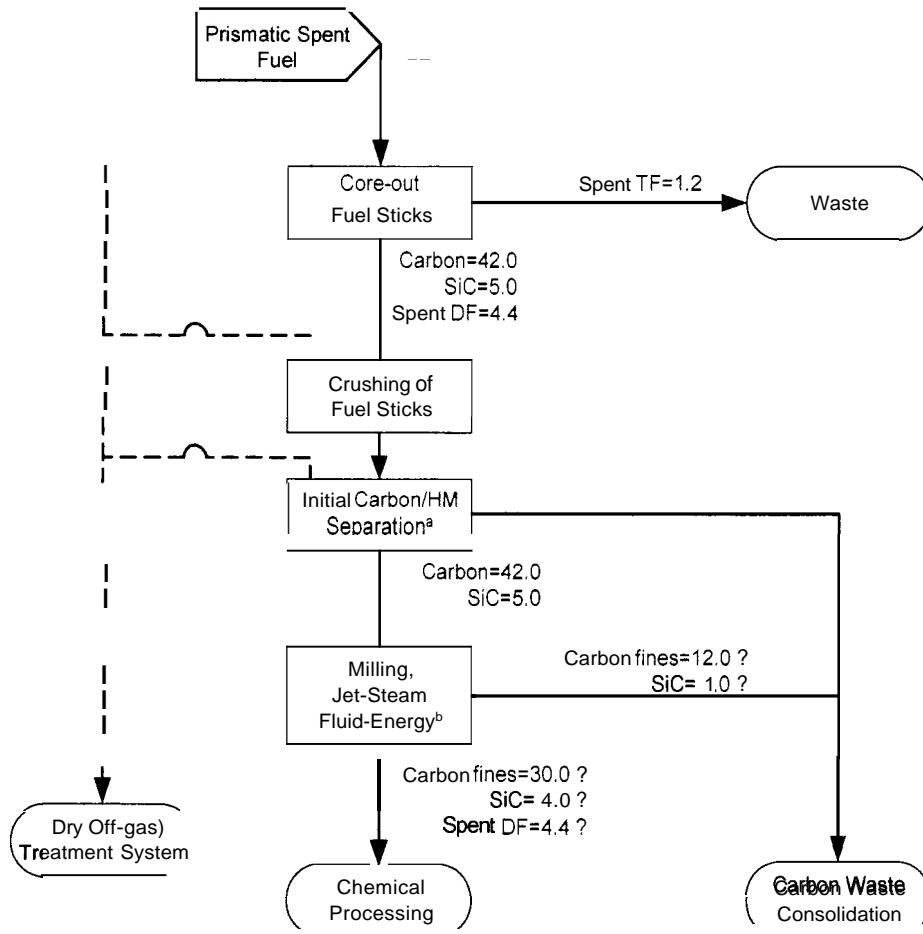
Figure 5.1 shows a flow sheet of the mechanical head-end common to the two processing options. This conceptual flow sheet incorporates some prior developments by GA related to the processing of TRISO fuel and the industrial experience of GrafTech related to carbon and graphite processing (including grinding, milling, acid leaching, filtering, etc.). The main processing steps are (1) removal of the DF from the graphite blocks; (2) crushing, grinding, and milling to expose the fuel kernels; and (3) optional solid-solid separation to remove some of the carbon and/or SiC.

The process starts with the removal of the DF compacts from the graphite blocks (block-end-cutting and rod-push-out machine). The fuel compacts, mostly intact, are then fed into a precrusher, which is likely to be a small jaw crusher located on top of a double-roll crusher, similar to the tabletop units that have been used before by GA. This system will minimize dusting while reliably breaking the compacts into small pieces that can be introduced into a roll crusher. Designed for remote maintenance, the roll crusher will be similar to the one that GA designed, built, and successfully operated under prototypical conditions (10-cm-wide by 10-cm-diam rolls, 78-kg/h throughput, >99.9% of the fuel particles crushed; Rickman, 1977). After the crushing operation, the projected average particle size should be about 40–200 μm .

A solid-solid separation using high magnetic fields has been suggested (Tsouris, 2002; Vandergriff, 2002) as a possible means to separate the carbon and SiC particles from the metal oxide particles. This or other techniques such as cyclonic or flotation separation require further evaluation. The major barrier is the requirement of a nearly 100% recovery of the fissile material contained in the oxide particles. This requirement translates into a nearly 100% efficiency in the solid-solid separation.

For the carbochlorination option, 150- to 200- μm particles may be adequate to feed into the actual chlorination step. However, a further milling step may be advantageous for the acid leaching. It is expected that the DF kernels will be difficult to dissolve in nitric acid, particularly defective fuel that will be unirradiated but must be recycled. The rate of dissolution is greatly enhanced by increasing the surface area exposed to the acid (achieved by reducing particle size). Accordingly, a steamjet grinder (suggested by Graffech) might be necessary to produce 5- to 20- μm particle sizes. This apparatus offers the advantage of not requiring any off-gas treatment, since the motive gas condenses and goes through the rest of the system as liquid water, which may then be recycled. Based on experimental data on the dissolution of ThO_2 , which were generated by GA, the roll crusher may prove sufficient. Although this hypothesis will require experimental verification, it should be noted as a possible process simplification. Larger particle sizes must be evaluated in terms of the dissolution rate and the type of dissolvent selected [e.g., using plain nitric acid without additives such as HF, Ce(IV), or Ag(I)].

Because a significant density difference exists between the lighter carbon and the SiC fraction (1.8–3.2 g/mL) and the heavier fuel kernels (~1 g/mL), the carbon and SiC particles ejected from the steamjet mill will be comparatively larger than the metal oxide particles, which is advantageous. In relative terms, the smaller oxide particles will be easier to dissolve, while the larger carbon and SiC particles will be easier to filter. Auxiliary solid-solid separation methods (e.g., magnetic separation) or the use of twojet mills in series should be evaluated as a means to achieve the required separation.



^a Solid/Solid separation may be unnecessary; carrying step until it is proven it is not needed.

^b The steam-jet fluid-energy mill has some separation capability to be determined.

Fig. 5.1. Mechanical head-end processes common to most processing options.

5.3 DIRECT-AQUEOUS-LEACHING FLOW SHEET

The conceptual dissolution process is shown in Fig. 5.2.

5.3.1 Description

The process can be described by the following main steps: (1) leaching and dissolution to dissolve nearly all fission products and fissile material, (2) washing and filtration to separate the insoluble solids (carbon, SiC, noble metals), (3) adjusting the resulting nitric acid solution to interface with the solvent extraction plant, (4) drying of the solids, and (5) compacting of the solids into a solid waste form. Additional solid waste from the separative process might be added to reduce the total number of different waste forms produced and/or to efficiently use repository space.

5.3.1.1 Harvesting of the DF compacts from the fuel elements

As previously mentioned, the process includes using a cutting wheel to slice the top and bottom of the graphite block to expose the DF channels and removing the fuel compacts by using pushing rods.

5.3.1.2 Crushing, grinding, and milling

The goal is to expose the fuel kernels to recover the fissile components. The optimum particle size is yet to be determined.

5.3.1.3 Solid-solid separation

All processing options would greatly benefit from a significant removal of the voluminous carbon and SiC fractions. A solid-solid separation using high magnetic fields has been suggested as a possible means to separate the carbon and SiC particles from the slightly paramagnetic metal oxide particles. Another possibility is the use of two jet mills in series. These techniques or others such as cyclonic or flotation separation require further evaluation. The major barrier is the requirement of a nearly 100% recovery of the fissile material contained in the oxide particles. This requirement translates into a nearly 100% efficiency in the solid-solid separation.

5.3.1.4 Leaching and dissolution

As previously noted, it is expected that the DF kernels will be difficult to dissolve in nitric acid, particularly unirradiated fuel to be recycled. The dissolution of spent fuel exposed to a very high burn-up might be easier than that for freshly prepared fuel. However, the process needs to be robust in order to handle the most difficult materials. Experimental determination of dissolution rates on actual and surrogate fuel will be necessary to ascertain (1) the optimum particle size for the oxide kernels, (2) a compromise between fast dissolution rates and filterability, and (3) the possible need for dissolution enhancers such as HF or strong oxidants (Ce^{+4} , Ag^{+2}). If possible, the use of plain nitric acid is the most desirable option to reduce requirements for reagents and subsequent production of wastes.

Generally, the use of two or more countercurrent dissolution steps can achieve a more-complete and faster dissolution in more-compact equipment than can be accomplished with a single large dissolver vessel. Accordingly, the present flow sheet contains two stages. The first stage will dissolve the bulk of the oxide kernels (90 to 99%), and the second stage will dissolve the remaining oxide (1 to 10%). The goal is to recover in excess of 99% of the fissile material. As shown, fresh nitric acid is used to remove the small fraction of oxide remaining after the first stage of dissolution. The resulting solution, which has a very low loading of fissile material, is first used to dissolve the bulk of the oxide of the following batch and is then sent to the solvent extraction step. A concentration step, evaporation, might be needed to adjust the concentration of fissile material to the optimum value required for the solvent extraction separative process.

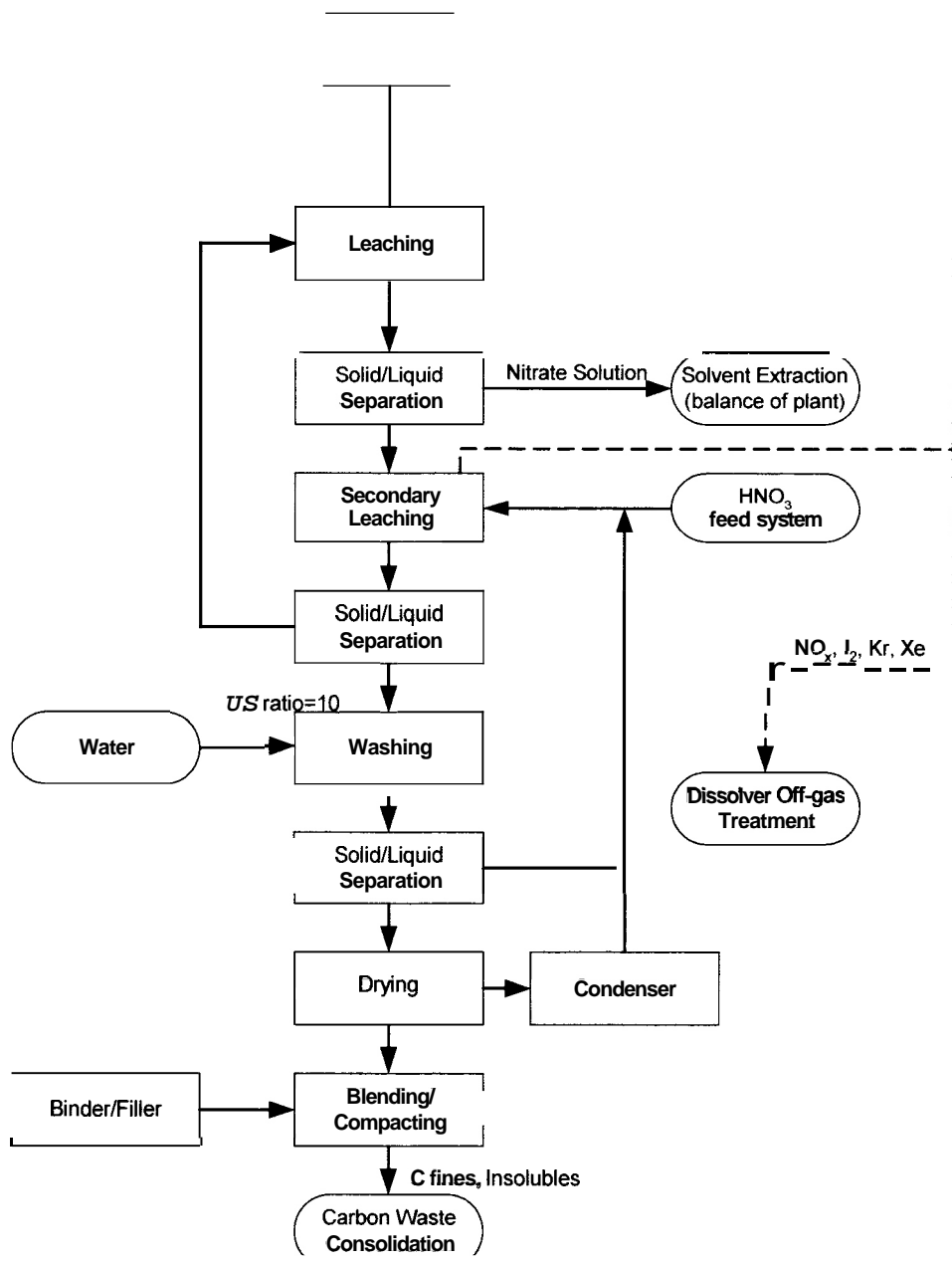


Fig. 5.2. Concept of countercurrent leaching process.

5.3.1.5 Washing and filtration

The main processing goal is to dissolve and recover the fissile content of the DF, leaving behind the carbon and SiC waste. Accordingly, it is crucial not only to completely dissolve the fuel kernels but also to effectively filter the insoluble solids. As the flow sheet is envisioned, a vacuum belt filter similar to that developed by GrafTech for strong acid applications will be used to separate the insoluble solids (carbon, SiC, and noble metals) during the dissolution and washing steps. To ensure the quality of the solution to be sent to the solvent extraction plant, a polishing filter will be used to capture solids that get past the vacuum belt filter.

5.3.1.6 Conditioning of the nitric acid solution

The acidity and concentration of metals in the nitric acid solution may need to be adjusted to interface with the solvent extraction plant. An evaporation and/or dilution step may be needed.

5.3.1.7 Drying of the solids

At completion of the dissolution and washing steps, the filtered solids (carbon, SiC, and noble metals) must be dried. Drying is a pretreatment step prior to waste consolidation. A conventional oven or, more likely, a semicontinuous microwave dryer will be used.

5.3.1.8 Compacting of the solids into a solid waste form

The concept is to compact the dry solids, probably using a binding agent such as tar to form compacts that may be reinserted into the empty channels of the fuel elements or may be cast into other forms to meet repository requirements. Details of this process are described in Sect. 6.

5.3.2 Reagents

For the aqueous processing options, the main reagents are water, steam for the jet mill, washing solutions, and nitric acid. Small amounts of HF or $\text{Ag}^{+2}/\text{Ce}^{+4}$ (recycled) may be added to the nitric acid to accelerate the dissolution.

For the carbochlorination process, chlorine and a chloride salt (recycled) are the main reagents. Other reagents may be needed as consumables in the off-gas system, as well as for the decontamination, waste treatment, and disposal steps.

5.3.3 Equipment

The main pieces of equipment are the following: (1) block-end-cutting and rod-push-out machine; (2) precrusher, which is likely to be a small jaw crusher located on top of a double-roll crusher; (3) compact-roll crusher; (4) steam jet mill; (5) solid-solid separator; (6) dissolver-washing-filtering system; (7) solution conditioning system; (8) solids dryer; and (9) waste form compacting unit.

5.3.3.1 Block-end-cutting and rod-push-out machine

As envisioned, the fuel element will be positioned horizontally using a rotating holding device. A couple of cutting wheels will slice the graphite to remove the top and bottom of the graphite block. The sliced ends will be retained and reused in the final waste form. A set of pushing rods, pneumatically or hydraulically operated, will be used to remove the DF compacts, which will fall into a hopper connected to the precrusher.

5.3.3.2 Precrusher

This apparatus is likely to be a small jaw crusher located on top of a double-roll crusher, similar to tabletop units previously used by GA. See Fig.5.3 .

5.3.3.3 Roll crusher

As shown in Fig. 5.4, the roll crusher designed for remote maintenance will be similar to the one designed, built, and successfully operated by GA. It is 10 cm wide with 10 cm-diam rolls and has an average throughput of over 78 kg/h. During the testing of the roll crusher, more than 99.9% of the fuel particles were crushed. After crushing, 98% of the particles were in the 40- to 200- μm size range.

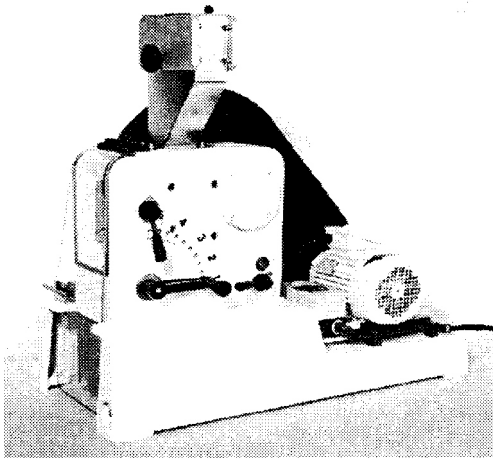


Fig 5.3. Example of a commercially available jaw crusher.

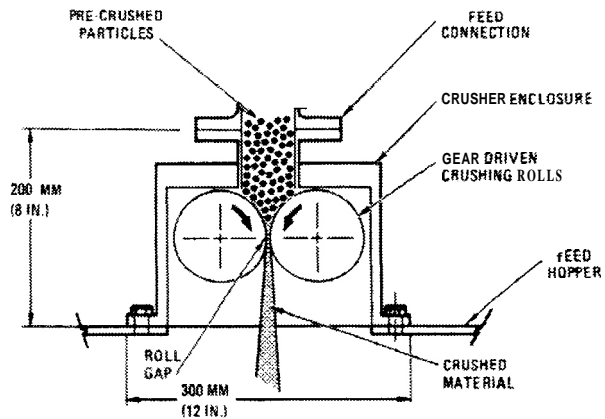


Fig. 5.4. Schematic of the GA double-roll particle crusher.

5.3.3.4 Jet mill

The jet mill will be an adaption of a commercially available unit shown in Fig. 5.5. A steamjet grinder (suggested by GrafTech) might be necessary to produce 5- to 20- μm particles sizes. It has the advantage of not requiring any off-gas treatment, since the motive gas condenses and moves through the rest of the system as liquid water to be recycled. Because there is a significant density difference between the lighter carbon and SiC fraction (1.8–3.2g/mL) and the heavier fuel kernels (~1 g/mL), the carbon and SiC particles ejected from the steamjet mill will be comparatively larger than the metal oxide particles, which is advantageous. In relative terms, the smaller oxide particles will be easier to dissolve while the larger carbon and SiC particles will be easier to filter.

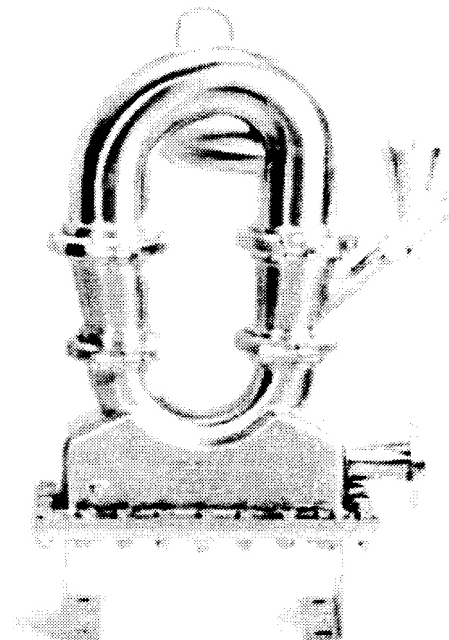


Fig. 5.5. Example of a commercially available steam jet mill.

5.3.3.5 Solid-solid separator

The solid-solid separation would be advantageous but not critical. Developmental work is needed to determine if the solid-solid separation can be achieved at nearly 100% efficiency. The list of suggested equipment includes a high magnetic-field separator, a cyclone, twojet mills in series, a flotation device, etc.

5.3.3.6 Dissolver-washing-filteringsystem

Several options are under consideration, including cylindrical or slab dissolvers and semicontinuous belt or carousel-type systems that combine dissolution, washing, and filtering.

A dissolver used at *Oak Ridge National Laboratory (ORNL)* for $\text{ThO}_2\text{-UO}_2$ binary scrap is shown in Fig. 5.6. This dissolver has an internal basket that holds the material while the liquid is recirculated. A similar design can be implemented for the dissolution of the TRISO fuel, except that the basket will have to be replaced by a very fine membrane to retain the very fine carbon and SiC particles. In this concept, reduced liquid-to-solid ratios should be sufficient.

The volume and geometry of the dissolver will depend on development results for the optimum liquid-to-solid ratio and on whether an effective solid-solid separation before dissolution could be practical. Assuming no separation of the carbon and SiC fraction, a conservative 5:1 liquid-to-solid ratio (by weight), and 10% free space, the volume of the dissolver required to accommodate one fuel element per batch would be around 160L. For this volume, a slab or annular dissolver should be considered. The maximum thickness for a critically safe slab (conservatively assuming 100% ^{239}Pu) is 2.2 in. The 160-L capacity can be achieved using a very reasonable 70-in.-high by 65-in.-wide slab (2.2 in. thick). An actual nuclear criticality safety (NCS) calculation using the expected isotopic mix in place of pure ^{239}Pu might allow a thicker slab. Additionally, the developmental work and a careful design might allow for a much lower liquid-to-solid ratio. These two factors should reduce the size of the dissolver and the amount of acid needed. However, even without optimization, the volume and size are quite functional. Based on the GrafTech experience, the traditional stationary dissolver may be replaced by a semicontinuous system based on a vacuum belt filter (a horizontal slab), as developed by Graffech for concentrated acid applications. This system could be tailored to incorporate several acid leaching, washing and drying steps. Each batch of solids would move with the belt as a thin filter cake into the different stages of leaching and washing. The liquid would move countercurrently from stage to stage. For example, pure water is used for the washing step. The resulting liquid (filtrate) is mixed with concentrated acid and used for the second leaching of the solids. The separated liquid from the second leaching step flows back to the first leaching step and becomes more concentrated in metal nitrates. Filtrate from the first leaching step is finally sent to the solvent extraction plant. In a similar concept, a carousel system could be envisioned to accomplish the multiple leaching, washing, and filtering steps.

5.3.5.7 Solution conditioning system

The solvent extraction process generally requires the removal of fine material and colloids to avoid problems in the separative equipment. Accordingly, a polishing filter (membrane surface) will be used to capture solids that get past the vacuum belt filter—either as a throwaway cartridge or as a cleanable module. The concentration of dissolved species and nitric acid may need to be adjusted to better meet the requirements of the aqueous processing plant. An evaporation and distillation column combination may be required to sufficiently concentrate the feed solution while recovering water for recycle.

5.3.3.8 Solids dryer

A semicontinuous belt system coupled with a conventional oven or, more likely, a microwave dryer will be used. The water removed may be condensed and recycled to limit the load on the off-gas system.

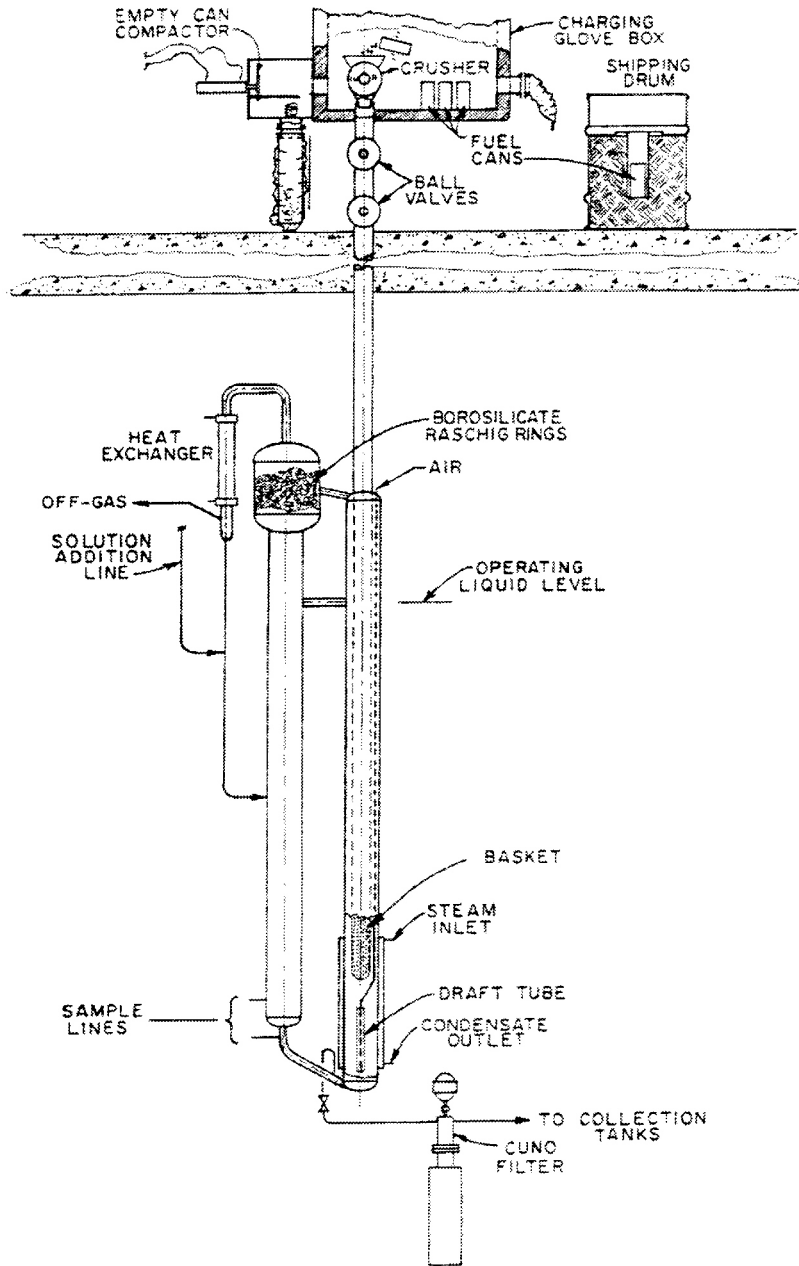


Fig. 5.6. ORNL pencil-tank dissolver.

5.3.3.9 Waste form compacting unit

The dried solid waste includes the carbon, SiC, and undissolved solids (e.g., noble metals). It may be advantageous to combine these wastes with denitrated fission products separated by the aqueous processing system. The wastes will be pressed into pellets that have dimensions similar to those of the original fuel compacts. This enables the pellets to fit into the discarded graphite fuel block. A binding material such as tar may be used. A pellet press will need to be designed, and the green pellets must be baked using a furnace.

5.3.4 Waste Streams

Paradoxically, the aqueous processing line will not produce significant quantities of liquid wastes because the bulk of the liquid is sent to the separations process. Only small volumes of secondary liquid wastes from the off-gas system and decontamination operations will be generated.

As previously noted, the solid waste—mostly carbon, SiC, noble metals, and probably fission products separated by the solvent extraction process—will be blended and compacted as a waste form. (A binder reagent may be added). Details are provided in Sect. 6.

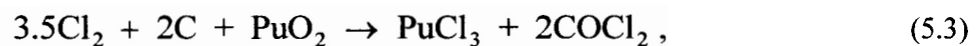
5.4 PYROPROCESSING FLOW SHEET

The conceptual pyroprocessing scheme is shown in Fig. 5.7. Pyroprocessing, like aqueous processing, starts with a mechanical head-end. A dry-rolling crushing operation is probably sufficient for the pyroprocessing option during which most of the gaseous fission products will be released. The fine particles (carbon, SiC, and MO_x) will be then introduced into a molten salt bath [e.g., LiCl/KCl (mp = 350°C) or the denser CsCl/KCl (mp = 616°C)]. Sparging with an inert gas, such as N₂, can ensure complete removal of the gaseous fission products (I₂, Kr, Xe) to be treated by the off-gas system. The actual chemical processing starts with the introduction of Cl₂ gas into a closed loop with recirculation. A cooled condenser will retain the chlorination by-product SiCl₄ (bp = 57.6°C) while allowing the Cl₂ gas (bp = -34.6°C) and the COCl₂ (bp = 8.3°C) to be recirculated. The SiCl₄ can later be scrubbed using water or an alkaline solution, forming a precipitate of SiO₂ and hydrochloric acid (or NaCl). If some use could be found for the acid, the scrubbing solution could be filtered and distilled to generate a more concentrated hydrochloric acid.

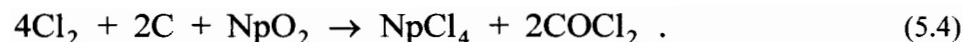
A heated coil (>350°C) may be used to thermally decompose COCl₂ to carbon monoxide and chlorine or to CO, and CCl₄. Carbon tetrachloride acts as a chlorinating agent similar to the combination of Cl₂ and carbon.



The accumulated CO₂ will be periodically vented through the off-gas system. Because chlorine does not react directly with carbon except in the presence of metal oxides, only a small fraction (~5%) of the carbon would be consumed. For example,



and



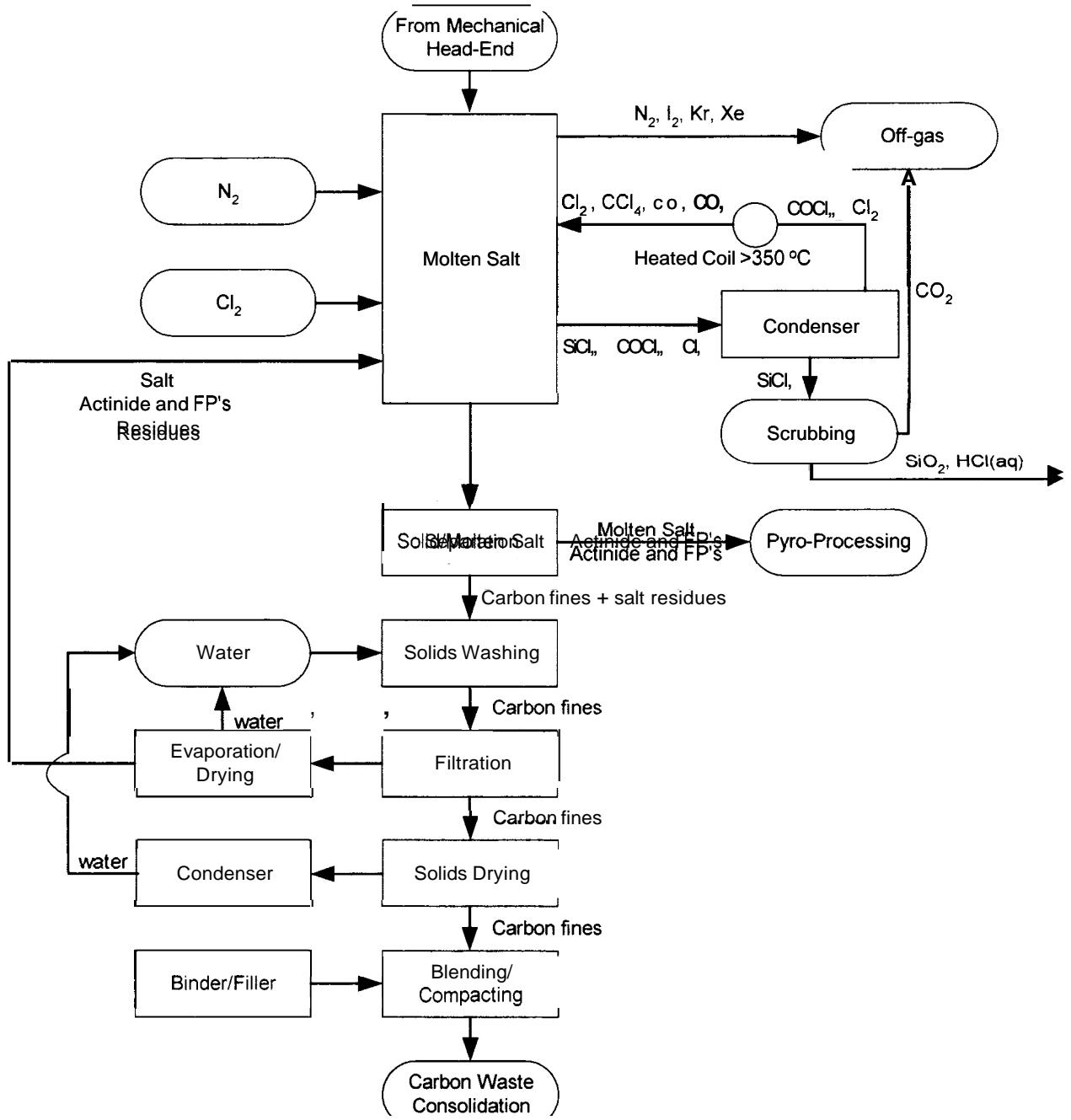


Fig. 5.7. Pyroprocessing flow sheet.

Note that the actual chlorination process involves several equilibrium reactions between the species carbon, Cl_2 , MO_x , CO , CO_2 , and CCl_4 . Chlorine will also react with the SiC coating layer, forming volatile SiCl_4 and carbon. The compound CCl_4 forms only at very high temperatures and will react with the oxide kernels in the same way that carbon and Cl_2 do.

All species from the spent fuel kernels, including the noble metal fraction, should completely dissolve by chlorination. One of the key aspects to be resolved is the handling of the solids, that is, introduction of the fuel compacts into the molten salt, the clean removal of the excess carbon waste, and the transfer of clean molten salt to the separation process equipment. However, a practical solution should be achievable during the development stage.

After chlorination, the filtered solids will entrain some quantity of fissile and fission products dissolved in the salt. Since most chlorides are highly soluble, water washing should be a simple and very efficient way to remove and recover these entrained fissile and fission products from the carbon fines. As shown in Fig. 5.7, the spent washing solution can be evaporated to dryness. The water can then be recycled for further washing, and the dried-solids residue reintroduced into the molten salt bath.

The washed carbon fines should be relatively free of contaminants. After drying, these fines can be compacted into a consolidated carbon waste form, as described in Sect. 6.

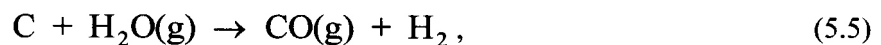
5.5 BACKUP OPTIONS

The GrafTech industrial-scale plant includes all the carbon processing steps shown in the aqueous option but at a much larger scale than required for a pilot plant that processes TRISO-coated fuel. Accordingly, there is a significant degree of confidence in the viability of the proposed flow sheets. The major efforts are expected to involve the adaptation to a much smaller scale and the need for remotely operated processes inside hot cells or canyons. A collaborative effort of industry (GA and GrafTech) and the U.S. Department of Energy (DOE) complex appears to be the most effective way to successfully proceed.

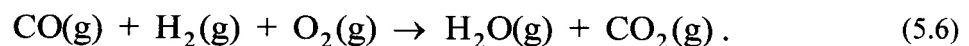
Should insurmountable difficulties be encountered during the R&D effort, several backup options are available. In the past, significant development work was performed on two alternatives in which the carbon was burned in air to CO_2 , and the resulting ashes dissolved in nitric acid. Alternatively, the carbon can be gasified by using steam. In all cases the DF compacts will be removed as previously described by slicing the top and bottom of the graphite blocks using a cutting wheel, followed by removal using pushing rods. The actual burning or gasification of the carbon can be performed in one or two stages, as described in the following sections.

5.5.1 Grind-Burn-Mill-Burn-Leach

In the grind-burn-mill-burn-leach option, the fuel compacts are crushed using a small jaw crusher and milled with a double-roll crusher, similar to the tabletop units that have been used before by GA. The resulting material is then burned in air, where the external carbon reacts with oxygen to form CO_2 , or is gasified by using steam:



followed by



In both cases, the resulting CO₂ needs to be trapped for disposal either as a solid (most likely as CaCO₃, formed via the use of lime) or as a gas or supercritical fluid (for injection into a deep well or deep sea disposal site). The steam option appears to be preferable because it is easier to control and does not produce significant amounts of secondary toxic species compared with the burning in air. Once the external carbon is consumed, then the SiC-coated fuel particles need to be broken. This can be accomplished using a roll crusher similar to the one that GA designed, built, and successfully operated under prototypical conditions (see Sect. 5.2). For the pyrochemical option, the ground material can be introduced into the carbochlorination unit. For the aqueous option, the material may be subjected to a second burning or gasification step and the resulting ashes dissolved in nitric acid.

5.5.2 Grind-Mill-Burn-Leach

This option is similar to the previous one, except that the initial grinding described above is followed by the use of a roll crusher to ensure that the SiC coating is breached and the inner carbon coating exposed. The carbon (inner and outer layers) is then burned or gasified as described in Sect. 5.5.1. The ashes are either dissolved in nitric acid (for further aqueous processing) or reacted with a halogen (Cl₂ or F₂) in a molten salt (for the pyroprocessing option).

6. WASTE MANAGEMENT

6.1 ISSUES AND GROUND RULES

In the processing of spent nuclear fuel (SNF), waste management operations have been estimated to contribute up to 40% of the total costs. Consequently, it is essential to integrate waste management processes with the separations processes, the means of transportation, and the disposal facilities. The waste forms should be selected to minimize environmental impacts and total system costs. Different SNF fuel processing techniques often imply different waste forms and different waste management strategies. Four sets of waste management operations are described herein for four different sets of process options. In these analyses, the following general assumptions are used.

- *Scale.* It is assumed that large quantities of HTGR SNF are processed. The quantities are sufficient that the transportation system and a section of the repository system are optimized to receive wastes from processing HTGR SNF. If only small quantities of a particular type of SNF are to be processed, the most cost effective strategy is generally to use the same strategies as used for LWR SNF. This approach can become very expensive for disposal of large quantities of wastes that have physical and radiochemical properties that are very different from those of LWR SNF.
- *Waste disposal.* The design of the waste processing and disposal systems is integrated to minimize total costs. In the United States, utilities are charged a flat rate of 0.1 ¢/kWh for disposal of HLW or SNF. All repository transport and disposal costs are to be paid from this fee. If waste forms are produced that increase transport or disposal costs, these will ultimately be reflected in the rate charged the utilities for waste management. Consequently, in a large system, the total system costs, not the costs of SNF processing, should be minimized.
- *Regulations.* The regulatory requirements for the system are current requirements, accounting for the scale of operations.

6.2 CHARACTERISTICS OF HTGR SNF AND IMPLICATIONS FOR WASTE MANAGEMENT

6.2.1 Characteristics of HTGR SNF

The composition of an HTGR SNF assembly is shown in Table 2.3. The unique waste management characteristic of processing HTGR SNF is carbon (90 kg per fuel assembly), with its radioactive ^{14}C . This is the dominant waste from SNF processing (by volume and mass). The large volumes and masses imply potentially a large impact on plant size and plant cost. Carbon management controls many of the decisions associated with the choice of waste management processes. As noted earlier, each fuel assembly has DF and TF. The DF is to be processed, while the TF is removed, put into new fuel blocks, and sent to an accelerator for further burning.

The mass ratio of fuel and fission products to nonfuel components in HTGR SNF is more than 30 times greater than in LWRs. This impacts not only the processing of SNF but also the transport and disposal. The design of a repository is based on the characteristics of the SNF. If the SNF is radically different from LWR SNF, the optimum design of the repository will be different as well.

The requirements for management of the carbon depend on its intrinsic radiological characteristics and any impurities from leaking fuel microspheres. The unavoidable radionuclide is ^{14}C ($T_{1/2} = 5760$ y) from the neutron irradiation of stable ^{13}C in natural graphite. Carbon-14 is also produced by the neutron irradiation of nitrogen impurities in the graphite. In addition to the ^{14}C , there are two other radionuclides typically found in graphite (Wickham, 1999): tritium (^3H) ($T_{1/2} = 12.5$ y) from neutron irradiation of lithium impurities and ^{36}Cl ($T_{1/2} = 308,000$ y) from the neutron irradiation of chlorine in the form of chlorides. The activity levels are controlled by the impurities in the initial graphite. Tritium is often the primary short-term hazard, whereas ^{36}Cl is the very long-term hazard. Repository performance assessments (White et al., 1984; Poinssot et al., 2002) indicate that ^{36}Cl can be an important radionuclide in terms of the long-term performance of the repository. Preliminary analysis (Su, 1995) for a fuel assembly with 112.3 kg of graphite projected the following concentrations of key radionuclides in the graphite 10 years after reactor discharge: 5.82×10^{-1} Ci ^3H per fuel assembly (0.04 ppm lithium in unirradiated graphite), 1.27×10^{-1} Ci ^{14}C per fuel assembly (100 ppm nitrogen in unirradiated graphite), and 4.24×10^{-4} Ci ^{36}Cl per fuel assembly (3 ppm in chlorides in unirradiated graphite).

6.2.2 Historical Perspective on Carbon Management

There is an important historical note in context of managing carbon containing ^{14}C from HTGR SNF processing. Significant work, including small-scale hot cell tests and large cold tests, was done on the processing of HTGR SNF in the 1960s and early 1970s. It was originally thought that the carbon associated with HTGR SNF could be managed by burning the SNF, converting the graphite to CO , cleaning impurities from the resultant CO_2 , and releasing the CO_2 with its ^{14}C to the atmosphere. Atmospheric dilution would be used to minimize health impacts.

As the research progressed, it was recognized that the quantity of ^{14}C released to the atmosphere could present a hazard to the population near the plant via CO uptake in plants consumed for food. There was also a concern about long-term global increases in atmospheric ^{14}C levels. Carbon-14 is produced naturally by high-energy particles from space that bombard the atmosphere but was also produced by atmospheric weapons testing. The pulse of ^{14}C from weapons testing (Alley et al., 2002) began to provide an understanding of its behavior in the environment. The result of these studies and analysis was the conclusion that the ^{14}C could not be released to the atmosphere. This was confirmed in the more recent analysis conducted by the DOE New Production Reactor Program in the United States and by European evaluations (Holt, 1999; White et al., 1984; Department of the Environment, 1986).

Research programs in the early 1970s on processing HTGR SNF led to the recognition that the ^{14}C could not be released to the atmosphere. A limited amount of work was done on removal of the CO from the off-gas with a scrubber using calcium hydroxide. The final product is calcium carbonate (CaCO_3).

The method is viable but expensive and generates very large quantities of wastes—the volumes are 10 to 20 times that of the initial carbon. Furthermore, the burning and processing of the large volume of radioactive gases are expensive. Because of these issues, new methods to manage carbon from HTGR SNF are being examined.

While only small quantities of coated-particle graphite-matrix fuels have been processed and most of the research was conducted in the early 1970s, there is a large body of more recent research on the treatment and disposal of irradiated graphite (with ^{14}C) from graphite-moderated reactors. In these reactors, the graphite was not part of the fuel. Graphite-moderated reactors include production reactors in Russia, England, France, and the United States, which produce materials for nuclear weapons; 26 Magnox reactors in Great Britain; 14 Advanced Gas-Cooled Reactors in Great Britain; 6 Magnox reactors in France; 18 RBMK power reactors in Russia; and a variety of reactors built in other countries. This work is reported in a variety of conference proceedings, including the IAEA Technical Community Meeting on “Nuclear Graphite Waste Management” held in Manchester, England, in October 1999. This source of information provides much of the technical basis to consider new methods to manage carbon with ^{14}C when processing HTGR SNF.

6.2.3 Waste Management Strategies

The early research indicated strong incentives to avoid burning of graphite and collection of the CO , as CaCO_3 . This resulted in consideration of methods to mechanically separate most of the carbon from the fuel compacts—the strategy described in this report. The DF is then processed for recovery of fissile and fertile materials, and the TF is repackaged in new graphite blocks and sent for additional neutron irradiation by a reactor. (Alternatively, the TF can be repackaged for disposal in a repository.) The graphite remains as solid carbon—the high-density form of carbon. This results in two classes of wastes from the processing facility that require disposal: the wastes from processing the DF and the graphite.

These wastes can be sent to the repository separately or together. If they are sent together, appropriate wastes from processing the DF can be incorporated into the graphite block by filling the coolant channels and other voids. This procedure requires that the HLW from processing be converted into thin compacts and placed back into the block. This is a potentially viable but mechanically complex option. The other alternative is to treat each waste separately. The rationale for this strategy is based on two considerations: (1) the very different properties of the waste streams and (2) the potential to optimize processing and disposal operations. This second option (i.e., separate treatment) is described herein. The defining characteristics of the two wastes are as follows:

- **Graphite.** This is a high-volume waste with no significant heat generation. The low-heat characteristic potentially allows low-cost disposal methods, as discussed in Sect. 6.3.
- **DF HLW.** This is a new type of HLW that is fundamentally different from traditional HLWs that have been created in the past—independent of the chemical or physical form of the waste. DF HLW generates significant decay heat from cesium and strontium, but this decay heat disappears within a few hundred years. Processing removes the actinides, which generate heat over long time periods. (Historically, HLW has included americium and curium, which resulted in decay-heat generation for many thousands of years.) These considerations have potentially major implications in terms of the repository. Geological methods for the disposal of DF HLW are described in Sect. 6.5.

6.3 SEPARATION AND DISPOSAL OF GRAPHITE BLOCKS FROM HTGR SNF

The volume and mass of the graphite in the SNF suggest that the preferred waste management strategy in processing HTGR SNF is to mechanically separate most of the graphite from the fuel compacts. Graphite is the second-highest-density carbon form (after diamond); thus, maintaining the

carbon as graphite minimizes waste volumes and masses. This reduces by 74% the mass of material (Table 2.3) to be further processed. Equally important, it reduces the potential off-gas volume by an equivalent fraction. Radioactive gas-handling equipment at atmospheric pressure requires large volumes of expensive shielded space. The single exception is if the CO₂ can be directly geologically sequestered. If this option is available, burning may be the preferred option. (See Sect. 6.5 for details.)

Three issues are associated with graphite waste management: methods to mechanically separate graphite from the fuel compacts, classification of graphite as a waste form, and graphite disposal.

6.3.1 Separation of Graphite Block from Fuel Compacts

As described in Sect. 3.2, the first step in processing the SNF is separation of the graphite block from the fuel compacts. This technology has been demonstrated several times (Saurwein et al., 1981; McCord, 1984). There are strong economic and waste management incentives for separating the bulk of the graphite from the fuel compacts. The viability of this process depends on the fuel designer choosing designs that allow separation of the fuel compact from the graphite block. This, in turn, depends on complex tradeoffs between reactor design, fuel fabrication, and SNF processing.

In some fuel designs, separation of the fuel compacts and the graphite blocks is simple and allows removal of the fuel compacts in the graphite block at the reactor. In such cases, the fuel compacts may be shipped to the processing plant without the graphite blocks. An example of this type of fuel design (Fig. 6.1) is the operating High-Temperature Engineering Test Reactor (OECD-NEA Nuclear Science Committee, 2000) in Japan. This 30-MW(th) helium-cooled test reactor is designed to reach very high helium discharge temperatures (950°C).

6.3.2 Classification of Graphite as a Waste Form

The graphite blocks contain radioactive ¹⁴C from irradiation of the graphite, radionuclides (³⁶Cl, ³H) formed from irradiation of impurities in the graphite, and radionuclides that migrated from the fuel microspheres. It is likely that geological disposal of this waste is required. This is based on several considerations.

- **Concentration.** Based on the concentration limits used to classify wastes in the United States (10 CFR 61), the graphite would be a Class C waste if ¹⁴C were the only radionuclide present. Class C wastes are the most radioactive wastes for which shallow land disposal may be used. Wastes with higher concentrations of long-lived radionuclides require deep geological disposal. For a waste containing only one radionuclide, ¹⁴C, the waste by definition is **Class C** because its ¹⁴C concentration is between **0.8** and **8 Ci/m³**. The graphite (assuming full compaction and 100ppm nitrogen impurities) has a ¹⁴C concentration of 2.5 Ci/m³. However, the irradiated graphite may exceed Class C limits and require geological disposal based on the concentrations of long-lived radionuclides.
 - **Chlorine-36.** The current regulations for shallow land disposal (10 CFR 61) were designed primarily for low-level wastes from **LWRs** and hospitals. Many long-lived radionuclides, such as ³⁶Cl, that are now known to be major radionuclides in terms of health effects, were not considered when the regulations were implemented. The potential impacts of ³⁶Cl have received considerable attention. For a large-scale deployment of HTGRs, a regulatory ruling will be required. The tables used to classify wastes for shallow land disposal are not applicable to this waste form.
 - **Carbon-14.** The ¹⁴C content is dependent on fuel burn-up. With a higher loading of fuel in the graphite block and more neutron irradiation, the ¹⁴C content could exceed the Class C limit. If shallow land disposal of graphite is used, this places a potential constraint on future fuel designs.

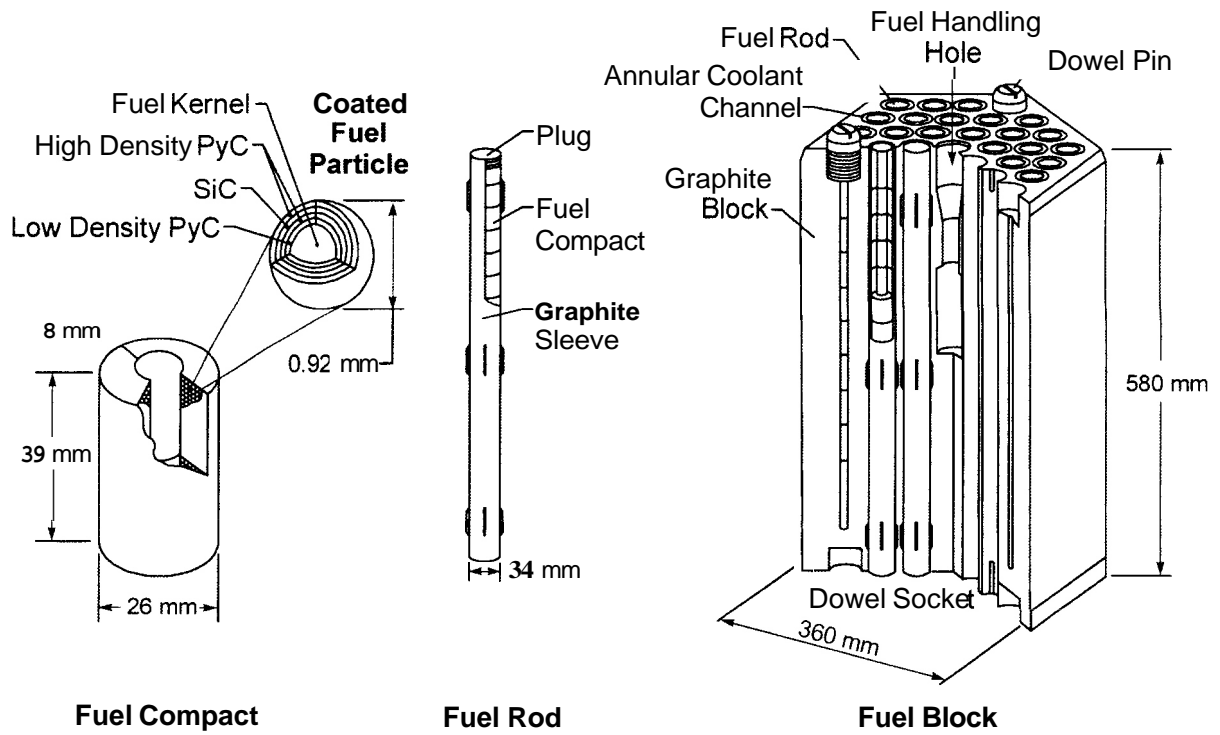


Fig. 6.1. High-temperature engineering test reactor fuel designed for 950°C exit helium temperatures with fuel rods and separate graphite block.

- *Other radionuclides.* The radioactivity of the irradiated graphite approaches the lower boundary for wastes that require geological disposal. To allow for shallow land disposal, it must be shown that (1) no impurities in the graphite add significantly to the radioactivity, (2) there was no leakage of radionuclides from the fuel in each graphite block during operation, and (3) the disassembly process did not leave any fuel debris with the graphite block. It appears difficult to demonstrate that these conditions can be met in a large-scale system because the radioactivity of the graphite is close to the boundary for wastes requiring geological disposal. Alternatively, each block could be measured for its radioactivity. However, many of the radionuclides that determine the waste classification are alpha and beta emitters, which are extremely difficult to measure in a large solid object. These practical considerations suggest that it would be very difficult, probably impossible, to demonstrate that graphite is Class C waste.
-
-
- *Quantity.* The quantity of waste has a significant impact on its acceptability for shallow land disposal. The U.S. regulatory structure (10 CFR 61) for shallow land disposal of radioactive wastes contains two components. The first part of 10 CFR 61 defines the general requirements for shallow land disposal. Specifically, it states: “A maximum concentration of radionuclides is specified for all wastes so that at the end of the 500 year period, remaining radioactivity will be at a level that does not pose an unacceptable hazard to an intruder or the public health and safety. Waste with concentrations above these limits is generally unacceptable for near surface disposal.”

The second component of the regulatory structure is the classification of wastes into categories (A, B, and C). This classification system is a method to make rapid judgments concerning the likely acceptability of a particular waste for shallow land disposal. However, it does not by itself ensure the acceptability of any waste for this form of disposal. **An** example of this is the U.S. Nuclear Regulatory Commission (NRC) perspective on disposal of uranium. The NRC allows disposal of small quantities of uranium from fuel fabrication facilities as Class A low-level waste (lowest category of LLW) but has stated that disposal of large quantities of depleted uranium (DU) via shallow land disposal is unacceptable (Leeds, 2000). This is a practical recognition that the earth’s crust contains small quantities of long-lived radioactive materials that have acceptable consequences but that large quantities of long-lived radionuclides can have major health impacts. The concentration limits of long-lived radionuclides in Class A, B, and C wastes are for relatively small quantities of materials, not many thousands or tens of thousands of tons.

Carbon-14 cannot be released to the atmosphere because of local health effects. With a half-life in excess of 5000 years, there will be no significant decay of ¹⁴C within the 500-year limit defined by regulations for disposal of LLW. It appears unlikely that a material that is unacceptable for release to the general environment as **CO**, with massive dilution by the atmosphere, would be acceptable for an intruder to release from a shallow land burial site in a highly concentrated form.

- *Foreign regulatory limits.* Other industrial nations, such as Germany and France, require geological disposal of any wastes with significant concentrations of long-lived radionuclides, such as irradiated graphite.

6.3.3 Disposal of Graphite

- If irradiated graphite cannot be disposed of via shallow land disposal, the irradiated graphite blocks wastes would be consolidated, packaged, shipped to the repository, and disposed of in a separate section of the repository. The irradiated graphite would be the final waste form for disposal.

Many graphite-moderated reactors have been built; consequently, significant work has been performed on the consolidation and packaging of irradiated graphite containing ^{14}C for disposal. There has also been limited work on sealing graphite with organic coatings followed by high-temperature carbonization to reduce the graphite permeability to groundwater flow. Such options have been examined for graphite contaminated with a variety of fission products and actinides from failed fuel elements. It is assumed herein that if the graphite block for the HTGR SNF assembly contains significant quantities of actinides and fission products from failed microspheres, it will be processed and not directly disposed of.

The unique characteristics of this waste form indicate that the graphite is the preferred waste form for ^{14}C and may allow low-cost geological disposal.

- *Volume/mass.* Graphite is the high-density, low-volume form of carbon, with a theoretical carbon density of 2.25 g/cm^3 . In contrast, the most likely alternative processed carbon form is calcium carbonate (CaCO_3), with a carbon density of 0.35 g/cm^3 . Graphite is clearly the preferred waste form because of its very high carbon density.
- *Decay heat.* The ^{14}C has a half-life of >5000 years; consequently, the decay heat of the graphite is very low.
- *Chemical durability.* Graphite is one of the most durable materials known to man. Natural graphite has existed under various geological conditions for hundreds of millions of years. Less refractory carbon (coal) has existed for similar time periods under many geological conditions. Oxidation and leaching in groundwater are extremely slow. Because of its extreme durability, graphite was once considered as a material of construction for repository waste packages. It was ultimately rejected because it is brittle and thus has the potential for failure if large rock falls impact the container after repository closure. Evaluations of HTGR SNF under repository conditions also indicate superior performance of graphite as a waste form (Lotts et al., 1992).

The combination of properties implies the potential for low-cost disposal of the HTGR graphite blocks after removal of the fuel compacts. SNF and HLW disposal is expensive because of two factors, neither of which applies to irradiated graphite:

- *Decay heat.* Decay heat raises the temperature in the repository, which, in turn, degrades repository performance. Temperatures are controlled by limiting the decay heat per waste package to 11 kW and spreading the waste packages over more than 100 km of tunnels. With the low decay heat of ^{14}C , waste packages can be of any size and the waste can be stacked in large low-cost caverns rather than distributed over many kilometers of expensive tunnels to control the maximum repository temperature. The waste packages need not be separated to distribute the decay heat and minimize repository temperatures.
- *Wastepackage/wasteform performance.* The repository must contain the radionuclides for 10,000+ years. For SNF and traditional HLW, this requires the use of expensive waste packages made of highly corrosion-resistant containers. The proposed Yucca Mountain (YM) waste packages have a volume of $\sim 7 \text{ m}^3$, with an estimated cost of \$500,000 per package. For graphite waste forms, high-performance waste packages may not be required.

No repository performance assessment has been performed for graphite waste forms containing radioactive ^{14}C . However, a performance assessment (Owen, 1999) was conducted for disposal of 500,000 tons of DU in the form of U_3O_8 in the proposed YM repository. This provides a starting point for considering disposal of a ^{14}C graphite waste form. Like the graphite, the DU generates almost no decay heat. Unlike graphite, DU is somewhat soluble in groundwater. The performance assessment indicated that the DU could be disposed of in steel drums (no expensive waste package) with the drums fully filling a disposal drift (no expensive spacing of drums in tunnels). The estimated incremental cost was ~ 250 million dollars for 500,000 tons or \$500/ton. Depending upon the other impurities in the graphite, this may be an option for disposal of the graphite in steel drums or boxes.

If the other radionuclides in the irradiated graphite necessitate packaging of the graphite to improve disposal performance, there are packaging options that are significantly less expensive than the traditional $\sim 7\text{-m}^3$ SNF waste package (Forsberg, 2000a, 2000b, 2000c). All of these packaging options require low decay-heat-generation rates. One example is to build a large waste package in the repository. The larger the waste package, the smaller the surface-to-volume ratio and the smaller the investment in waste packages per unit volume. An example of a large waste package is the Swedish SFR silo (Fig. 6.2). Several of these silos have been built at SFR, the Swedish disposal site for low- and intermediate-activity wastes. The silos were built in caverns located about 100 m deep and located under the Baltic Sea. They are connected to the mainland by a 1-km-long tunnel. Each silo is ~ 25 m in diameter and 40 m high. The silos can accept both contact and remote-handled wastes. The facility has been operating for ~ 15 years.

6.4 OPTIONS FOR WASTES FROM PROCESSING DF COMPACTS

The general waste management strategy for processing HTGR SNF is to remove, by mechanical means, as much graphite as possible from the SNF assembly as an initial process step. (Sects. 2.4 and 5.2). After graphite removal, four alternative waste management options have been identified (Fig. 6.3) for the wastes from processing DF components. Each is based on how the carbon is removed from the separated fuel compacts and the final waste forms produced for disposal.

6.4.1 Traditional: Burn SNF Compacts and Recover CO, as a Solid

The historical HTGR process was to burn the fuel assembly, remove various radionuclides from the off-gas, and scrub the CO_2 from the off-gas using a calcium hydroxide scrubber (Fig. 3.1). The calcium hydroxide reacted with the CO , to produce calcium carbonate—the final ^{14}C waste form. The newer version of this process is to remove most of the graphite block before burning the fuel compact. This greatly reduces the quantities of off-gas to be processed and the calcium carbonate waste to dispose of.

After removal of the carbon by burning, the ash residue is a mixture of oxides similar to LWR fuel pellets—except for the SiC shards. Nitric acid is used to dissolve the fissile materials, fertile materials, and many of the fission products. The dissolved fertile, fissile, and fission products are processed by modified aqueous processing techniques, with the resultant HLW converted to HLW glass. The final composition of the HLW glass (Forsberg, 2002) may contain up to 28% waste oxides; however, typically the waste loading in HLW glass is about half this amount. The process also produces secondary waste streams including tritium, iodine, and krypton that must be packaged and properly disposed of.

The nitric acid does not dissolve everything. The undissolved residue consists of undissolved noble metal fission products and SiC hulls. The noble metal fission products include a number of long-lived radionuclides and generate significant decay heat. Because of the SiC, this is a significant-volume HLW stream. There are three potential options for its management.

- **Low-heat waste.** The radionuclides that generate most of the heat in this residue have half-lives of a few years. If this waste were stored for several decades, the resultant waste would have a relatively low rate of heat generation. While this waste stream will require geological disposal, it may be feasible to treat the waste in a manner similar to graphite (see Sect. 6.3.3).
- **Mix with HLW glass.** The primary component of HLW glass is silica (SiO_2). Oxidation of the SiC yields SiO_2 . If the SiC can be oxidized separately or within the glass melter, this silicon (in the form of silicon oxide) can be the primary component of the final HLW glass. This is a very attractive solution in terms of minimizing wastes. A contaminated radioactive waste replaces a required nonradioactive component of the HLW glass. However, it is unclear whether a practical method for SiC conversion can be developed. Under most conditions, SiC is an extremely inert ceramic that is known to be very difficult to oxidize at a reasonable rate.
- **HLW solid.** The residue can be consolidated into a monolithic waste form and treated as a type of HLW.

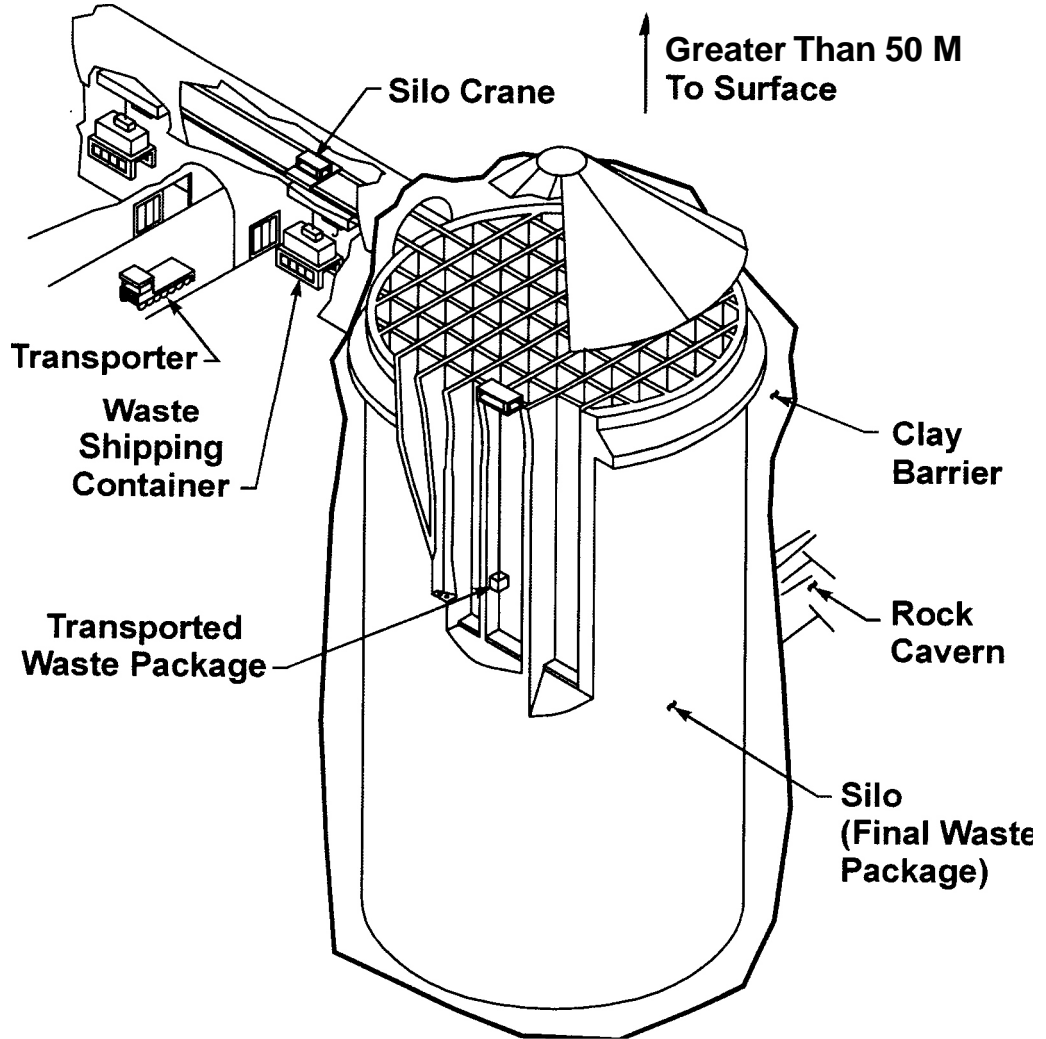


Fig. 6.2 Swedish SFR silo for intermediate wastes.

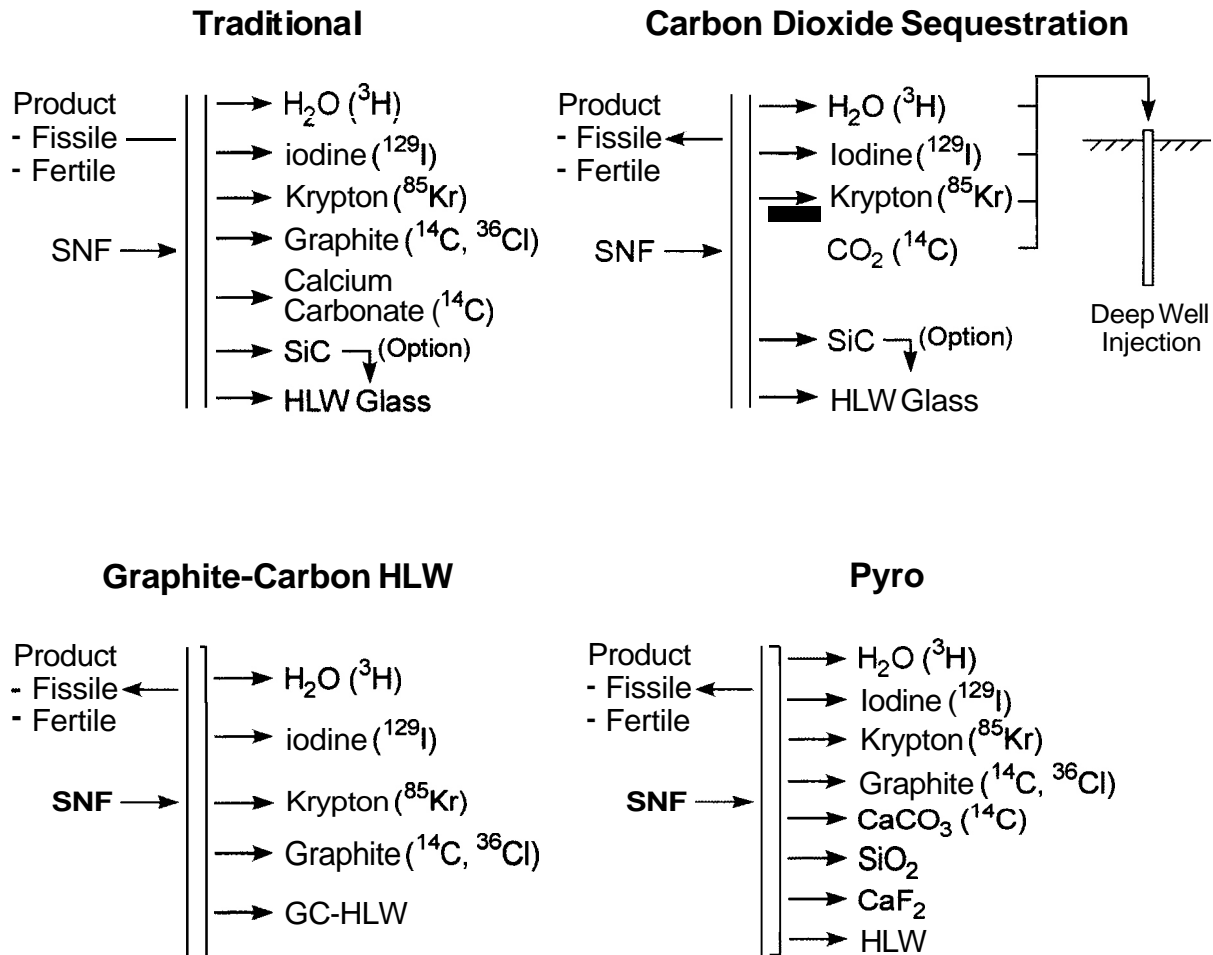


Fig. 6.3 Alternative waste products from different HTGR process options.

6.4.2 Carbon Dioxide Sequestration: Burn SNF Compacts and Sequester Carbon Dioxide and Other Volatile Radionuclides

The DF compacts can be burned with the volatile CO₂, tritium, krypton, and perhaps iodine injected into deep geological structures containing saturated brine (saltwater) solutions. The CO₂ and other components are dissolved in the brine groundwater. The existence of the brine groundwater implies that the geological stratum is isolated from fresh groundwater, which is typically above the brine water. There is no mixing between the two layers. The brine solution also ensures that the water will not be used for drinking or irrigation. This type of disposal may be equivalent to geological disposal of HLW glass in a traditional repository. Some fraction of the CO₂ will react with the rock and become a solid compound. This option is potentially a very low cost option that simultaneously minimizes risks by minimizing processing and handling.

This approach to CO₂ sequestration is the mainline approach for the geological sequestration of CO₂ from the combustion of fossil fuels. Carbon dioxide sequestration methods are being developed because of concerns about global warming from changes in the composition of the atmosphere caused by addition of CO₂. Carbon dioxide sequestration experiments and limited production operations (Kane and Klein, 2001) are under way in Europe, with the largest operations disposing of 20,000 metric tons per week. Current production operations are several orders of magnitude greater than the CO₂ releases from a large HTGR processing facility. If CO₂ sequestration is done on a large scale to limit atmospheric releases from fossil power plants, billions of tons will be sequestered per year.

If this method of CO₂ disposal from an HTGR processing facility is used, it is highly desirable to couple the injection of these gases with CO₂ sequestration from fossil power plants. Combining the *two* streams dilutes by many orders of magnitude the gases from the HTGR facility and provides a secondary safety factor (dilution) for disposal of selected radionuclides. There remain many technical and institutional questions with this strategy.

Except for treatment of volatile gases, the remainder of the process is identical to the traditional process as described in Sect. 6.3.1.1, with the same waste forms produced. If this disposal option for CO₂ is viable, there may be incentives to also burn the graphite block and sequester this CO₂.

6.4.3 Graphite-Carbon HLW: Crush SNF Compacts and Leach Selected Radionuclides with Nitric Acid

The third option (Fig. 6.4) is a new waste management option partly described earlier in this report. The fuel compacts are mechanically removed from the graphite block. The block, with its ¹⁴C, becomes a low-heat waste form for disposal in a repository. The compacts are crushed and leached in nitric acid. The nitric acid dissolves uranium, plutonium, higher actinides, and many fission products. This solution is sent to a processing plant for recovery of the fissile and fertile materials. The leaching process leaves a residue of graphite particles, SiC hulls, and noble metal fission products. The separations facility using aqueous separations processes produces an aqueous HLW stream consisting of nitric acid, the soluble fission products, and trace quantities of actinides. The dissolver residue and the aqueous HLW stream are mixed. Reagents are added to denitrate the slurry, with the subsequent precipitation of many fission products onto the dissolver residues. (Alternatively, the aqueous HLW stream is thermally denitrated with the resultant oxides mixed with the dissolver residue.) The aqueous slurry is fed to a heated extruder with an organic binding agent. The heated extruder evaporates the water and mixes the organic binding agent with the solids. The solid product is heated at temperatures from 800 to 1000°C to produce a final waste form. The heating process destroys the organic and produces a carbon-graphite waste form.

In this process, the graphite-carbon HLW form contains most of the radionuclides from the SNF. The other waste streams include the graphite SNF block and the gaseous waste streams (tritium, iodine, and krypton). A single waste treatment process and a single HLW form minimize the number of process steps and thus may minimize the total costs.

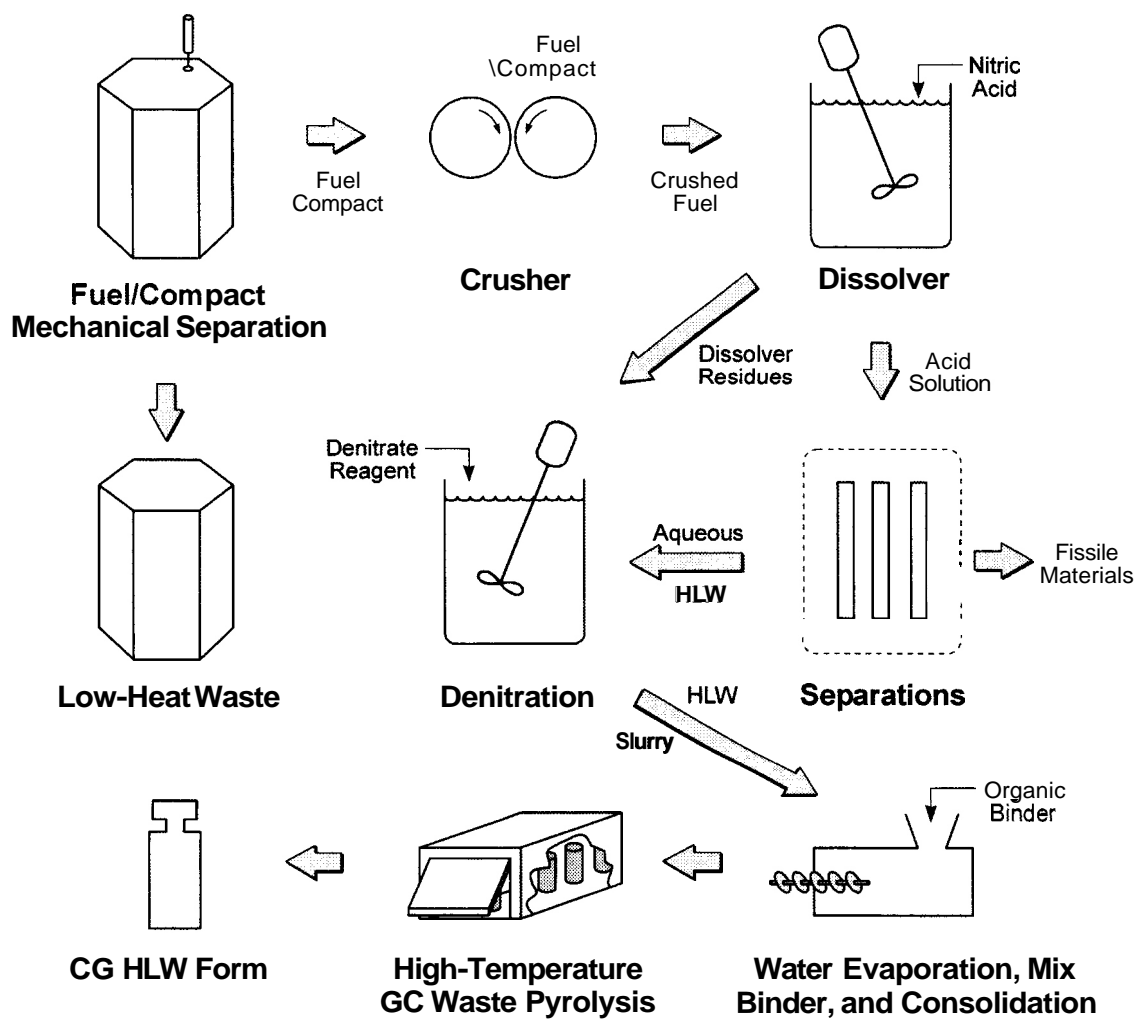


Fig. 6.4. HTGR processing to produce graphite-carbon HLW form.

6.4.3.1 Process status

Most of the process steps have been demonstrated; however, significant development is required.

- *Nitrate destruction.* Destruction of nitrate in nitric acid solutions by chemical methods is currently done in some SNF processing facilities. In this case, it would be expected that as the nitrate is destroyed, the radionuclides in solution would precipitate as oxides onto the solid graphite fines in the slurry.
- *Water evaporation and binding of the graphite.* The aqueous slurry would be mixed with an organic binder and fed to a screw extrusion system. The heated extrusion system would evaporate the water, mix the binder with the solids, and extrude solid HLW logs.

This technology has been used commercially to solidify a variety of radioactive liquid waste streams. At the LaHague SNF processing facility in France, the largest commercial facility of this type in the world, secondary high-activity liquid and slurry wastes were solidified by this process. Process improvements ultimately eliminated this particular waste stream, but the technology was used for many years on an industrial scale. For this application, it is desirable to minimize the quantity of binder to minimize the final waste volume and maximize waste form performance.

- *Carbonization.* The HLW logs would be baked at high temperatures to decompose the organic binder to produce amorphous carbon and graphite. This is a standard process to produce a variety of carbon products. The organics must be destroyed to avoid hydrogen generation in the repository from radiation and to avoid organics that can complex radionuclides and enhance migration from the waste form to the environment. The carbonization process is designed to reduce the long-term permeability of the waste form to air and groundwater.

Firing to higher temperatures produces a more graphitic product, but as the temperature increases, more cesium is volatilized, which must be captured by the off-gas system and recycled back to the solidification system. This is a major issue in HLW glass vitrification where the process operates at $-1\ 150^{\circ}\text{C}$ but would not be expected to be significant at the lower process temperatures.

6.4.3.2 Waste form performance

There are multiple requirements on the waste form, and the viability of the process depends upon producing an acceptable waste form.

The processing operations involve producing a solid, low-permeability waste form by addition of an organic binder and a carbonization cycle that decomposes the organic binder to amorphous carbon and graphite. This process generates an off-gas containing hydrogen and determines the thermodynamic state of each element in the final waste form. The thermodynamic chemical state of most of the fission products is similar to that found in SNF: the rare earths, cesium, and strontium will be oxides in their normal thermodynamically stable state. Any uranium will be in the form of uranium dioxide. The noble metal fission products will remain as noble metal fission products, as found in SNF or HLW glass. Some elements will change chemical form. Iron may be found in the metallic state rather than the oxidized form found in HLW glass.

The process will drive the neptunium and technetium to their lower valence states in the graphite-carbon HLW form. These two radionuclides control the long-term performance of the repository. Under chemically reducing conditions, their solubility in groundwater is minimized.

The fission products and any residual actinides would be in the carbon waste in at least three forms.

- **Particulates.** The noble metal fission products will remain unchanged and be particulates embedded within the carbon waste form.
- **Intercalated layers.** The graphite is a layered structure, where certain types of atoms are known to embed themselves between these layers. Any atoms between these layers of carbon will be extremely difficult to remove from the graphite. Some alkali metals (such as sodium) are known to migrate into these layers. There is the potential that some radionuclides such as cesium may go into these layers, but experiments will be required to quantify which radionuclides are trapped by this mechanism. Any radionuclide that is embedded between these layers should have outstanding waste isolation. Depending on the results of experiments, it may be desirable to condition the graphite fines to maximize the sorption of radionuclides within these layers.
- **Embedded fission products.** Many of the fission products, such as the rare earths, will have precipitated onto the carbon fines. They will be trapped within the graphite structure but not necessarily chemically bound to the graphite.

There are multiple potential mechanisms for waste form failure. Each must be considered individually.

- **Direct oxidation.** In an oxidizing environment such as the proposed YM repository, the carbon will oxidize over time. Measurements and analysis indicate that the time for significant graphite oxidation is on the timescale of hundreds of millions of years (Lotts et al., 1992). Gross oxidation attack on the graphite is not a significant mechanism of waste form degradation.
- **Mechanical breakup.** Mechanical breakup of the waste form will expose surface areas to leaching of radionuclides. One secondary oxidation mechanism could contribute to waste form breakup. If oxygen can diffuse into the waste form and high concentrations of uranium, iron, and certain other cations exist, then the cations can be oxidized to produce oxidized products with lower densities. The volume changes could assist waste form breakup.
- **Leaching.** If the waste form is permeable, selected radionuclides could be leached from the waste form by groundwater.

The above considerations suggest that the carbon waste form has the potential for excellent performance, provided that the permeability of the waste form to air or groundwater is minimized. Permeability can be minimized by the use of organic binders that are then carbonized to convert the organic to amorphous carbon. Significant research and development has been undertaken to develop graphite and carbon waste forms with very low permeability. Multiple graphite and carbon products have this property.

6.4.3.3 Waste loading

The fission product loading of the waste form is determined by the composition of the fuel compact. Based on several theoretical considerations (but no experimental work), the allowable waste loading may be considerably higher than that defined by combining these two waste streams. This may have important economic implications. The aqueous processing steps for LWR SNF and the HTGR SNF are similar. The potential exists to build a single processing facility with specialized front-end equipment for the two types of SNF. Under such a scenario, it may be feasible to use this waste form for disposal of both the HTGR and LWR SNF high-level wastes. A single HLW processing facility would process all HLW. This may result in minimization of total waste volumes while producing a very high-quality waste form.

Based on volume considerations (not considering the graphite block), the graphite-carbon HLW form would require about half as many waste packages as for LWR SNF per unit of energy output from the respective reactors. The current design basis for YM has an LWR SNF waste package with an internal volume of 7.3 m³ and a decay-heat limit of 11 kW. The design basis is a package containing 21 pressurized-water reactor (PWR) SNF assemblies (–1 0 metric tons initial heavy metal) with a typical burn-up of 30,000 MWd/tonne. In terms of energy, the waste package accepts the wastes from the production of 300,000 MWd of energy. For the proposed graphite-carbon HLW, the same waste package accepts the wastes from modular high-temperature gas-cooled reactors (MHTGRs) that produced –700,000 MWd of energy, assuming an average waste density of 2 g/cm³.

6.4.4 Pyrometallurgical: Crush SNF Compacts and Leach

A number of pyrometallurgical HTGR SNF processes have been proposed. These options are in a very early state of development. As with the other process options, there are strong incentives to reduce the material to be processed by separation of the fuel compacts from the graphite fuel block. The waste products will depend on the specific flow sheet. Figure 5.7 shows the likely waste products that are produced if the fuel is destroyed by using a fluorinating agent. While there are many process options, the likely waste forms can be identified: calcium carbonate for the carbon (¹⁴C), calcium fluoride for the fluorides, and silica (sand) for the silicon in the SiC. (Fluorination processes offer the advantage of being able to quickly attack SiC.) The requirements for low cost and waste form stability limit the number of practical waste forms. These three high-volume waste forms would be low-heat wastes. Some could be low-level waste—depending on the efficiency of the process for separating radioactive components from nonradioactive components in the off-gas system.

6.5 STORAGE, TRANSPORT, AND REPOSITORY CONSIDERATIONS FOR HLW

6.5.1 Repository Capacity

The HLW from the processing of HTGR DF—independent of the process used or the chemical form—is fundamentally different from traditional HLW. Traditional HLW generates decay heat from (1) cesium and strontium, with half-lives of –30 years, and (2) higher actinides. The most important actinide in terms of heat generation in traditional HLW is ²⁴¹Am, with a half-life of –470 years. In contrast, the processing of DF removes all the actinides. The only significant sources of decay heat are cesium and strontium, which decay away much faster than the actinides. This has potentially major implications in terms of waste management and repository capacity.

Temperatures in the repository must be limited to avoid waste form, waste container, tunnel, and rock degradation. The disposal drifts have a temperature limit to avoid excess stresses that can cause tunnel collapse. The rock has a temperature limit to prevent degradation of its capability to retard radionuclides and to avoid major changes in groundwater composition. Each component has a different temperature limit. To control temperature limits, the decay heat generated from each package is limited.

In a repository, the heat is conducted from the waste form, through the waste package, across various gaps to the tunnel wall, through the rock, and to the atmosphere. The heat conduction process is slow. It may take 1000 years for heat generated today to reach the earth's surface. As a consequence, both the instantaneous heat generation rate and the cumulative heat generation is important in determining repository temperatures. While the instantaneous heat generation rate from cesium and strontium in fresh waste is higher than from the actinides, after 100 years the actinides become the important source of heat. This has several implications (Croff, 1994; Forsberg, 2000a, 2000b, 2000c).

- **Repository capacity per unit of energy produced.** Integrated over time, the decay heat from the HTGR driver fuel HLW will be much less than that from traditional HLW—assuming that the original SNF in both cases produced the same total quantity of energy in the reactor. The HTGR driver fuel HLW contains almost no actinides. The total repository capacity will increase by a factor of 2 or more. This is independent of the volume of the HLW.
- **Ventilated repository.** The YM project is evaluating alternative repository designs. Among the leading design options is the concept of a ventilated repository, in which the repository is ventilated by natural circulation or fans for decades to a century or more. This effectively increases the repository capacity because a significant fraction of the decay heat from cesium and strontium is removed by ventilation. For SNF or conventional HLW, this provides some increase in repository capacity—but the benefit is limited because of the longer-lived actinides such as ²⁴¹Am. For the HTGR driver fuel HLW, a ventilated repository provides a major increase in repository capacity. Every 30 years, one-half of the existing repository capacity is returned to be reused because one-half of the decay heat has vanished. The same effect is obtained by storing the HTGR driver fuel for many decades before disposal to allow decay of cesium and strontium.

6.5.2 Waste Form Temperature Limits

Each waste form has a different temperature limit. If the temperature limit is exceeded, the waste form will degrade, which will, in turn, degrade its performance in the repository. The temperature limit for SNF is 350°C, to avoid clad degradation. The temperature limit for borosilicate HLW glass is 400°C, to avoid early devitrification of the glass. The temperature limit for a graphite waste form has not been defined but should be considerably higher than that for other waste forms, probably in excess of 600°C. This has several major implications.

- **HLW log size.** The size of an HLW log is determined by the waste heat-generation rate and temperature limit and by the thermal conductivity of the waste form. For example, current commercial HLW glass logs produced by the LaHague facility in France (Forsberg, 2002) are limited to a diameter of 43 cm to avoid overheating the center of the log. The maximum decay-heat output per glass log (height = 1.335 m) is 4 kW. The thermal conductivity of the proposed graphite-carbon HLW form is not known; however, the thermal conductivity of SiC is 20 times that of glass and the thermal conductivity of graphite is over 50 times that of glass. The higher thermal conductivity and higher temperature limits for a carbon waste form allow for larger HLW log sizes, reducing the number of HLW logs and associated handling costs in storage, transport, and disposal. Alternatively, the high-temperature capability allows processing of shorter-cooled SNF and HLW with much higher decay-heat loads.
- **Transport.** If the waste form can operate at higher temperatures, transport casks can accept more wastes without exceeding the temperature limits of the waste form.
- **Storage.** If a waste form can operate at a higher temperature, it is easier to reject heat to the environment. This allows the use of larger, lower-cost storage casks or other storage systems.

6.6 WASTE TREATMENT, TRANSPORT, AND DISPOSAL RECOMMENDATIONS

The waste management issues associated with the processing of HTGR SNF are very different than those for LWR SNF. The following areas have been identified as high-priority areas in terms of future research and development.

- *Graphite separations.* Major cost savings are possible if easy separation of the graphite blocks from the fuel compacts can be achieved. The viability of this option depends upon the design of the fuel. The options to ensure easy separation of the fuel block from the fuel compact need to be evaluated and understood.
- *Repository design.* Processing of HTGR driver fuel will generate two waste streams with properties that are significantly different from those of SNF or traditional HLW glass. **All** of the HTGR processing options are likely to generate large volumes of low-heat radioactive wastes: graphite or another waste form containing the ^{14}C . The HTGR driver fuel HLW is also fundamentally different. It generates high levels of decay heat; however, unlike traditional HLW with minor actinides, the decay heat is only from cesium and strontium. The decay heat decreases much more rapidly with time. Much larger quantities of each of these wastes per unit of energy generated in the reactor can be placed in a repository such as YM—if the repository design is modified to take advantage of their unique properties. Repository design options must be investigated simultaneously with the processing of HTGR driver fuel to minimize total system costs. The potential is to significantly lower disposal costs.
- *Graphite-carbon HLW forms.* Experimental work is required to confirm the viability of manufacturing carbon HLW forms. If the initial work indicates that the waste form is significantly better than alternative waste forms and relatively easy to manufacture, then the waste form should be considered for HLW streams from processing other **types** of SNF. If even a small fraction of the SNF that is processed is HTGR SNF, the graphite blocks would provide carbon as required.
- *Addition of SiC to HLW glass.* The backup waste form to the graphite-carbon HLW is the traditional HLW glass. The second-largest waste stream is SiC. A careful examination should be undertaken to determine if the silicon in this waste is that required for HLW glass. This would significantly reduce waste volumes.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The excellent performance characteristics of the TRISO-coated fuels make these type of fuels highly attractive for gas-cooled reactors that operate at high temperatures. The carbon and SiC coatings can withstand very high temperatures without sustaining damage, and their resistance to chemical attack in the environment makes them **an** excellent waste form for disposal of spent fuel. They are also an excellent option for recycle and transmutation because of their ability to achieve very high burn-ups. However, historically the spent TRISO-coated fuels are considered difficult to handle for the recovery of the fissile content.

Our present analysis has identified two very attractive and promising processing options that, if developed, will greatly simplify the recovery of fissile species from spent TRISO-coated fuels. Simple processing steps, waste minimization, economy of reagents, and the utilization of existing industrial-scale processes and equipment were very important considerations in the design and selection of both processing options. To achieve economy of scale, both options can be directly interfaced with LWR fuel processing plants. Selection of one of the options therefore depends on the type of LWR fuel processing plant that will be deployed.

One of the options produces a nitric acid solution that can be introduced into an aqueous-based separation scheme typified by existing industrial-scale PUREX-processing plants. The other produces a chloride salt that can be fed into pyroprocessing separation schemes, which are presently under active development.

Graphite-block fuel elements containing the TRISO-coated fuels are composed primarily of carbon, either as the graphite of the block or as the pyrolytic and amorphous carbon materials contained in the fuel compacts. The mass of the SiC shell is also greater than the mass of the fuel kernel. The graphite block represents the bulk of the carbon. The unused fissile material represents **-3.6%** of the mass of the compacts, and the combined carbon and SiC is **-87%** of the mass of the compacts (the remainder being fission products). To reduce the costs associated with processing these fuels, it is important to separate the carbon to the greatest extent practical without resorting to methods that chemically combine the carbon with other additives. In addition, the waste carbon may be reused to fabricate a waste form that has very desirable characteristics over geologic time periods.

7.2 RECOMMENDATIONS

It is recommended that methods for processing TRISO-coated fuels focus initially on the processing steps needed to place the fissile materials in aqueous solution. This permits the aqueous nitrate product from a custom head-end to be fed to the solvent extraction systems of a PUREX-based LWR spent fuel processing plant. Mechanical separation and nitric acid dissolution do not convert the carbon to other forms, thus keeping the carbon in the most compact. Mechanical separation is judged desirable for all processing schemes to reduce the production of carbon compounds having greater mass and volume than the original carbon. The mechanical head-end should therefore support either aqueous processing or pyroprocessing techniques. Nitric acid dissolution is expected to effectively solubilize the fuel and fission products (except the noble metals) and permit separation from the carbon fines. There is a risk that recovery will not be as **high** as desired. Washing of entrained nitrate solution from the wet carbon fines could be problematic, or the fines could sorb a portion of the product. Should dissolution become problematic, a fallback position is to resort to oxidation of the carbon, but only as small a quantity as is practical. In either case, a significant quantity of elemental carbon remains from the processing of the fuel. It is further recommended that a graphite-carbon HLW waste form be explored as a means not only to disposition the excess carbon but also to immobilize the fission product wastes arising from the processing of the spent fuel.

7.2.1 Key Elements That Need to Be Developed and Tested

The key elements, or unit operations, that need to be developed and tested are identified and described in this section. It is anticipated that demonstration at a meaningful scale implies equipment capable of processing the equivalent of 1 to 2 fuel elements per day, or about **22 to 44 kg** of compacts per day. Proof-of-principle experiments need not be **performed** at this scale; a smaller scale will suffice. However, purchased mechanical equipment at this scale could reduce overall costs by functioning for both initial scoping tests and demonstrations.

7.2.1.1 Crushing and milling

Size reduction and breaking the SiC shell are important to providing access for leaching of the spent fuel. A jaw crusher is recommended for breaking the compacts into sizes appropriate to feed a roller mill. The roller mill would then break the SiC shell and reduce the particle size. Further size reduction in a fluid-energy jet mill provides for rapid dissolution. These pieces of equipment should **(1)** be robust, providing long life with little or no maintenance; **(2)** be adaptable to remote operation; **(3)** support easy maintenance, repair, and replacement; and **(4)** be fitted with a containment and off-gas system for contamination control and trapping of volatile fission products.

7.2.1.2 Carbon-kernel separation

Separation of the finely divided carbon from the oxide fuel kernels simplifies the operation of the dissolution process. The lower the ratio of carbon to oxide fuel, the smaller and more reliable will be the dissolver. After crushing the density of the filler carbon is -1.9 g/cm^3 , compared with the coated particles, which have a density of -2.2 g/cm^3 . Mechanical separation could be difficult at this stage. However, after milling, the density of the carbon particles would be -2.0 g/cm^3 , compared with the oxide particles, which have a density of -11 g/cm^3 . The fluid-energy jet mill has an intrinsic capability to effect a degree of separation. This should be investigated as should other solid-solid separations methods.

7.2.1.3 Multistage leaching and dissolution of oxide particles

The leaching-dissolution process needs to be proven and demonstrated. Reagents need to be evaluated, particularly in regard to the need for adding either hydrofluoric acid or the use of an electrochemical dissolver. Operating parameters including solution recovery, carryover (by carbon and SiC sludges), stage efficiency, and overall efficiency need to be determined.

7.2.1.4 Solid-liquid separation

Solid-liquid separation is required to separate the dissolver (nitrate solution) from the carbon and SiC fines. A fabric belt filter may be applicable and could be integrated with the dissolver. Issues to be investigated include (1) adaptation to hot cell environment, (2) reliability and robustness of the system, (3) determination of need for filtering aids, (4) remote maintenance and parts replacement, (5) contamination control, and (6) requirements for moist off-gas control.

7.2.1.5 Carbon waste consolidation

Consolidation of the carbon waste into a durable form needs to be examined. Issues to be addressed include (1) drying, (2) type and quantity of binding agent per unit quantity of waste, (3) carbonization or sintering of the waste form, and (4) preliminary testing of the waste form to ascertain acceptability at the repository.

7.2.2 Approach

Testing and development on the key elements will be done using a phased approach. Initial tests will be conducted using cold surrogates to simulate the properties of the actual fuel compacts that are important to the particular step to be developed. For example, processing aspects related to grinding and milling will be initially tested using compacts made from quartz, glass or alumina spheres in place of actual TRISO particles. Further tests will be done using compacts having surrogate TRISO-coated particles (e.g., kernels made with ZrO_2 , HfO_2 , UO_2 , etc.). Solid-solid and solid-liquid separation and dissolution will be initially tested using appropriate mixtures of carbon, pyrocarbon, porous carbon, SiC, and metal oxides of the expected particle sizes and composition. As development progresses and TRISO-fuel compacts become available, final testing will be done using actual fuel compacts.

To test and develop the proposed processing options in the most efficient and economical way, it is proposed to establish a collaboration with relevant industrial partners to adapt existing industrial-scale processes and equipment and to fully utilize the experience gained during previous studies.

7.2.3 Collaboration with Industrial Partners

As previously indicated, the processing of TRISO fuel implies handling relatively large amounts of carbon in order to recover a small amount of fissile material. Accordingly, the need for the industrial

expertise related to carbon processing is self-evident. After a search of possible industrial partners, a very promising contact was established with the R&D group of GrafTech International, Ltd. (formerly Union Carbide Carbon Company). Through a couple of conference calls and a visit to their research and industrial facilities located near Cleveland, Ohio, it was established that GrafTech has significant experience directly related to the processing of TRISO-coated fuel, including (1) carbon technology and nuclear-grade-graphite manufacturing; (2) crushing and milling; (3) acid leaching; (4) filtering of fine-carbon slurries; and (5) binding, compacting, and shaping of carbon forms. At present, a formal collaboration agreement is being negotiated in support of the R&D efforts. It is also proposed to extend this collaboration toward the goal of building a pilot plant.

General Atomics is recognized as the industrial leader in the field of HTGRs and TRISO-coated fuels. Accordingly, maintaining a close collaboration with GA is essential. At present, this collaboration is based on a direct participation of GA in the development of HTGRs and TRISO-coated fuels for DOE. In addition, W. S. Rickmann (formerly with GA and coauthor of this report) is providing his expertise to the present R&D studies based on his significant current and past involvement with HTGRs and TRISO-coated fuels.

It appears that interest in HTGRs and TRISO-coated fuels is also shared by other countries such as France. As agreements develop, a significant international collaboration may also be established.

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