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High Temperature Gas-cooled Reactor (HTGR) Graphite Pebble Fuel: Review of Technologies for Reprocessing

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EXECUTIVE SUMMARY

This report reviews literature on reprocessing high temperature gas-cooled reactor graphite fuel components. A basic review of the various fuel components used in the pebble bed type reactors is provided along with a survey of synthesis methods for the fabrication of the fuel components. Several disposal options are considered for the graphite pebble fuel elements including the storage of intact pebbles, volume reduction by separating the graphite from fuel kernels, and complete processing of the pebbles for waste storage. Existing methods for graphite removal are presented and generally consist of mechanical separation techniques such as crushing and grinding and chemical techniques through the use of acid digestion and oxidation. Potential methods for reprocessing the graphite pebbles include improvements to existing methods and novel technologies that have not previously been investigated for nuclear graphite waste applications. The best overall method will be dependent on the desired final waste form and needs to factor in the technical efficiency, political concerns, cost, and implementation.

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LIST OF ABBREVIATIONS

AVR	Arbeitsgemeinschaft Versuchsreaktor: a prototype pebble bed reactor at Julich Research Center
BISO	bi-isotropic: coating for fuel particles with two different isotropic layers
CEA	Alternative Energies and Atomic Energy Commission in France
EPA	Environmental Protection Agency
FWHM	Full Width at Half Max
HEU	Highly Enriched Uranium
HLW	High Level Waste
HTGR	High Temperature Gas cooled Reactors
HTTR	High Temperature Test Reactor
HV	High Voltage
IPyC	Inner Pyrolytic Carbon layer
JUPITER	Juelich Pilot plant for Thorium Element Reprocessing
LEU	Low Enriched Uranium
LIBS	Laser Induced Breakdown Spectroscopy
LLW	Low Level Waste
M	Molar: mol/L
MW	Microwave
N	Normal: equivalent concentration of H+ or OH-
OPyC	Outer Pyrolytic Carbon layer
ORNL	Oak Ridge National Laboratory
PBR	Pebble Bed Reactor
PNNL	Pacific Northwest National Laboratory
PWR	Pressurized Water Reactor
PyC	Pyrolytic Carbon
RAPHAEL	ReActor for Process heat Hydrogen And ELectricity
RF	Radio Frequency
SCDEH	South Carolina Department of Health and Environmental Control
SRNL	Savannah River National Laboratoy
SRS	Savannah River Site
THTR-300	Thorium Hochtemperaturreaktor 300
TRISO	Tri-Isotropic: coating for fuel particles with three separate isotropic layers
VHTR	Very High Temperature Reactor

1.0 Introduction

This review investigates the processing of graphite-based nuclear fuel generated during the development of high temperature gas cooled reactors (HTGR) by the Federal Republic of Germany. The pebbles were rigorously designed to be mechanically robust fuel containers that are capable of withstanding extremely harsh environments. It is this durability that has proven difficult in the past for the end-of-service processing of the fuel elements into a stable waste form for storage in a repository. However, since only 3% of the pebble is fuel related waste, there are significant gains to be had by volumetric reduction of the waste. This literature review will primarily focus on the removal of the graphite matrix and kernel coatings. Other concerns and technologies will be briefly addressed.

2.0 Background

Since the first sustained nuclear reaction in the Chicago Pile-1, graphite has been used in a variety of nuclear applications. Graphite continues to be used for its high density for enhanced moderation, high irradiation stability, high thermal conductivity, high strength, high oxidation resistance, low coefficient of thermal expansion, and low elastic modulus. High purity graphite is required to be free of neutron absorbing materials such as boron. These properties make graphite useful for reactor components and incorporation into fuel components. The concept for HTGRs was first proposed by Farrington Daniels in 1942 at Oak Ridge National Laboratory. (BK McDowell, 2011) The basis of the reactor allows for much higher operating temperatures resulting in increased efficiencies. The encapsulation of the nuclear fuel in graphite provides several enhanced safety measures. The graphite matrix acts as a moderator, enhances heat transfer from the kernel surface to the pebble surface, exhibits high mechanical strength for resisting external forces, is resistant to corrosive attack from impurities and coolant, and has high dimensional stability during irradiation with fast neutrons. (H. Nickel, 2002) (A.W. Mehner, 1990) Two avenues of graphite encapsulated fuel progressed: the U.S. developed prismatic based reactors where the fuel is in a cylinder contained within a large graphite block with cooling channels, and Germany along with several other countries pursued pebble based reactors where the fuel is dispersed through a spherical graphite matrix and with large quantities stacked in the reactor with cooling gas flowing between the pebbles.

2.1 Reactors

Several test reactors have been built since the 1960s by several countries including Germany, the U.K., France, Belgium, the U.S., Russia, India, Japan, China, South Africa, and the Republic of Korea for the testing of various fuel component designs. (Karl Verfondern, 2007) Germany (Federal Republic of Germany during the research and development stage) designed and built two test reactors that utilized graphite-fuel composites of the pebble form. The Arbeitsgemeinschaft Versuchsreaktor (AVR) operated from 1967 to 1988, and the Thorium Hochtemperaturreaktor 300 (THTR-300) operated from 1985 to 1991. A simple schematic of a pebble bed reactor is given in Figure 2-1.

While the reactors tested a large number of different fuel configurations, all of the fuel components were incased in very similar graphite pebbles. The pebbles are an existing nuclear waste concern for Germany. This, combined with a resurgence of interest and research into pebble bed reactors, creates a need and opportunity for improving the lifecycle of nuclear graphite to further the advancement of nuclear power.

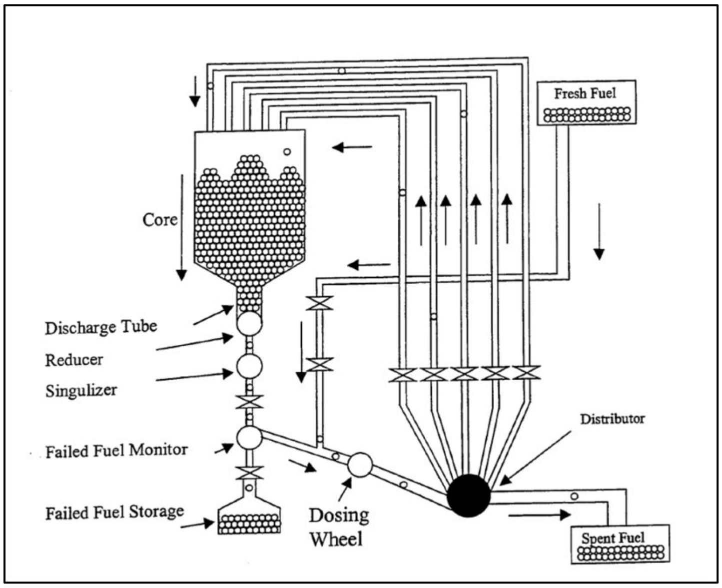


Figure 2-1: Simple pebble bed reactor (PBR) schematic adapted from Ref (Owen, 1999).

2.2 Fuel Components Materials & Properties

The pebbles are graphite spherical fuel elements 60 mm in diameter with individually coated fuel particles dispersed through the 50 mm diameter core, leaving a 5 mm thick outer graphite shell. (L. Wolf, 1975) The spherical coated fuel particles or kernels are 400-780 µm in diameter, depending on the fuel type, with approximately 10,000-20,000 kernels per pebble. (Andreas Wilden) (Heinz Nabielek, 1984) A diagram of the fuel pebble components is shown in Figure 2-2.

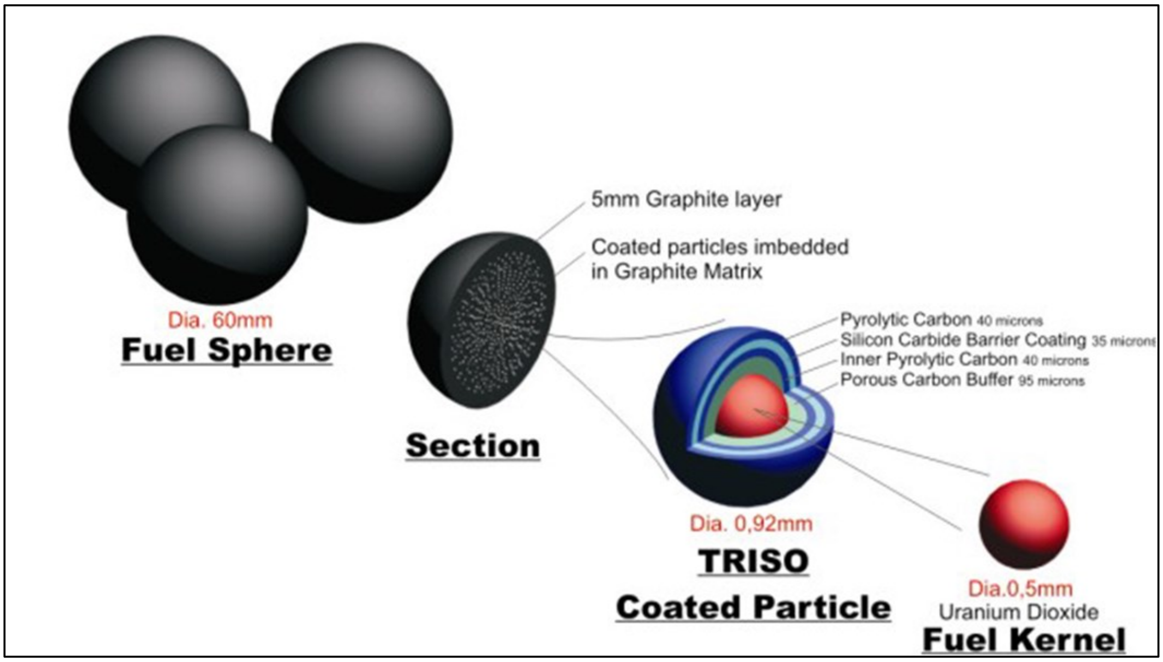


Figure 2-2: Schematic of spherical fuel pebble components provided by Robert A. Pierce.

A total of three kernel variations were used in the German HTGR pebbles: laminar, bi-isotropic (BISO) and tri-isotropic (TRISO) configurations shown in Figure 2-3, although the last two types comprise the majority of the fuel. The laminar design consists of a single pyrolytic carbon layer that was deposited using conditions that produced extremely anisotropic material and properties that had a laminar appearance under polarized light microscopy. While this kernel configuration was initially used in the U.S. Peach Bottom, U.K. Dragon, and German AVR reactors, it was quickly abandoned after fission recoil damage was observed that caused early failure and release of fission products. (Stansfield, 1991) This complication led to the development of the BISO kernel coating system with the nomenclature based on the two types of isotropic layers surrounding the central fuel kernel. The BISO kernel has a center fuel particle of 400-500 µm in diameter. This fuel particle is then coated in a low density isotropic pyrolytic carbon layer, ~85 µm in thickness, which is designed to allow for absorption of fission products and swelling for protection of the outer layers from recoil damage. Finally, a dense outer layer of isotropic pyrolytic carbon ~75 µm thick is deposited as a containment layer for the fission products. High density pyrolytic carbon is polycrystalline with each crystallite having anisotropic properties with an isotropic crystallite orientation. (Karl Verfondern, 2007) While the BISO kernel variation retains strong oxide-forming fission products, the BISO coating does not retain metallic fission products effectively at high temperature and still allows for the diffusional release of metallic fission products such as cesium, strontium, and silver at elevated temperatures. This complication led to the addition of a SiC layer that better retains the metallic fission products with the exception of Ag. (Stansfield, 1991) (H. Nickel, 2002) This and the desired stability at higher temperatures (>950 °C) was obtained with development of the TRISO kernel coating system. The nomenclature for this kernel variant is from the three types of isotropic layers even though it has a total of four separate layers. The TRISO coating starts with a fuel particle coated with the BISO variant of a low density PyC layer and high density PyC layer. This particle is then coated with a SiC layer ~25 µm thick that is followed by another ~35 µm layer of dense pyrolytic carbon. (L. Wolf, 1975) TRISO kernels, as compared to BISO kernels, offer improved retention of silver and cesium under normal operating conditions. (A.W. Mehner, 1990)

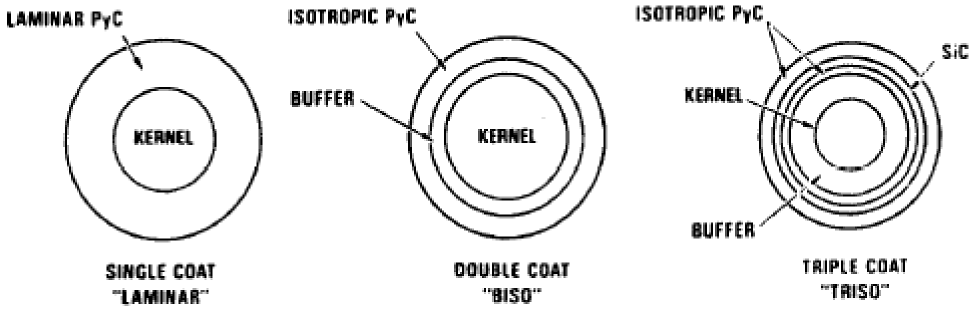


Fig. 3-1. The evolution of coated particle design took place by adding new materials and coating layers.

Figure 2-3: Diagram of Laminar, BISO, and TRISO coatings from Ref (Stansfield, 1991)

Table 2-1 provides a brief description of the composition and function of each of the BISO and TRISO kernel layers.

Table 2-1. Composition and Function of BISO and TRISO Kernel Layers [2]

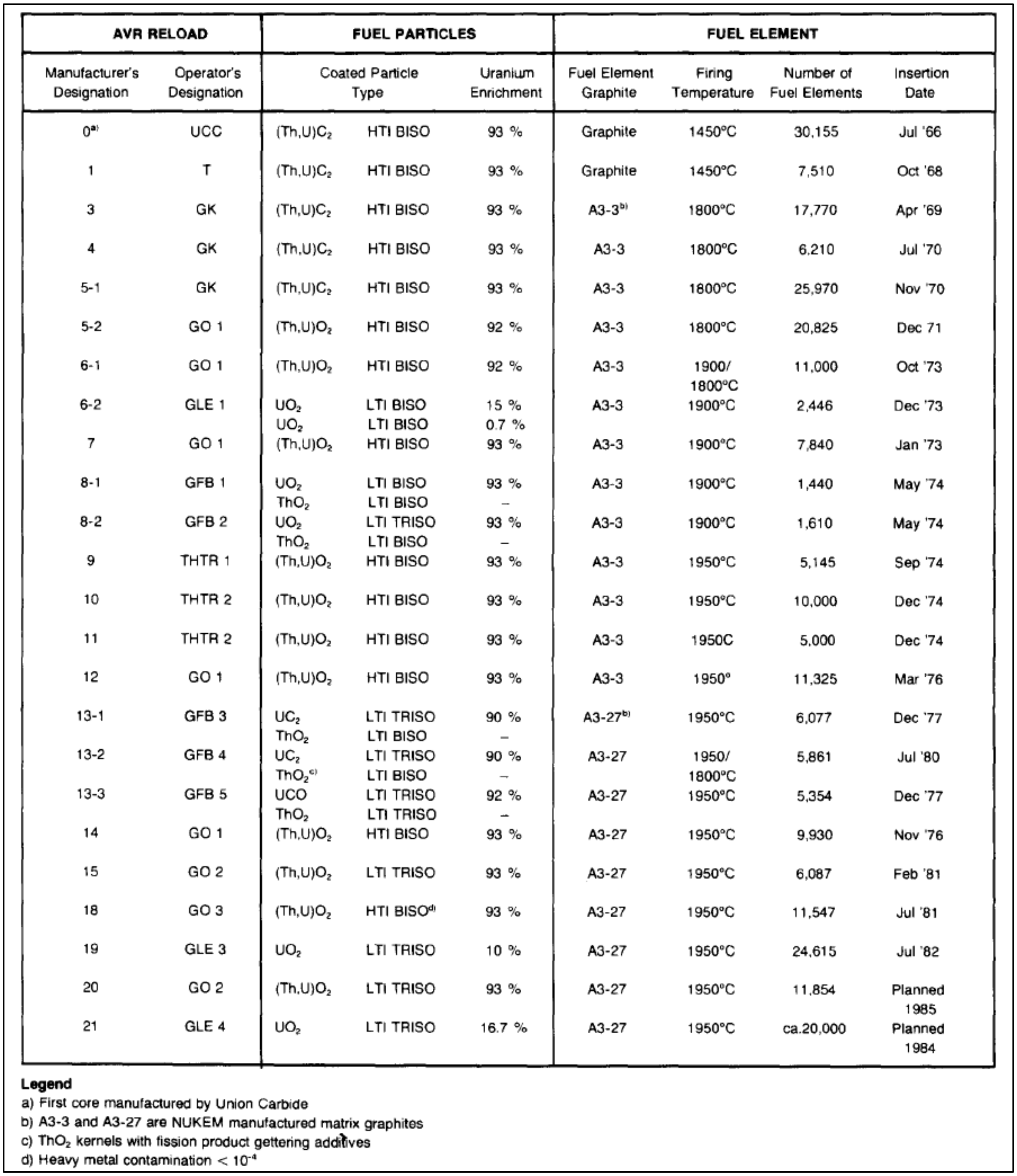
Layer	Composition	Function
First	Low density pyrocarbon	Sacrificial void volume for fission products
Second	High density pyrocarbon	Gas-tight; diffusion barrier for metallic fission products; protect kernel from Cl_2; reduce tensile stress on SiC layer
Third	High density SiC	Pressure retaining layer; primary metallic fission product diffusion barrier
Fourth	Outer high density pyrocarbon	Final diffusion barrier; protection for brittle SiC during fabrication; bonding surface for overcoat

The HTGRs in the Federal Republic of Germany used a mixed Th/U oxide fuel enriched to 93% up to 1981 before switching to a low enriched uranium fuel of 10% enriched uranium. (Andreas Wilden) The fuel elements were developed by the NUKEM/HOBEG Company and tested together with the HRB Company and the KFA Julick. (Owen, 1999) The THTR-300 reactor only used BISO fuel particles, while the AVR reactor used a mix of BISO and TRISO particles. (Andreas Wilden)

Since temperatures in excess of 1,800 °C are required for the fuel fabrication of the pebbles, oxide kernels were used, instead of carbide fuels, for more completely retaining U and Th and minimizing fuel dispersion during the fabrication heat treatments. (Stansfield, 1991) While the majority of German fuel particles were oxide kernels, over 5,000 fuel pebbles with highly enriched uranium (HEU) uranium oxycarbide (UCO) were loaded into the AVR in 1977. (Stansfield, 1991)

A representative inventory of AVR fuel elements manufactured by NUKEM/HOBEG is given in Table 2-2 and exact inventory of AVR and THTR can be obtained through collaboration partners. More than 290,000 pebbles of 5 different types and 15 variants (carbide/oxide, BISO/TRISO, HEU/LEU (low-enriched fuel)) containing >6 billion kernels and 80,000 graphite moderator pebbles were used in the AVR. Most pebbles were recycled several times and starting with reload charge 3 the shells were changed from machined graphite to pressed graphite matrix. [4] It is clear that with such a diverse inventory, which might not be segregated, special consideration is needed to develop a reprocessing technique that can be administered indiscriminately against the entire inventory and not just tailored to a certain kernel variety.

Table 2-2: AVR reload inventory from Ref. (Heinz Nabielek, 1984)



AVR RELOAD		FUEL PARTICLES			FUEL ELEMENT			
Manufacturer's Designation	Operator's Designation	Coated Particle Type		Uranium Enrichment	Fuel Element Graphite	Firing Temperature	Number of Fuel Elements	Insertion Date
0[a)]	UCC	$(Th,U)C_2$	HTI BISO	93 %	Graphite	1450°C	30,155	Jul '66
1	T	$(Th,U)C_2$	HTI BISO	93 %	Graphite	1450°C	7,510	Oct '68
3	GK	$(Th,U)C_2$	HTI BISO	93 %	A3-3[b)]	1800°C	17,770	Apr '69
4	GK	$(Th,U)C_2$	HTI BISO	93 %	A3-3	1800°C	6,210	Jul '70
5-1	GK	$(Th,U)C_2$	HTI BISO	93 %	A3-3	1800°C	25,970	Nov '70
5-2	GO 1	$(Th,U)O_2$	HTI BISO	92 %	A3-3	1800°C	20,825	Dec 71
6-1	GO 1	$(Th,U)O_2$	HTI BISO	92 %	A3-3	1900/ 1800°C	11,000	Oct '73
6-2	GLE 1	UO_2 UO_2	LTI BISO LTI BISO	15 % 0.7 %	A3-3	1900°C	2,446	Dec '73
7	GO 1	$(Th,U)O_2$	HTI BISO	93 %	A3-3	1900°C	7,840	Jan '73
8-1	GFB 1	UO_2 ThO_2	LTI BISO LTI BISO	93 % –	A3-3	1900°C	1,440	May '74
8-2	GFB 2	UO_2 ThO_2	LTI TRISO LTI BISO	93 % –	A3-3	1900°C	1,610	May '74
9	THTR 1	$(Th,U)O_2$	HTI BISO	93 %	A3-3	1950°C	5,145	Sep '74
10	THTR 2	$(Th,U)O_2$	HTI BISO	93 %	A3-3	1950°C	10,000	Dec '74
11	THTR 2	$(Th,U)O_2$	HTI BISO	93 %	A3-3	1950C	5,000	Dec '74
12	GO 1	$(Th,U)O_2$	HTI BISO	93 %	A3-3	1950°	11,325	Mar '76
13-1	GFB 3	UC_2 ThO_2	LTI TRISO LTI BISO	90 % –	A3-27[b)]	1950°C	6,077	Dec '77
13-2	GFB 4	UC_2 ThO_2[c)]	LTI TRISO LTI BISO	90 % –	A3-27	1950/ 1800°C	5,861	Jul '80
13-3	GFB 5	UCO ThO_2	LTI TRISO LTI TRISO	92 % –	A3-27	1950°C	5,354	Dec '77
14	GO 1	$(Th,U)O_2$	HTI BISO	93 %	A3-27	1950°C	9,930	Nov '76
15	GO 2	$(Th,U)O_2$	LTI TRISO	93 %	A3-27	1950°C	6,087	Feb '81
18	GO 3	$(Th,U)O_2$	HTI BISO[d)]	93 %	A3-27	1950°C	11,547	Jul '81
19	GLE 3	UO_2	LTI TRISO	10 %	A3-27	1950°C	24,615	Jul '82
20	GO 2	$(Th,U)O_2$	LTI TRISO	93 %	A3-27	1950°C	11,854	Planned 1985
21	GLE 4	UO_2	LTI TRISO	16.7 %	A3-27	1950°C	ca.20,000	Planned 1984

Legend

a) First core manufactured by Union Carbide

b) A3-3 and A3-27 are NUKEM manufactured matrix graphites

c) ThO_2 kernels with fission product gettering additives

d) Heavy metal contamination $< 10^{-4}$

3.0 Fuel Element Synthesis & Fabrication

As a large variety of graphite fuels have been produced, this review will primarily focus on German fuel production for the HTGR program. Note there are variations in dimensions and other characteristics of the kernels given the large variety contained in the inventory; therefore, approximations will be made for the purposes of this review.

3.1 Pebble Fabrication

The spherical fuel elements are a pressed from a mixture of 75% natural flake graphite, 15% petroleum coke, and 10% phenolic resin. This mixture is kneaded together with the resin, dissolved in methanol, and then dried and milled. At this stage some of the mixture is used as an overcoat for the kernels that are then mixed into the matrix. The graphite fuel matrix, designated A3, is poured into a mold and immediately mixed before being pressed at 300 kg/cm^2 to insure homogeneous dispersal of the kernels. This fuel core is then placed in a second mold, coated with additional matrix, and then pressed under near isostatic conditions to 3,000 kg/cm^2. The pressed core is then slowly heated to 800-900 °C under an inert atmosphere to crack the resin before being fired under vacuum at 1,800-1,950 °C. The pebble is then machined to a final diameter of 60 mm. (L. Wolf, 1975) Typical data or working assumptions for fuel elements: (L. Wolf, 1975)

- Matrix density = 1.70 g/cm^3
- Kernel size: AVR = 780 um & THTR = 400 um
- Heavy metal content AVR = 6 g/ball & THTR = 11 g/ball
- Particle volume loading factor: AVR = 5% & THTR = 9%.

3.2 Kernel Synthesis and Fabrication

With the numerous kernel variations used in the AVR and THTR it is not practical to list every synthesis method. A representative method is provided here as an example.

The initial mixed-oxide fuel particles for the THTR were made using the ‘solution process’. (L. Wolf, 1975) However, the ‘well known’ gel precipitation method was referenced (Advances in High Temperature Gas Cooled Reactor Fuel Technology, 2012) for the AVR and THTR-300 fuel components also referenced as in UO_2 kernel manufactured using the external gelation process. (Karl Verfondern, 2007) This method started with U_3O_8 powder dissolved in nitric acid forming a uranyl nitrate solution and pre-neutralized with ammonium hydroxide just prior to precipitation. (Karl Verfondern, 2007)

$$3U_3O_8(s) + 20HNO_3(aq) \longrightarrow 9UO_2(NO_3)_2(aq) + 10H_2O + 2NO(g)$$
$$2UO_2(NO_3)_2(aq) + NH_4OH(aq) \longrightarrow 2UO_2(NO_3)_{1.5}(OH)_{0.5}(aq) + NH_4NO_3(aq)$$

Polyvinyl alcohol (PVA) is added to a U-Th nitrate solution and then dripped through an ammonia solution forming the microspheres that were then washed in isopropanol. The microspheres were dried and sintered in H_2 at ~1,600 °C. The BISO fuel elements were coated with low density (~1.1 g/cm^3) porous carbon buffer and an outer higher density (~1.8 g/cm^3) pyrolytic carbon layer. The TRISO elements add a SiC layer at ≥ 3.2 g/cm^3 and a final high density compression pyrolytic carbon layer. All the layers are deposited in pyrolytic fluidized beds. (Advances in High Temperature Gas Cooled Reactor Fuel Technology, 2012) The inner buffer layer is deposited through the decomposition of acetylene (C_2H_2) at 1,400 °C and the dense carbon layer is deposited from methane (CH_4) at 1,900-2,000 °C or from acetylene, propylene/propene (C_3H_6) or propane (C_3H_8) at 1,400 °C. (L. Wolf, 1975) The SiC layer uses a process that “is similar to that applied by all countries engaged in the HTGR” and involves the decomposition of methyltrichlorosilane (CH_3SiCl_3) with hydrogen as the fluidizing gas. The particles then have an overcoat of matrix powder applied in a large rotating drum. (Karl Verfondern, 2007) (L. Wolf, 1975) (Advances in High Temperature Gas Cooled Reactor Fuel Technology, 2012)

TRISO particles characterized by NUKEM GmbH can be approximated by a Gaussian distribution centered at 0.92 mm with a full-width at half-max (FWHM) of 0.074 mm. (P.R. Hania, 2012) X-ray computed tomography of 31 pebbles produced in the 1980s for the German HTGR program (samples were from GLE-4 from an AVR reloading batch and HFR-K5/6 final proof test samples for MODUL-type reactors) was analyzed for kernel distribution with an example of the distribution given in Figure 3-1. The number of kernels observed was slightly lower ~2.4% than the average or expected value. There were some areas of low kernel density and the kernel loaded matrix center of mass is slightly off-center with respect to the pebble center of mass. The nearest neighbor distances for the kernels were determined to be ~1.125 mm. (P.R. Hania, 2012) This was a concern as TRISO particles that are closely spaced have a strong chance of 'hard contact' or direct particle-to-particle contact during the pressing stage of the pebble fabrication, (P.R. Hania, 2012) (H. Nabielek, 1990) which could lead to the failure of the kernel shell and possible release of material.

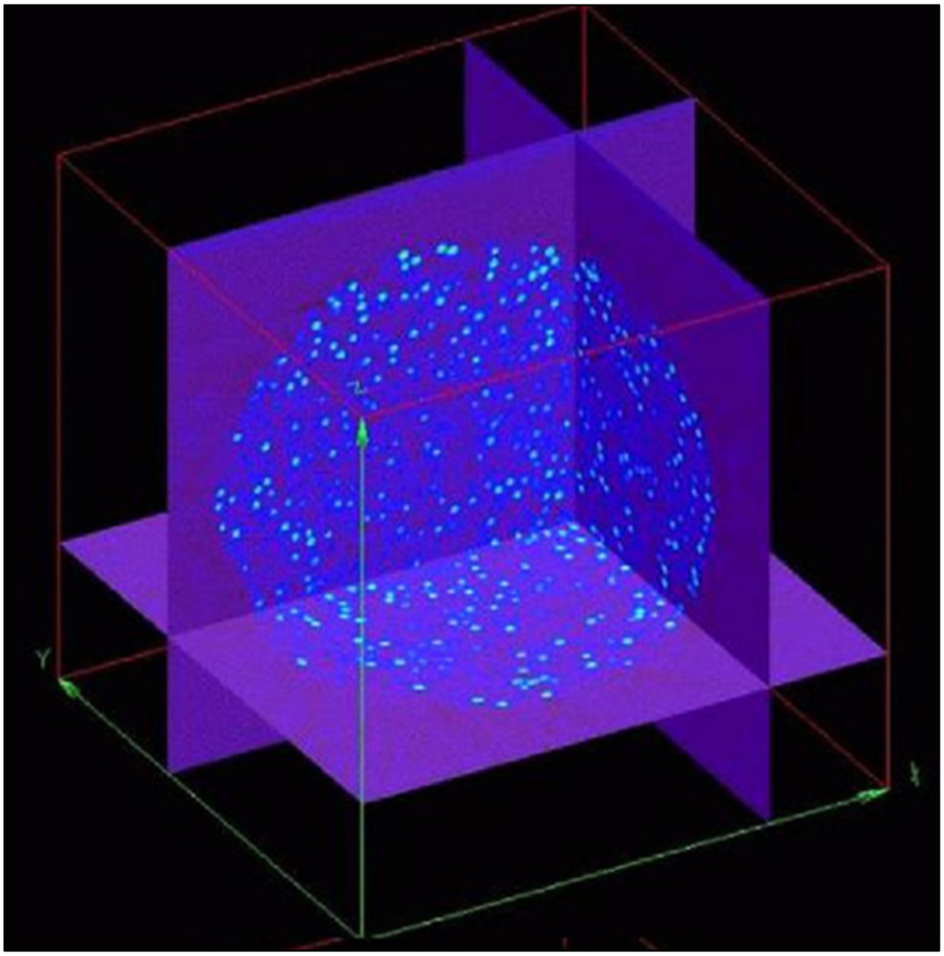


Figure 3-1: CT image of kernel distribution in AVR pebble from Ref (P.R. Hania, 2012).

There are some similarities and differences between the U.S. and German fuel elements aside from prismatic or pebble configuration related to fabrication methods. The U.S. and FRG had an exposed heavy metal fraction contamination in the fuel compacts and SiC defect fraction of $\leq 6x10^{-5}$. (Stansfield, 1991) Also, the average defect fraction of $3.9x10^{-5}$ was noted by Ref (Karl Verfondern, 2007). The German fabrication of TRISO particles was on an industrial production scale using strict process control. Incorporation of fuel production improvements resulted in only $\sim 10^2$ defects found in $3.3x10^6$ kernels.

Additionally, the three main TRISO layers were coated in a continuous manner in the German process, whereas the U.S. process was interrupted between each layer with quality control measurements. (D.A. Petti, 2003) The high rate of coating deposition, 4-6 µm/min used by the Germans compared to 1-4 µm/min from U.S. methods generated a very isotropic pyrocarbon that is more radiation resistant but also has somewhat more surface porosity for the inner pyrocarbon layer of the kernel. The inner layer interface of pyrocarbon/SiC is more tightly bonded in the German fuel than in the U.S. fuel because the SiC is deposited into the pyrocarbon as a result of the higher surface porosity shown in Figure 3-2. The debonding of this layer is believed to be related to the strength of the bond along the interface and as such the 'German fuel never exhibits debonding under irradiation.' (D.A. Petti, 2003)

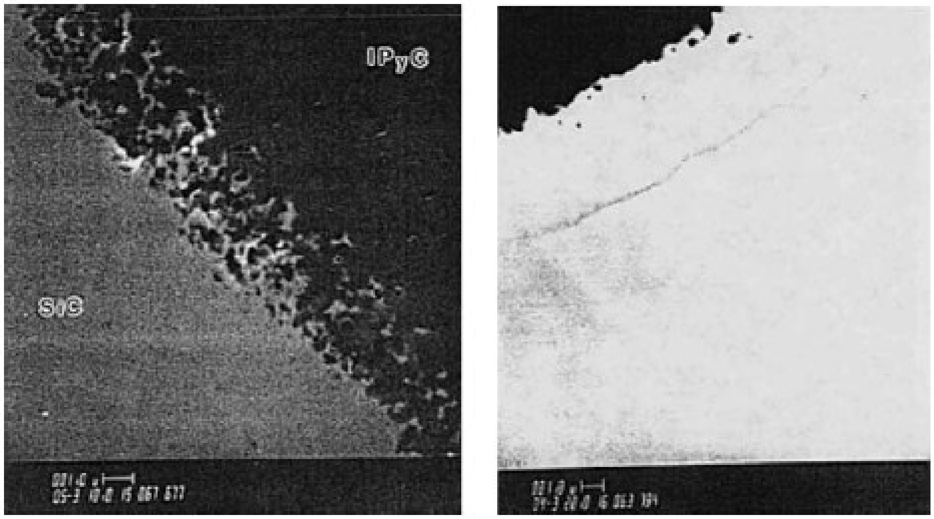


Figure 3-2: IPyC/SiC interface comparison, German (left) and U.S. (right). "The difference in contrast in the two pictures is associated with lighting techniques used in the examination" Notice the interface demarcation. From Ref (D.A. Petti, 2003) that referenced "Saurwein and Schilling, 1993" (General Atomics Doc. No. 910647).

The SiC microstructure for German fuel is small equiaxed grains, compared to the US large columnar thru-wall grains from hotter deposition conditions, and is primarily a function of process temperature and is shown in Figure 3-3. With smaller grains and higher tortuosity the SiC layer 'should in principle retain metallic fission products better than the large thru-wall columnar U.S. SiC with more direct grain boundary pathways through the layer' and experimental data suggest that microstructure has a role in the Ag release. Additionally, diffusivity of cesium through columnar SiC is an order of magnitude higher than that through laminar SiC. (D.A. Petti, 2003)

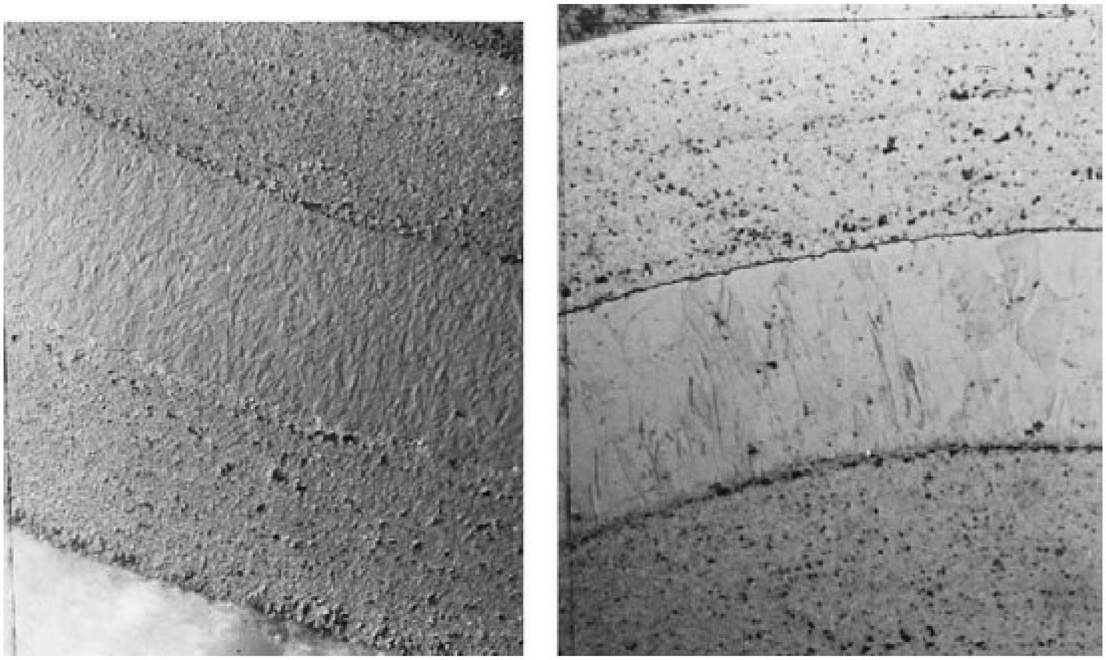


Figure 3-3: SiC microstructure comparison, German (left) and US (right). From Ref [9] that referenced "Saurwein and Schilling, 1993" (General Atomics Doc. No. 910647).

3.3 Failure Mechanisms

Several failure mechanisms of the kernels are possible and are of concern for graphite and fuel reprocessing as fuel element failures would affect the radionuclide distribution, structure, and morphology, and generate other concerns.

Pressure vessel (kernel coating) failure can be caused by internal gas pressure buildup from the release of fission gases and excess oxygen released from UO_2 ('rare earth and other fission products tie up about 1.6 atoms of oxygen per fission, leaving an excess of 0.4 atoms') that reacts with the buffer forming CO into the porous buffer layer exerting tensile forces on the IPyC and SiC layers. Given the quality of IPyC and SiC layers in the German fuel, "no indications of pressure vessel failure were observed in the German irradiations". (D.A. Petti, 2003)

Irradiation causes PyC to shrink in both radial and tangential directions, after an initial swelling in the radial direction. With strongly bonded PyC/SiC the shrinkage generates a strong compressive stress in the SiC layer offsetting the deposited tensile stress. If there is a high enough tangential stress in the PyC it can cause cracking through the PyC layer and stress concentrations in the SiC layer causing failure of the SiC layer as well. (Karl Verfondern, 2007) (D.A. Petti, 2003) "Post irradiation examination of German fuel did not reveal any shrinkage cracks in the IPyC layer," unlike many U.S. fuel irradiations. (D.A. Petti, 2003)

Dimensional changes observed in irradiated AVR fuel elements measured over years of testing from fast neutron fluence (up to $5x10^{21}$ cm^{-2}) resulted in a decrease in pebble diameter of <1.0 mm even with abrasion and corrosion under normal operation. There was no significant change in crushing strength. (A.W. Mehner, 1990)

Kernel migration, or amoeba effect, is the ‘movement of the kernel in the coated particle toward the TRISO coating,’ and with excessive migration the kernel can penetrate the TRISO leading to failure. The migration of a kernel is associated with the transport of carbon down a temperature gradient and the movement of the kernel up the gradient. As this process is strongly dependent on temperature and gradient, fuels with a higher power density, prismatic, have a greater propensity for kernel migration, whereas lower density fuels, pebbles, do not. As such, kernel migration (D.A. Petti, 2003) (Karl Verfondern, 2007) “has not been observed in German irradiation experiments or in AVR and THTR operation due to low power densities and the lack of a sufficiently steep thermal gradient”. (D.A. Petti, 2003)

The transport of fission products to the SiC layer can cause damaging interaction and potential failure. With UO_2 kernels, palladium is a very important concern as well as some noble metal fission products. While not a failure mechanism, the transport of Ag through intact particles could be an issue for reprocessing the fuel elements as it can deposit on cold surfaces. Again, German fuel has not been observed to have evidence of chemical reaction between fission products and SiC layers after irradiation experiments. The switch from HEU to LEU might have an unintended consequence of increasing the amount of Ag and Pd as the yields are 25-50 times higher for Pu than U. (Karl Verfondern, 2007) (D.A. Petti, 2003) Another report states that the inventory of ^{110}Ag in LEU is 10 times higher than that in HEU. [3]

Fission product Pd reacts with SiC forming palladium silicide locally or forming nodules. The reaction can be presented as:

$$2Pd + SiC \longrightarrow Pd_2Si + C$$

The reaction was observed to have expanded or progressed in both the radial and circumferential directions and the corrosion rate was mainly dependent on temperature. The reaction proceeds through four steps as depicted in Figure 3-4: 1) Pd birth, 2) release from kernel, 3) diffusion through PyC, 4) reaction with SiC with the rate limiting action being step 2, as steps 3 and 4 are fast. (Kazuo Minato, 1990)

Research from the Japan Atomic Energy Research Institute (JAERI) for the High Temperature Test Reactor (HTTR) measured the interaction distance of Pd-SiC to be dependent on cubic root of Pd release. A maximum penetration depth of 11 μm, less than SiC layer thickness, was calculated for the expected lifetime of the fuel. While the relative mass of SiC is much greater that the mass of Pd generated in the kernels, the reactions are highly localized and complete penetration of SiC layer through “worm holes” is possible under high burnup conditions or extended high temperatures and could form additional pathways for the release of fission products from the kernel. Similar to Ag, Pd can be formed at a rate of 25-50 times more in high burnup LEU fuels than either high burnup HEU fuel or low burnup LEU. (X.W. Zhou, 2011)

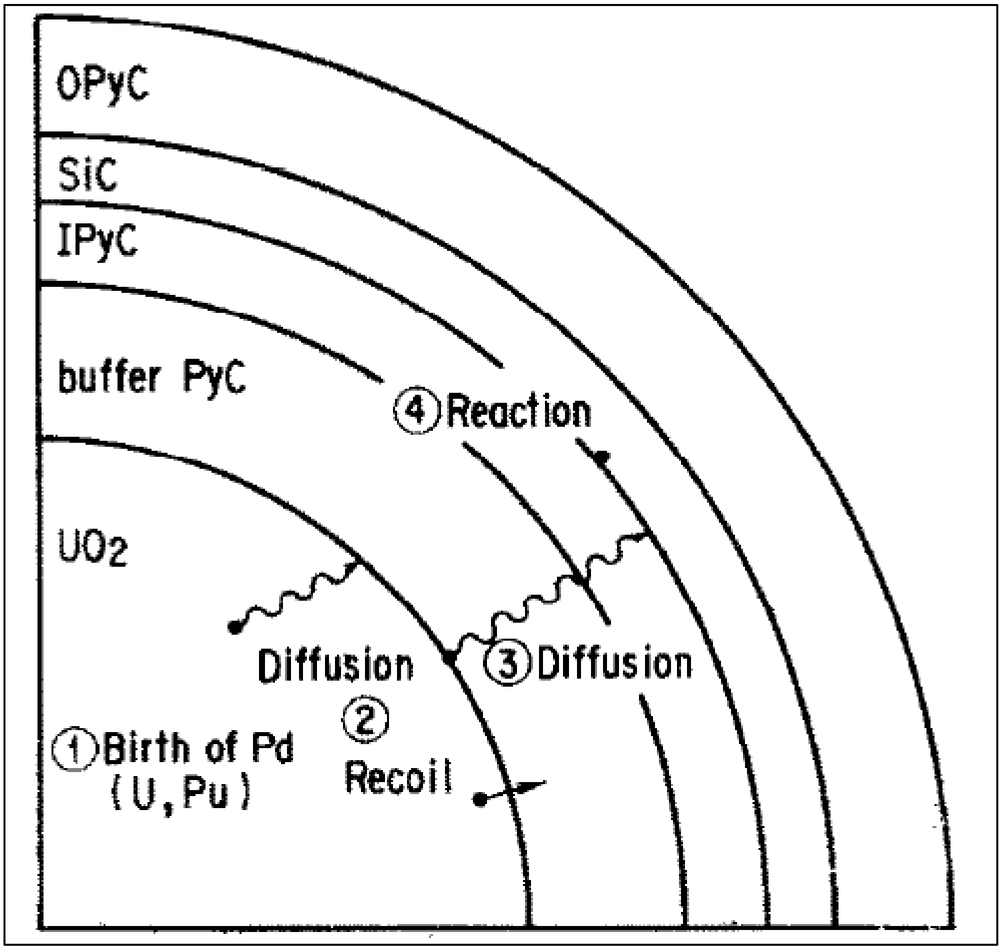


Figure 3-4: Pd-SiC corrosion schematic representation from Ref (Kazuo Minato, 1990)

Other mechanisms for kernel failure include the compromise of the SiC layer if the inner PyC layer is permeable or cracked and allows CO generated by the irradiation of UO_2 to react with the SiC forming SiO. (Karl Verfondern, 2007) Also, failure of the OPyC can occur through the result of intrusion of liquid matrix material during fabrication by the U.S. methods, whereas German manufacture used powder based matrix fabrication techniques and kernels made by that method have not exhibited this failure mechanism. Additionally, the final soft over coating layer reduces 'out of roundness' and limits stresses from particle-to-particle contact during manufacture of the pebbles. (D.A. Petti, 2003) At temperatures >2,000 °C SiC undergoes thermal decomposition. (D.A. Petti, 2003)

4.0 Options for Disposal of AVR & THTR-300 Pebbles

While the final decision regarding reprocessing of the graphite-based composite fuels will include substantial influence from political, environmental, and local sentiments, there are several technical options that exist for the disposal of the pebbles:

- Storage of intact pebbles
- Volume reduction
- Complete processing

The first option is as simple as described: storing the pebbles in the current condition in casks or other suitable containers. The second option of volume reduction includes the removal of the graphite matrix component of the pebble and then either the storage of intact BISO or TRISO kernels or an additional process for removing the kernel claddings and storage of intact fuel particles. The final option of complete processing encompasses the removal of graphite matrix and processing of fuel material for either repurposing or repository level storage. There are several considerations and methods for each option that include but are certainly not limited to processing cost, feasibility, generated waste, waste release, transportation, risks, stability of storage, storage volume, and cost of storage. A composite image is given in Figure 4-1 showing AVR spent fuel management in Hot Cells at FZJ and AVR canister storage with storage in CASTOR casks.

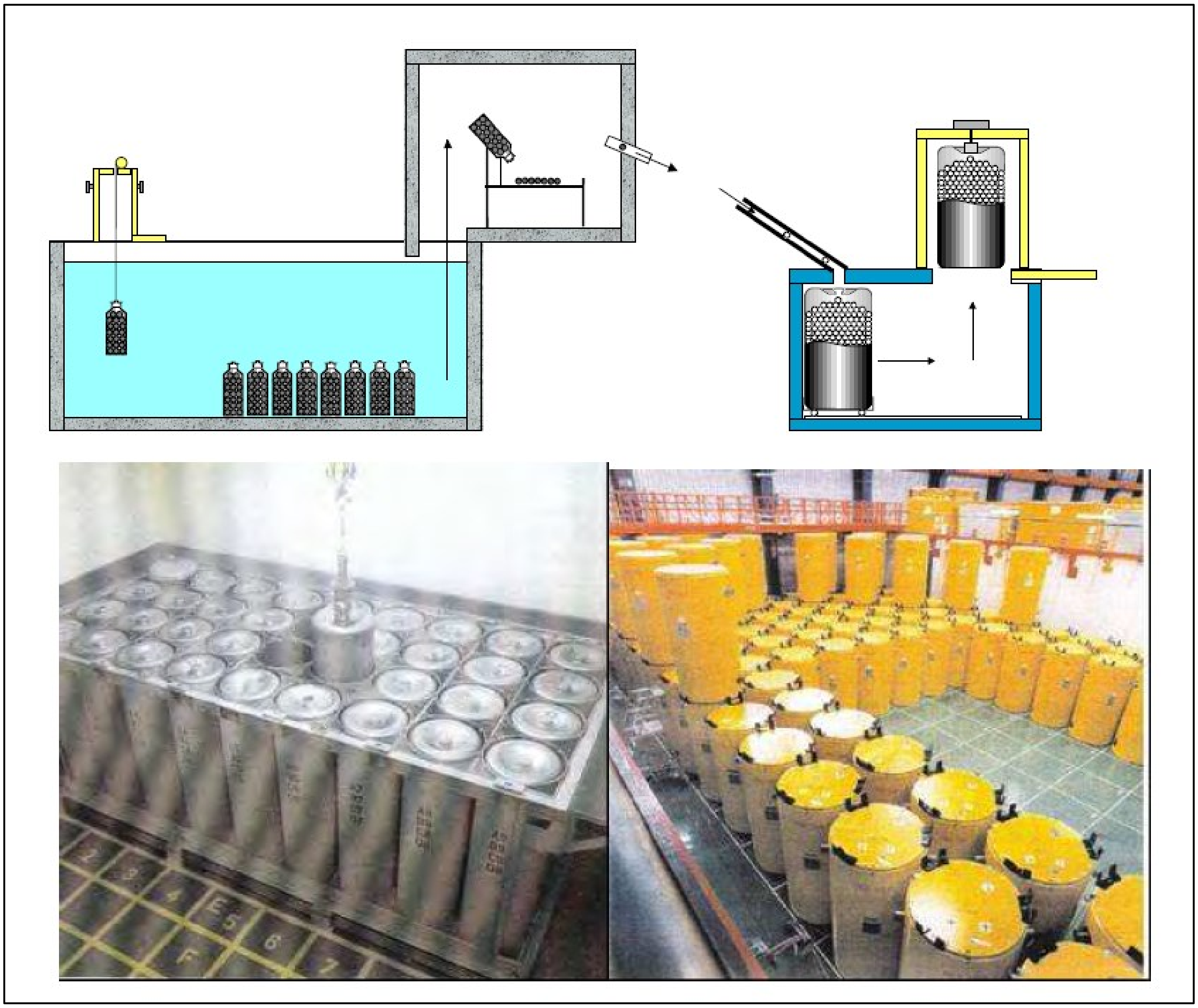


Figure 4-1: "AVR spent fuel management in Hot Cells at FZJ (top) AVR canister storage (bottom left), storage in CASTOR casks (bottom right)" from Ref (K. Verfondern, 2007)

4.1 Storage of Intact Pebbles

In terms of complexity this is by far the simplest option. The vast majority of radionuclides are contained within the kernels that are encased in the pebbles. This would have the lowest risk and probability of release from handling and processing events. If the current casks are no longer useable then the pebbles could be transferred to another container system either as free pebbles or encased in foam or cement and stored at a secure facility. Reference (A.L. Lotts, 1992) reviews in detail the following considerations for graphite matrix fuel storage:

1) Regulations on allowable release rates for radionuclides
2) Regulations on organics
3) Regulations on combustibility of waste
4) Regulations covering repository acceptance criteria

One major limiting technical concern is the large storage volume and limited storage space, and associated costs. This option likely has the highest inherent non-proliferation measures due to the large volume of material, the difficulty associated with extracting useful materials, and the inclusion of thoriated pebbles. Basic volume calculations are given in Table 4-1 for the pebbles and (Pressurized Water Reactor)PWR 21 canister dimensions are given in Table 4-2.

Table 4-1: Volumetric calculations for pebble inventory.

1.00E+06	Total number of pebbles
3	Pebble radius (cm)
113.1	Pebble vol. (cc)
1.13E+08	Total pebble vol. (cc)
113.1	Total pebble vol. (m^3)
188.5	Total vol. (m^3) at 60% packing factor

Table 4-2: PWR 21 canister dimensions

533.5	Outer Length (cm)
165	Outer Diameter (cm)
506.5	Inner length (cm)
141.0	Inner diameter (cm)
7.91E6	Inner vol. (cc)

As of Progress Report #16, Yucca Mountain thermal loading criteria are that a fully loaded spent fuel canister (PWR 21 waste canister: outer length = 5.34 m, diameter = 1.65 m) cannot exceed 18 kW, resulting in a range of 80-100 metric tons of uranium per acre. For comparison a 112 MWe PBR has a larger expected waste volume generation rate of 29 m^3/yr as compared to a 1000 MWe PWR of only 10 m^3/yr, but has a lower waste package loading of 0.194 kW/m^3 to 4.538 kW/m^3 and a lower fission product waste loading of 5.8 kg/m^3 to 136.1 kg/m^3. As a result, even though the PBR generates 2.9 times more waste volume, the waste has lower activity and heat generation and can therefore have a higher packing density in a repository. With 100% packing factor, 69,929 pebbles can fit in one PWR 21 canister. With a 60% packing factor for closest packing 41,957 pebbles would fit. Theoretically 800,000 pebbles could be loaded into a container and remain under the heat constraints. For equivalent reactor outputs of 1,000 MWe, a PBR would require 1.33 acres as compared to 10.06 acres for a PWR, or 5.3 m^2/MWe compared to 40.7 m^2/MWe. (Owen, 1999) If canisters are specifically designed for pebble storage taking advantage of the inherent stability of graphite there could be significant gains packing density compared to existing canisters. At ambient conditions it would take an estimated 1E9 years to oxidize through the outer 5 mm layer compared to hundreds or thousands of years for failure of Zircaloy cladding and the corrosion of metallic canisters associated with a PWR. Similarly graphite has superior leach rates when compared to other storage materials as tabulated in Table 4-3

Table 4-3: Leach rates of waste matrix materials from (Owen, 1999) that reference: Gray W.J., "A study of the Oxidation of Graphite in Liquid Water for Radioactive Storage Applications," Radioactive Waste Management and the Nuclear Fuel Cycle, Volume 3, Number 2, pages 137-149, 1982.

Material	Leach Rate (g/cm^2-day)	
	250 °C	99 °C
Synroc	$4x10^{-5}$	$6x10^{-6}$
Waste Glass	$8x10^{-3}$	$4x10^{-4}$
Al_2O_3	$4x10^{-5}$	$2x10^{-6}$
ZrO_2	$6x10^{-5}$	$6x10^{-5}$
Graphite	$1x10^{-8}$	$3x10^{-10}$

For additional details a Master's thesis from MIT by Paul Owen, "Waste Characteristics of Spent Nuclear Fuel from a Pebble Bed Reactor," goes through several calculations of storing PBR fuel in greater depth. (Owen, 1999)

4.2 Storage of Intact Fuel Kernels

With the limitations of the intact pebble storage option, at least an initial volumetric reduction needs to be considered. This option carries moderate risk for release of radionuclides during processing as some level is contained throughout the graphite matrix. In addition to the physical removal and handling of pebbles which could be done remotely, the kernels would need to be separated from the bulk graphite matrix. The separation method could be mechanical, chemical, or a hybrid method. Each of these methods would include problems, the first two including: complex machinery, dust generation, and production of large volumes of hazardous waste streams. The most commonly researched topics for the removal of the graphite matrix are mechanical crushing and oxidation through burning, fluidized beds, or salt dissolution. Volumetric reduction could arguably offer the largest benefit related to storage through removing 97% of the waste volume and only requiring the incorporation of the remaining 3% volume into repository level storage systems. Basic calculations are given in Table 4-4 Depending on the separation method, the graphite matrix could be stored in a low level waste system or exhausted and completely eliminated from storage concerns. This method would carry the concern of proliferation as the fuel elements would be in an isolated form.

Table 4-4: Basic calculations for the storage volume of isolated kernels.

1.00E+06	Total number of pebbles
3	Pebble radius (cm)
113.1	Pebble vol. (cc)
1.13E+08	Total pebble vol. (cc)
94	Graphite vol. %
6.79E+06	Fuel vol. (cc)
6.79	Fuel vol. (m^3)
11.3	Fuel vol. (m^3) at 60% packing factor

4.3 Reprocess Entire Fuel Element

This option likely offers the most favored end result of the fuel; however, it is the most complex, carries the most risk, the highest waste generated, and highest radionuclide release rates. After the removal of the graphite matrix the additional removal of the two carbon layers for BISO kernels would be required. The TRISO kernel processing would require the outer carbon layer to be removed followed by cracking or removing the SiC layer and finally (similar to the BISO) removal of the inner carbon layers. The additional processing adds to the complexity and with higher complexity would come higher risk of failure or incidents. As more fuel components will be processed, invariably more waste will be generated that will have to be processed, stored, or remediated. The fuel kernels have the highest amount of fuel and fission products and by removing the protective kernel layers and dismantling the fuel particles, these radionuclides will be released into the processing system.

4.4 Disposal concerns

4.4.1 Carbon-14

One of the main processing concerns with the removal of the graphite matrix is presence of ^{14}C. The issue regarding ^{14}C depends on the method chosen for processing the graphite matrix. If the graphite is retained in solid form then the concern falls under normal storage methods and regulations for radionuclide release and leaching. If the graphite is processed with an oxidation method then the CO_2 must be exhausted or sequestered since there is currently no effective method for removing only $^{14}CO_2$. (G.D. DelCul, 2002) If a molten salt digestion or halogen volatilization method is used there remains a large volume of ^{14}C concentrated waste.

The distribution of ^{14}C in pebbles is inhomogeneous. There are low levels that are more or less homogeneous throughout pebble due to the carbon and oxygen reactions. The majority of the ^{14}C contained in the pebble is mostly inhomogeneous in distribution and has higher concentration at the edge or surface of the pebble in the outer 5 mm due to air/N_2 infiltration and the resulting nitrogen reaction as shown by the precursor cross section and isotopic abundance in Table 4-5. The reactions for ^{14}C production from Ref: (Smith, 2014) are:

$$^{14}N + n \longrightarrow {}^{14}C + p$$
$$^{13}C + n \longrightarrow {}^{14}C + \gamma$$
$$^{17}O + n \longrightarrow {}^{14}C + \alpha$$

Table 4-5: Properties of ^{14}C precursors (Smith, 2014)

Species	Capture cross section (Barns)	Isotopic abundance (%)
^{14}N	1.8	99.63 (^{14}N:N)
^{13}C	0.0015	1.07 (^{13}C:C)
^{17}O	0.235	0.04 (^{17}O:O)

The Idaho State University has produced research on the characterization of ^{14}C in nuclear graphite. (Smith, 2014) (Dunzik-Gougar, 2014) (Tara E. Smith, 2013) As the primary production of ^{14}C is the nitrogen neutron capture and as graphite naturally adsorbs air during manufacturing and fuel handling the highest concentration of ^{14}C is in the first 5 mm of the graphite surface.

Table 4-6: Nuclide inventory of AVR graphite (Johannes Fachinger, 2008)

Specie	Specific Activity (Bq/g)
^{3}H	884,000
^{14}C	95,000

^{137}Cs	1940
^{154}Eu	560
^{60}Co	27,000

Mechanisms for removal of ^{14}C from a CO/CO_2 stream are dependent on the distribution and level of graphite removal required. Adjusting the graphite separation processing is a possible solution so that the first 5 mm of the pebble are controllably removed and only those products are addressed for ^{14}C storage or exhaust. If CO_x sequestration is required, solutions could be adapted or modified from conventional 'green' CO/CO_2 removal techniques.

Cryogenic isotopic separation of ^{14}CO, $^{14}CO_2$, or $^{14}CH_4$ is one option. Ontario Hydro in Canada obtained a patent for the removal of $^{14}CO_2$ from an isotopically mixed waste stream. The gas is chilled to create dry ice that is then volatilized providing a substantially pure carbon dioxide gas. This is reduced to carbon monoxide that is liquefied and separated with fractional distillation. The ^{14}CO is oxidized and absorbed onto a metal hydroxide forming carbonate salt. (Francis H. Chang, 1994)

Another isotopic separation method is possible through plasma chemical reactions in a CO glow discharge that form a ^{14}C enriched carbon film on the plasma reactor walls. (Shinsuke Mori, 2006) This occurs due to the "disproportionation reaction of vibrationally excited CO molecules:

$$CO(v) + CO(w) \longrightarrow C + CO_2$$

This occurs as heavier isotopic CO molecules are preferentially excited due to the vibration-to-vibration (V-V) energy exchange among the vibrational states of the molecular gases."(more references available)

A research group at Idaho State University used highly porous graphite foam, POCOFoam®, for ^{14}C studies; however, the intent was for high surface area for nitrogen adsorption to produce more ^{14}C during irradiation testing and not as an analogous structure representation. (Tara E. Smith, 2013) (Dunzik-Gougar, 2014) It might be possible to identify a graphite or foam density that would be indicative of irradiated graphite for use during testing of reprocessing methods.

4.4.2 Radionuclides: presence, release, storage

C-14 has been addressed specifically above, there is a broad range of other radionuclides that must be considered for reprocessing of the entire fuel element and it is not practical to review them all here.

5.0 Existing Methods for Volume Reduction of Irradiated Graphite Fuel Components

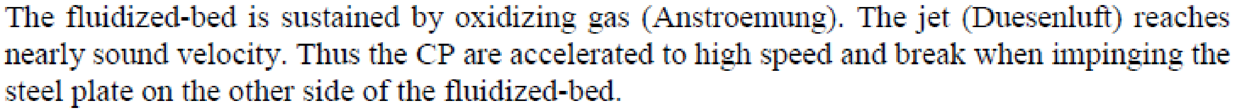
5.1 <u>Background</u>

Graphite matrix fuels have been used since the 1960s for a variety of projects in addition to significant amounts of graphite that have been used as moderators, reflectors and other reactor components. As such, there has been a substantial amount of research conducted on the remediation of irradiated graphite for two main purposes. In all graphite waste programs the volume reduction is a major factor as storage of Low-Level Waste (LLW) or High-Level Waste (HLW) can be space limited and costly. The other main consideration is the removal of the graphite in matrix type fuels for the reprocessing of the fuel components. There are two main methods for graphite removal: mechanical and chemical. The mechanical methods can include grinding, crushing, and fragmentation. The chemical methods can include oxidation, acid digestions, molten salt digestion, and halogen volatilization.

Multiple pathways exist for processing pebbles: Stepwise involving multiple methods for the removal of matrix graphite, separate/isolate the kernels, remove kernel cladding, and process fuel particles. Single or continuous methods can complete separation and processing in a single step or with a single method.

5.2 Mechanical Methods

The Juelich Pilot plant for Thorium Element Reprocessing, JUPITER plant, was developed in 1970 to investigate several methods for the separation of graphite from the fuel elements as depicted in Figure 5-1. (Lensa, 2008) At JUPITER the graphite moderator and carbon fuel coatings were removed by a process using a hammer mill to fragment the pebble into suitable size particles for fluidized-bed burning with oxygen at 800-850 °C. Fine particulate matter is recycled and off-gas passed through packed-bed absorbers. The fuel elements were treated in a Thorex-reagent HNO_3/HF solution followed by extraction with TBP/n-Dodecane producing U/Th nitrate solution. Several methods were investigated for the required additional separation for the SiC layer in the TRISO kernels. Two gas based processes included the *jet stream* method, Figure 5-2, which injects compressed air into a fluidized bed of kernels that are accelerated and impinge against a plate, thus cracking the SiC layer. The particle break rate is dependent of the cross-section and pressure of the jet and distance to impact plate.



The fluidized-bed is sustained by oxidizing gas (Anstroemung). The jet (Duesenluft) reaches nearly sound velocity. Thus the CP are accelerated to high speed and break when impinging the steel plate on the other side of the fluidized-bed.

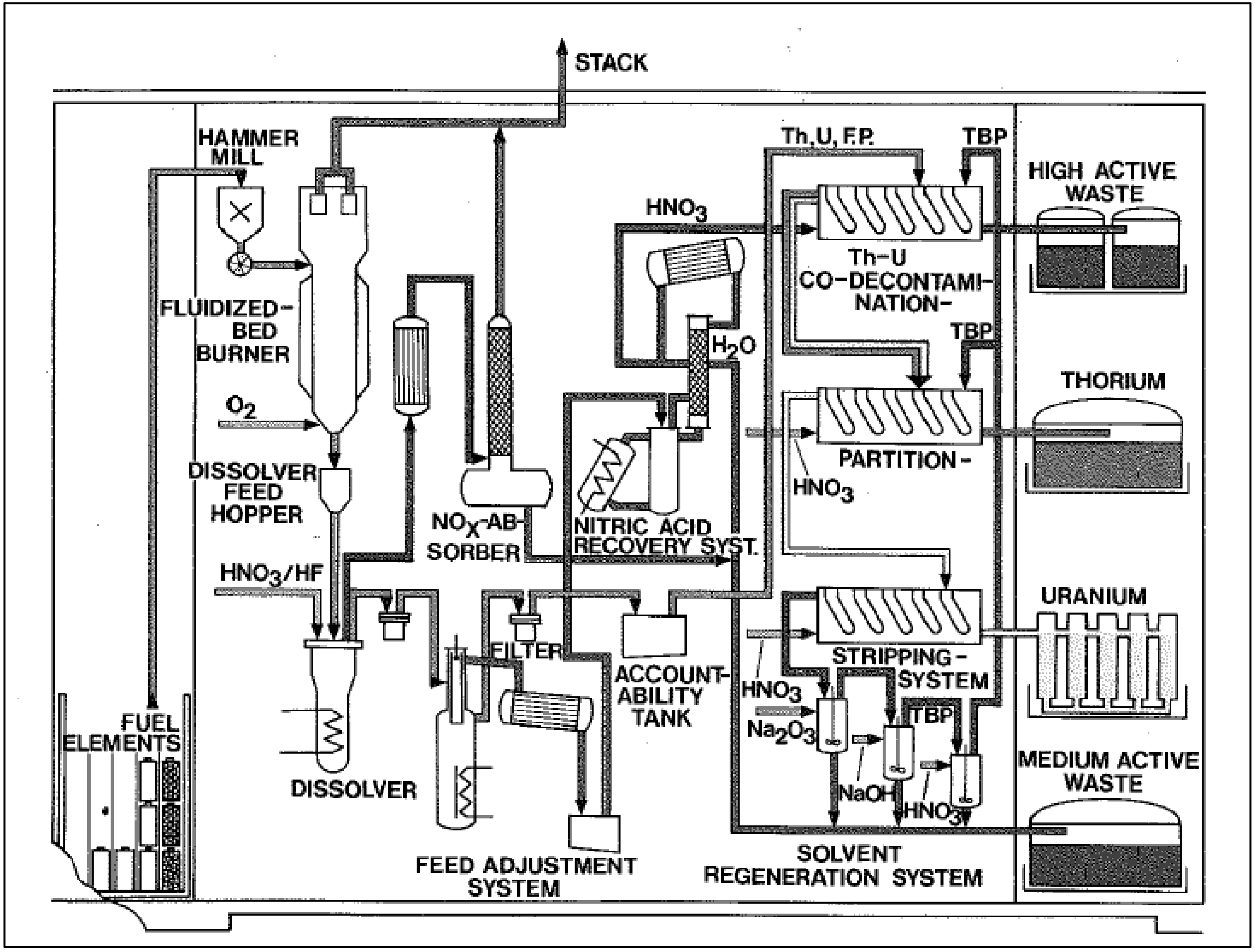
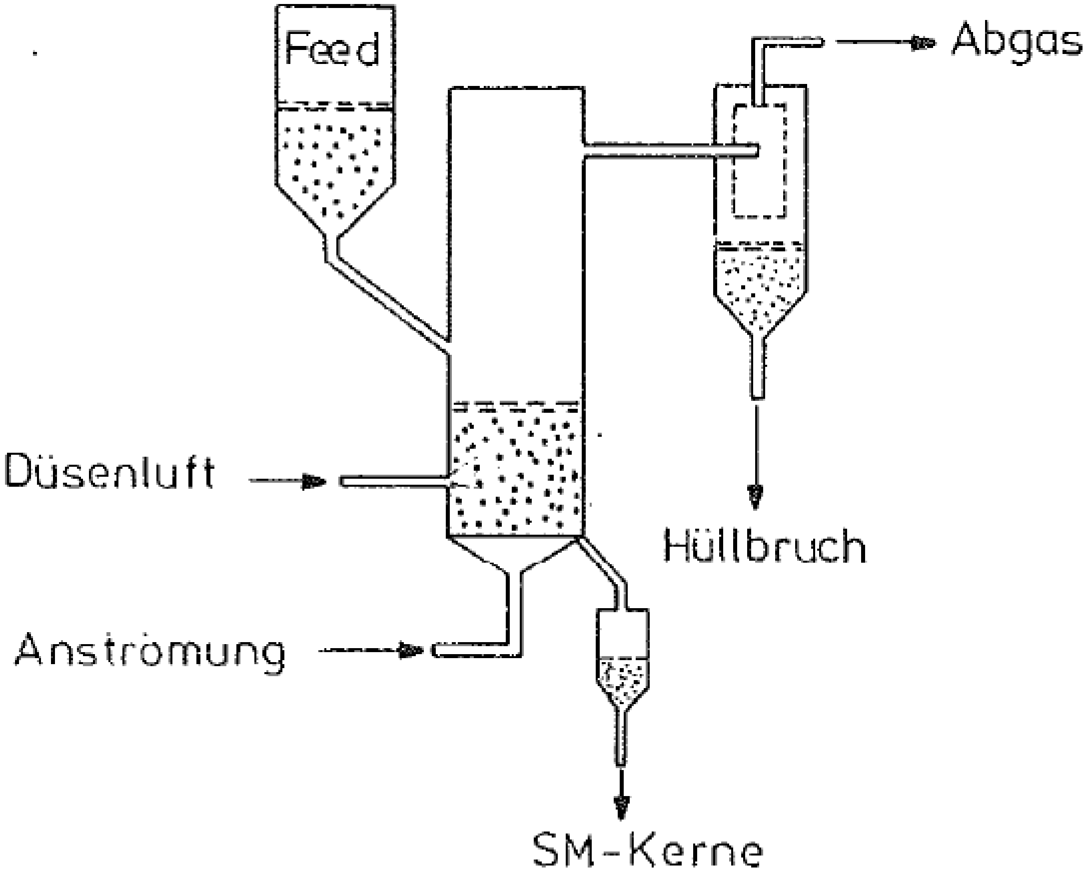


Figure 5-1: Process Schematic of JUPITER Plant from Ref (Lensa, 2008)



The fluidized-bed is sustained by oxidizing gas (Anstroemung). The jet (Duesenluft) reaches nearly sound velocity. Thus the CP are accelerated to high speed and break when impinging the steel plate on the other side of the fluidized-bed.

Figure 5-2: Jet stream method from Ref (Lensa, 2008)

Advantages of this method over crushing include whole layers are removed, layer fragments are relatively large, and low equipment maintenance; however, it does produce a dust fraction of 1% and the heavy metal fraction in the fragments was between 0.37-1.5%. The second and similar method, the *particle jet mill,* Figure 5-3, accelerates the particles within an injection tube before exiting and impinging on a plate. This fracture rate is dependent on the method by which the kernels are injected into the jet, jet pressure, and the acceleration distance. This produces a low dust fraction of 0.2% between 0-40 µm.

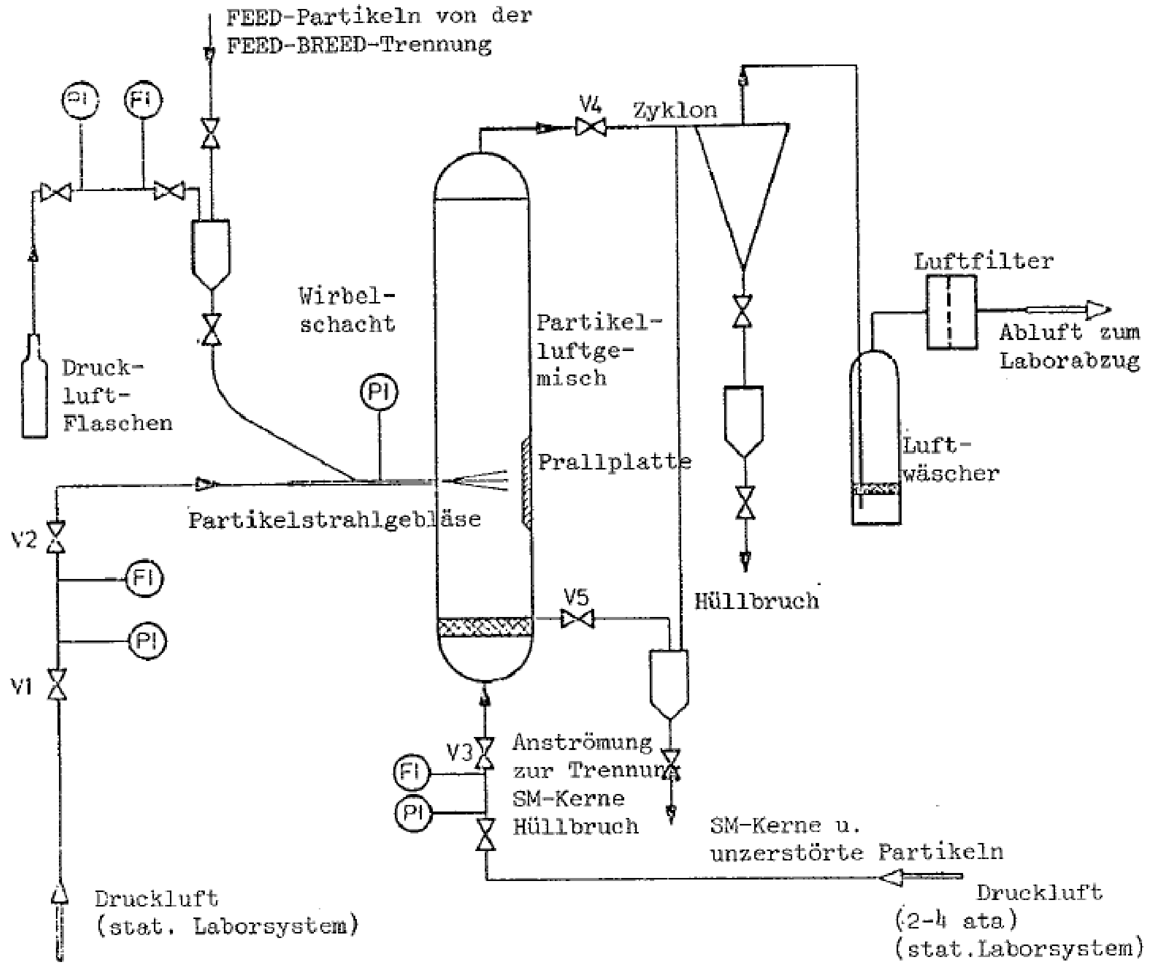


Figure 5-3: Particle jet mill from Ref (Lensa, 2008)

Two mechanical methods include the *diamond disk mill* method (Figure 5-4), which cracks the SiC layer by feeding the particles into a mill gap between one rotating disk and a stationary diamond disk with a butterfly screw. Both the break fraction and size distribution are dependent only on the size of the mill gap. This method produces a dust fraction of 1.5% that is below 40 µm. The *double-roll-crusher* (Figure 5-5) passes the kernels through two counter-rotating rollers with a defined mill gap. These tests were conducted in the USA at General Atomic Co. and additional information can be found in relevant reports*.

*Reports were cited by title but documents could not be retrieved for further review:
1) J.W. Baer, J.B. Strand; Interim Development Report: Engineering-Scale HTGR Fuel Particle Crusher, GAC, San Diego USA, GA-A 15073 UC-77, September 1978
2) C.A. Heath; Reprocessing Development for HTGR-Fuels; GA-A 13279, February 1975

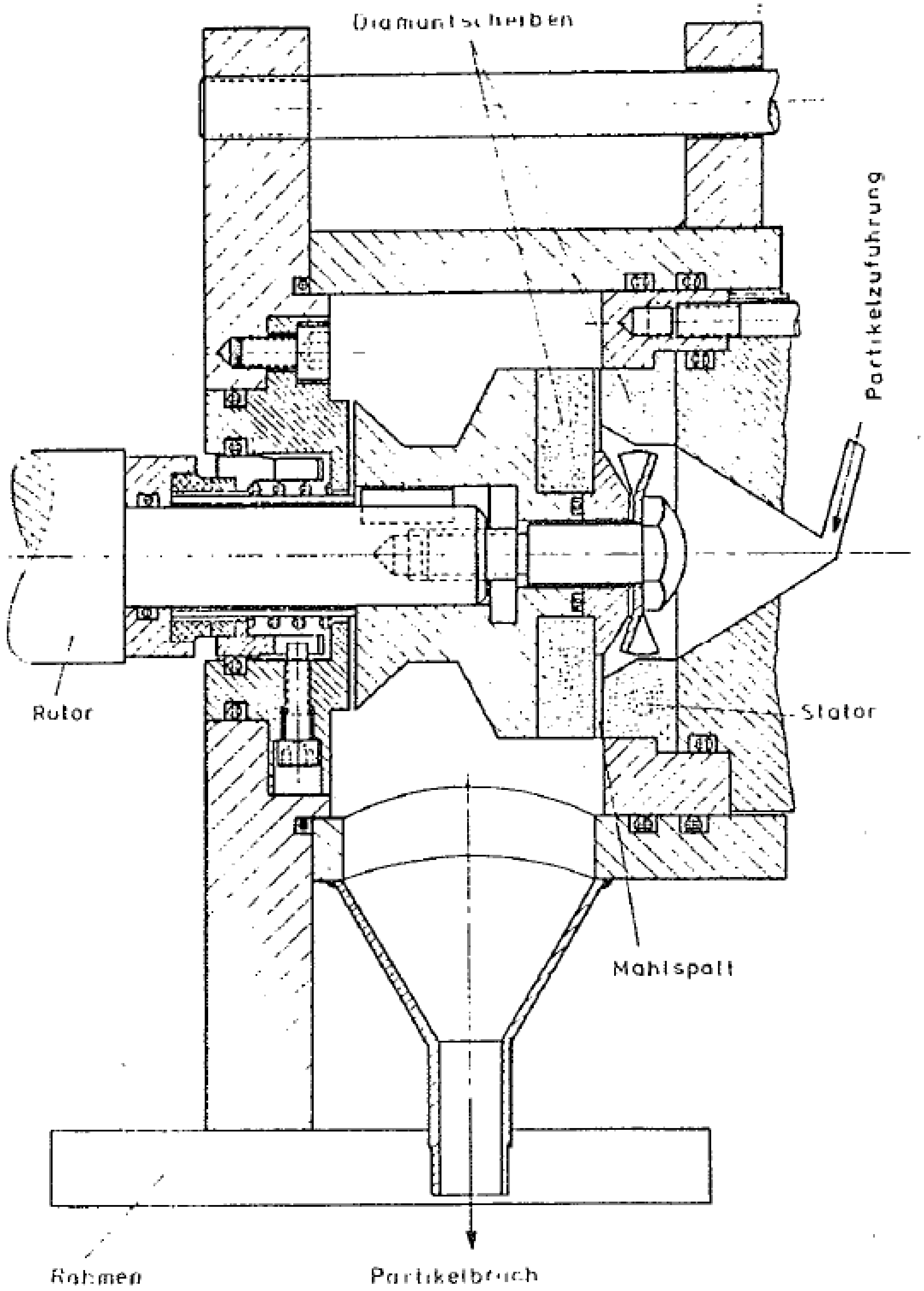


Figure 5-4. Schematic of a Diamond Disk Mill tested at Forschungszentrum Juelich. (Lensa, 2008)

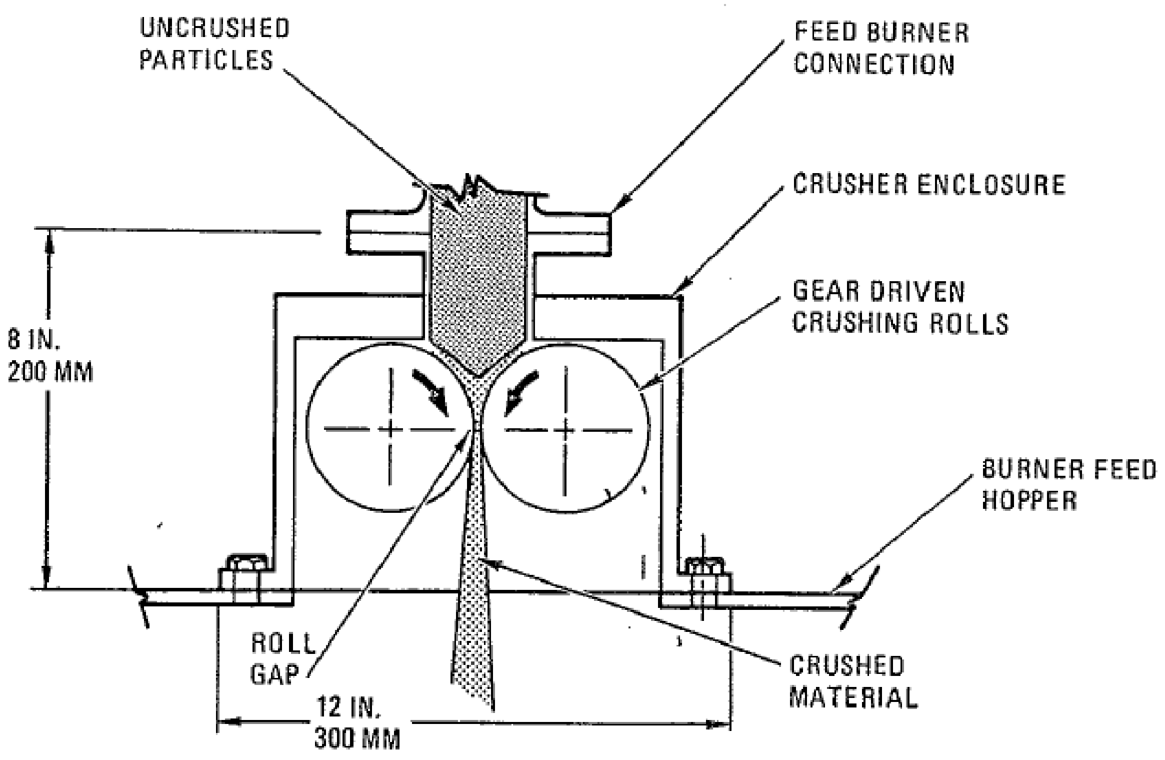


Figure 5-5: Double-Roll-Crusher from Ref (Lensa, 2008)

An additional method was investigated for cracking the TRISO shell of UC_2 fuel kernels as part of the ReActor for Process heat Hydrogen And ELectricity (RAPHAEL) project. (Lensa, 2008) Previously isolated kernels were loaded into a Retch milling machine, depicted in Figure 5-6, and milled for 15 minutes with a calibrated distance between the two working faces slightly larger than the fuel kernel diameter. The fuel kernels were separated from the fragments through two different sized mesh sieves. Initial results indicated that the fuel kernels still retained some of the pyrocarbon buffer layer that was subsequently removed by a 90 minute ultrasonic bath. This technique is rather simple and successfully isolated the fuel kernels from the protective layers, although it would likely have similar maintenance issues as the other mechanical separation methods. The method is conducted underwater preventing the release of dust; however, it would generate a secondary liquid waste stream.

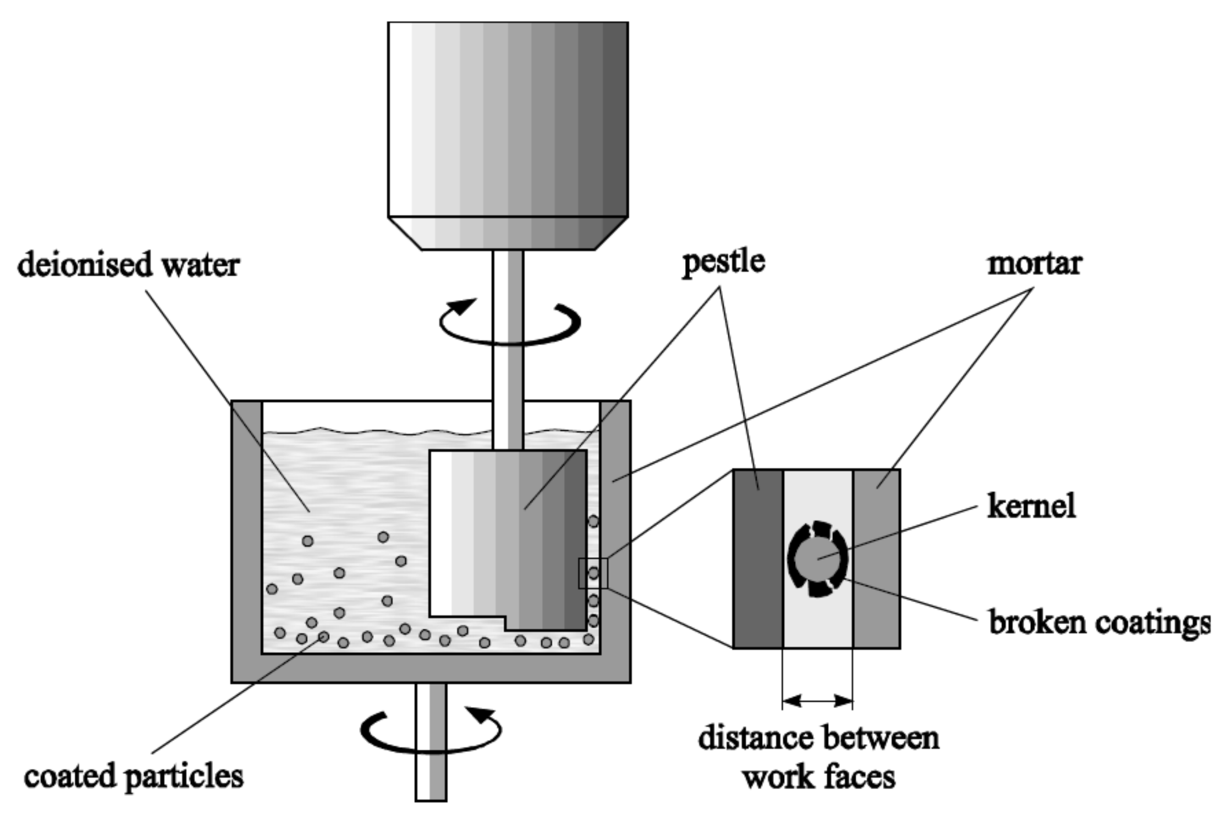


Figure 5-6: Isolation of fuel kernels from coated particles by Retsch milling (Lensa, 2008)

5.3 Chemical Methods

Graphite, especially nuclear grade, is difficult to burn compared to other carbonaceous material such as coal or biomass. The higher thermal conductivity and heat capacity of graphite reduce oxidation rates whereas the other carbonaceous material undergoes the formation of insulating porous ash that reduces radiation losses and the increased porosity allows oxygen to reach the underlying carbon. Since graphite has high thermal conductivity, as it oxidizes heat is rapidly transported away from the reaction zone and, combined with a high emissivity, there are large black-body radiation losses that further slow the reaction. (Characterization, Treatment and Conditioning of Radioactive Graphite from Decommissioning of Nuclear Reactors, 2006) Other carbonaceous materials have substantial amounts of impurities relative to nuclear graphite that catalyze the oxidation reaction. The oxidation rate of matrix components differs: petroleum coke graphite < nuclear grade natural graphite< thermoplastic formaldehyde resin carbon. (Luo Xiaowei, 2004)

Graphite oxidation has three main mechanisms: chemical, in-pore controlled, and boundary layer controlled. At low temperature, slow oxidation occurs with absorbed and adsorbed oxygen and is rate limited by the chemical reaction. At intermediate temperatures, oxidation is controlled by in-pore diffusion of oxygen and the chemical reaction as the consumption of reactant gas is consumed and must be replaced. At higher temperatures, the oxidation is at the graphite surface as the reaction occurs more rapidly than in-pore diffusion and is limited by mass transfer to the outer surface. (Luo Xiaowei, 2004) (Hans-Klemens Hinssen, 2008) Preferential oxidation of graphite occurs at the edges of surface pores and can provide a route for oxygen to enter the interior. Oxidation also increases the reactive surface area leading to an increase in oxidation. During oxidation, if a stagnant gas layer is formed then oxygen must diffuse through the layer. (Wei-Ming Guo, 2008)

While these oxidation reaction issues are focused on gas phase oxidation mechanisms, there is a fair amount of carryover to liquid phase digestion techniques as there will still be transport and diffusion related steps. Addressing these issues for either liquid or gas fluid methods should contribute to increase the processing returns.

One caveat with chemical removal mechanisms is that most methods still use some type of mechanical means to break the graphite into smaller pieces prior to chemical treatment either for ease of handling in bench top and pilot scale facilities or to increase reaction rates.

A patent by Richard Gay, Rockwell International Corporation, describes a 'Method for Disposing of Radioactive Graphite and Silicon Carbide in Graphite Fuel Elements 1995'. A salt bath of molten alkali carbonate is used with a small amount of catalyst sodium sulfate in air at 1,000-1,100 °C as a method for disposing of graphite and SiC. (Gay, 1995) These conditions supposedly substantially increase the oxidation rate of graphite and SiC. This method uses a lower temperature than incineration (1,200 °C), does not require multiple steps to burn the outer graphite, separate the SiC coated kernels, mechanically crack the SiC, and incinerate the inner graphite, which generates fine particulate matter. The reactions are as follow:

$$C + O_2 \xrightarrow{Na_2CO_3 + Na_2SO_4} CO_2$$
$$SiC + 2O_2 \xrightarrow{Na_2CO_3} SiO_2 + CO_2$$
$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2$$

Or if a calcium salt is used:

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

Joseph Farrell and Paul Haas at Oak Ridge National Laboratory (ORNL) in 1967 developed another method for the oxidation of nuclear-grade graphite using nitric acid with flowing oxygen at elevated temperatures and high pressure. (Joseph B. Farrell, 1967) The experiments found that increasing temperature from 275 to 300 °C increased the reaction rate as did increasing the acidity from 1N to 4N; however, corrosion of the containment vessels was noticed at the lower pH values. Higher reaction rates were achieved with a rocking container as compared to the stationary condition. Pressure over the solution was ~1,600 psig. The researchers did not address kernel separation, the SiC layer, or heavy metals.

L.M. Ferris at ORNL in 1967 conducted experiments on prototype Peach Bottom reactor fuel that had been crushed in a hammer mill and then pulverized in a double roll crusher and tested under boiling HNO_3. (Ferris, 1967) The report referenced that the reaction of nitric acid with graphite proceeds slowly, even with boiling nitric acid, whereas uranium dissolves readily in hot nitric acid, and ThO_2 and $(Th/O)_2$ are soluble in HNO_2/HF solutions. The samples were leached for 5 hrs in boiling 13 M HNO_3. Even going to 21.5 M solutions for 24 hrs kept uranium losses due to the graphitic residue to 0.2-0.5%. There was also soluble carbon in the solutions, more present at higher temperatures. Ferris concluded the process was 'only marginally feasible' and did not appear to get to desired levels of U and Th recovery.

Another set of ORNL experiments looked at the Burn-Leach process where ground particles of pyrolytic carbon coated UC_2 and ThC_2 in graphite matrix are burned in air/oxygen at 750 °C in a fluidized bed of mesh alumina and leached with fluoride-catalyzed nitric acid. The nonvolatile fission product oxides were leached from the alumina bed in a single leach of 5 hr with refluxing 13 M HNO_3-0.05 M HF, which resulted in 99.8% of the U and Th being recovered. (Oak Ridge National laboratory Status and Progress Report, 1966)

5.4 Volatilization through oxidation and halogenation reactions:

Graphite gasification occurs through a three step mechanism 1) reactant adsorption, 2) reaction between adsorbed reactant and carbon, and 3) desorption of products with the third step being facilitated by thermal treatment. (Tara E. Smith, 2013)

Halogenation is a potential volatilization method for complete pebble processing. The halogens reported in the literature, F and Cl, are highly reactive with a majority of the chemical species present in the pebbles. The halogens will react with carbon and silicon to form CX_4 or SiX_4, where X = F or Cl, and will react with uranium and plutonium to form UX_6 or PuX_6. This is advantageous because the vapor pressure for the tetra-X-ides is much higher than that of the hexa-X-ides and enables easier separation with a fairly large temperature difference instead of energy intensive cryogenic or distillation methods. Issues with this method include that the halogens are corrosive and represent a health concern. A method to partially mitigate the concerns would be to use a halogen donor molecule such as SF_6 instead of molecular and atomic F.

The USSR had a brief report published in 1983 (Trotsenko, 1985) on the treatment of HTGR fuel with F_2 based on the reactions:

$$UO_2 + 3F_2 \leftrightarrows UF_6 + O_2 - 252\ kcal/mol$$
$$PuO_2 + 3F_2 \leftrightarrows PuF_6 + O_2 - 165\ kcal/mol$$
$$C + 2F_2 \leftrightarrows CF_4 - 162.5\ kcal/mol$$
$$Si + 2F_2 \leftrightarrows SiF_4 - 360.1\ kcal/mol$$

This method allows for separation of the fluorides based on volatility and it is possible that the HTGR fuel elements can be fluorinated without the preliminary removal of graphite shells. However, this capability comes at the expense of increased fluorine consumption and waste generation and would need to be compared against mechanical separation methods. The fluorination step occurred at 1,300 K and condensation of U/Pu hexafluorides at -40 °C to separate from the highly volatile species (tetrafluorides).

In 1963, ORNL had a project that investigated the recovery of uranium from graphite-uranium carbide fuel that was representative of the Kiwi type fuel used in the Rover project. The process included oxidation of graphite in oxygen or air and subsequent direct fluorination of the ash with elemental fluorine. Uranium recovery of over 99.9% and the separation of U-fluorides from other fluorides were demonstrated. (Scott, 1963) Reactor wall temperatures were below 900 °C (usually 450 °C) and the internal fuel bed temperature was 1,320 °C. The Kiwi fuels used Nb-carbide liners for propellant gas passages complicating the isolating of uranium. (F.L. Culler, 1963) The UF_6 was separated from NbF_5 using NaF beds; however, the NbF_5 would not desorb from the NaF and the bed material would need to be exchanged frequently. This technique is advantageous since the oxidation and fluorination could occur in the same chamber.

Also in 1963, ORNL worked on the development of a chloride volatility process using uranium carbide impregnated graphite matrix from the Rover project KIWI B-1B fuel elements. (Johns, 1963) The U is isolated as UCl_4 where it may be further processed by aqueous solvent extraction (Darex) or fluoride volatility. Two processes were investigated for the treatment of ground or rough-crushed fuel. A combustion-chlorination method was used where the matrix is first oxidized/burned in pure oxygen at 800 °C for 5 hr and then chlorinated with 15/85 % vol. CCl_4/Cl_2 at 500 °C for 3 hr with the volatiles collected at room temperature. The chlorination at 500 °C was only required to obtain a rapid reaction and not the volatilization of uranium chlorides. The direct chlorination method treated the graphite/fuel matrix with chlorinating and chlorinating/oxidizing gases at 800 °C. A variety of gases were used with the most effective being carbonyl dichloride, $COCl_2$ (phosgene), although carbon tetrachloride, CCl_4, also worked with appreciable rates. Both methods had U recoveries of >99%. There were some corrosion related concerns dependent on processing parameters and materials. The researchers noticed more corrosion issues from the direct chlorination method. The major combustion components were U_3O_8, Nb_2O_5, and CO_2/CO. The chlorination with carbon tetrachloride vapor followed the reaction:

$$U_3O_8 + 4CCl_4 \longrightarrow 2UCl_5 + UCl_6 + 4CO_2\text{-27 kcal/mol (U)}$$

UCL_6, UCL_5, and UCL_4 can be volatilized easily at T > 200, 300, 550 °C, respectively. Also the decomposition reactions:

$$UC_6 \longrightarrow UCL_4 + Cl_2$$
$$UCl_5 \longrightarrow UCl_4 + Cl$$

occur very rapidly, turning the volatile chlorides into nonvolatile uranium tetrachloride (this was stated during the niobium chloride separation). The recovery of chlorine and carbon tetrachloride would be possible with a dry ice trap and they could then be recycled back into the process. One hazard is the production of small amounts of CO and phosgene, but the phosgene could be trapped along with the chlorine and carbon tetrachloride and recycled. It is then possible for the gas-phase removal of Cl from the uranium chloride based on the reaction:

$$3UCl_4 + 4O_2 \longrightarrow U_3O_8 + 6Cl_2.$$

In 1966, Brookhaven National Laboratory reported using the burn-fluorination process with a fluorine-nitrogen fluidized bed of inert fused alumina particles to volatilize U and Pu from graphite matrix fuel. (J.J Reilly, 1966) The fluidized bed is described as a stable heat transfer medium where the reaction can occur without corrosion and other problems associated with liquid heat transfer media and fused salts. The graphite matrix is highly enriched fuel used in the Rover Nuclear Rocket program: pyrographite-coated dicarbide (UC_2) particles dispersed in a graphite matrix. The most direct approach referenced by the researchers was to burn the fuel with oxygen resulting in volatile CO_2 and CO and nonvolatile U/Th oxides. In this set, the burn and fluorination were conducted in separate reactors for the following reasons:

- Continuous operation of the oxidizer instead of batch
- Two reactors do not have the frequent thermal cycling through wide temperature range
- Avoid alternate exposure to high temperature fluorine and oxygen
- Greater choice on construction materials

The major oxidation reactions were:

$$C(s) + O_2 \xrightarrow{\approx 750\,^oC} CO_2(g)$$
$$C(s) + \frac{1}{2}O_2 \longrightarrow CO(g)$$
$$3UC_2(s) + 10(O_2) \longrightarrow U_3O_8(s) + 6CO_2(g)$$

Followed by fluoride volatility reaction:

$$U_3O_8(s) + 9F_2 \xrightarrow{\approx 450\ ^oC} 3UF_6(g) + 4O_2(g)$$

UF_6 sumblimes, with a vapor pressure of 760 mm at 56.5 °C and triple point at 1137 mm at 64.02 °C. Total uranium recover was 99.25%. With the presence of Th, the two main (unbalanced) reactions are:

$$(Th - U)C_2 + O_2 \longrightarrow ThO_2/U_3O_8 + O_2$$
$$\frac{ThO_2}{U_3O_8} + F_2 \longrightarrow ThF_4 + UF_6 \uparrow + O_2$$

Thorium forms a nonvolatile fluoride and may contain some uranium hexafluoride requiring additional separation.

A French Alternative Energies and Atomic Energy Commission (CEA) paper on block-type HTGR spent fuel processing addresses several methods. (Michel Masson, 2006) A schematic of one of the processes ORNL developed for the initial grinding of graphite is shown in Figure 5-7 but noted breaking the SiC layer was particularly difficult. Other non-cited work referenced efforts in the 1960s-1970s of mechanical grinding the SiC causing significant tool wear from the abrasive charater of the SiC. Without citing specific reports, the authors indicate that processes combining grinding and combustion followed by dissolution in aquesous acid and the THOREX process studied in the United States and Germany only had U/Th recovery yields on the order of 95%, indicating that higher yields are required. Mechanical crushing techniques are described as “too destructive to ensure that the graphite is not polluted by actinides and/or fission products after processing”. The authors seem to be impressed with the pulsed current fragmentation method describing the electric arc as propagating preferentially through the solid or water and the method is capable of separating the kernels from the matrix and subsequently fracturing the kernel layers as shown in Figure 5-8. Another technique based on fission product vitrification using an induction furnace operated under oxygen is described. Pyrometallurgical processes are referenced for the dissolution of SiC in a eutectic mixture of 43.5% Li_2CO_3, 31.5% Na_2CO_3, 25% K_2CO_3 with a melting point at 387 °C, producing CO_2 and SiO_3^{2-}. The gas phase treatment reaction is described as:

$$2Cl_2(gas) + SiC \text{ -> } C(solid) + SiCl_4(gas).$$

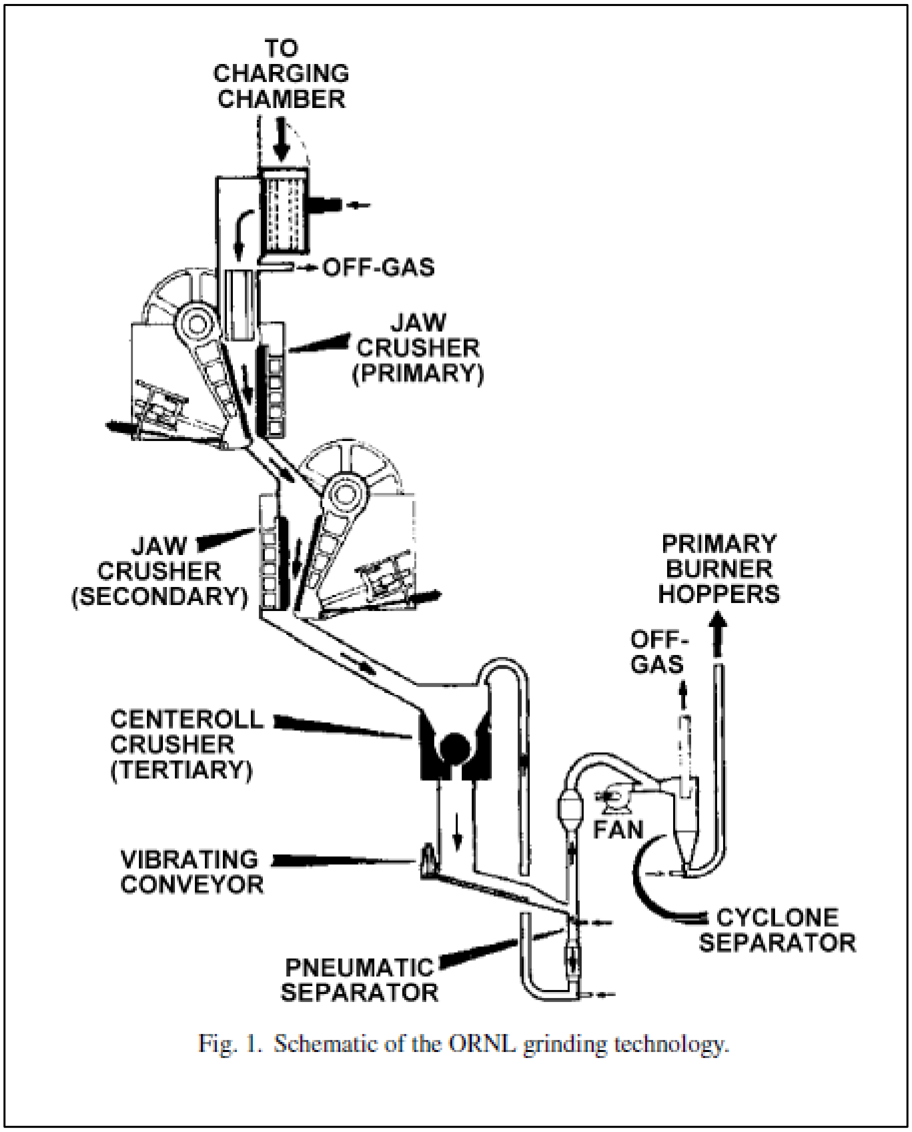


Figure 5-7: Schematic of the ORNL grinding technology. Ref: (Michel Masson, 2006)

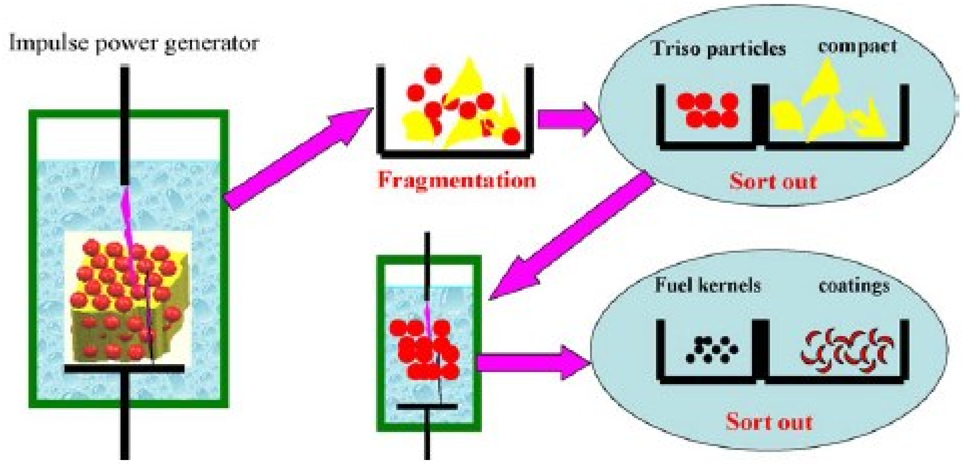


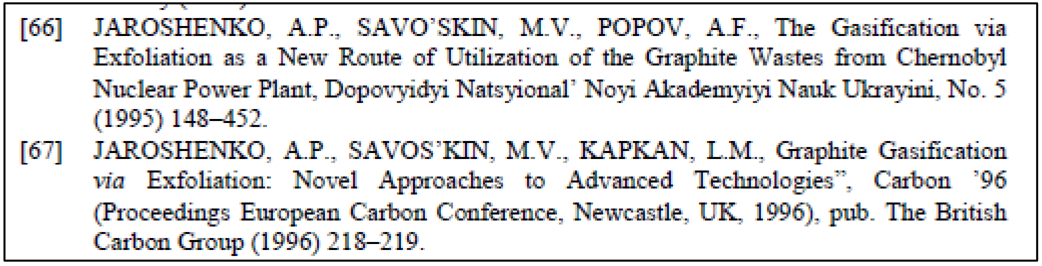
Fig. 5. Potential use of pulsed currents to fragment graphite from compacts and TRISO particle layers.

Figure 5-8: Fragmentation process using HV discharges from Ref: (Michel Masson, 2006)

A report from the Japanese efforts with reprocessing Very-High Temperature Reactor (VHTR) fuel in 1977 looked at burning the graphite sleeves with CO_2 at 800-1,000 °C with an unidentified catalyzer and fluorination of SiC with F_2. No results were reported. (Sueo Nomura, 1977)

Studsvik, Inc. and Bradtec Decon Technologies Ltd have described a pyrolysis technique for use in nuclear graphite disposal. (Bradbury, 1999) This technique is a patented Thermal Organic Reduction (THOR^{SM}) process utilizing pyrolysis/steam reforming technology ($C + H_2O \longrightarrow CO + H_2$). It still requires grinding to <1 cm size.

Another option for increased oxidation efficiency has been developed in Ukraine for a dry pretreatment process using fuming nitric acid, perchloric acid, and magnesium perchlorate or sulphuric acid at ambient temperature, then heated to 600 °C. This method achieved oxidation rates in air 4-27 times higher than oxidation of non-treated graphite. (Characterization, Treatment and Conditioning of Radioactive Graphite from Decommissioning of Nuclear Reactors, 2006) The following sources were referenced:



[66] JAROSHENKO, A.P., SAVO'SKIN, M.V., POPOV, A.F., The Gasification via Exfoliation as a New Route of Utilization of the Graphite Wastes from Chernobyl Nuclear Power Plant, Dopovyidyi Natsyional' Noyi Akademyiyi Nauk Ukrayini, No. 5 (1995) 148–452.

[67] JAROSHENKO, A.P., SAVOS'KIN, M.V., KAPKAN, L.M., Graphite Gasification *via* Exfoliation: Novel Approaches to Advanced Technologies", Carbon '96 (Proceedings European Carbon Conference, Newcastle, UK, 1996), pub. The British Carbon Group (1996) 218–219.

Closed chamber incineration research was conducted through a collaboration of the Nuclear Systems and Materials Department Reactor Technology Center at Pacific Northwest National Laboratory (PNNL) and the Energy Conversion and Storage Research Headquarters of the Institute of Gas Technology in 1994. (D.J. Senor, 1994) The process uses an enclosed combustion chamber coupled with molten carbonate fuel cells that allow for the destruction of irradiated graphite without the release of radioactive cation release, only the release of combustion gas, and at least partial conversion of SiC layers into SiO_2. The liquid electrolyte is typically Li_2CO_3 and K_2CO_3 and contained in a porous $LiAlO_2$ matrix operating at 600-700 °C. "Any cations carried with the oxidant gas from the combustion chamber to the fuel cell stack will tend to collect within the cathode due to the presence of the electric potential." The oxidant gas is removed by:

$$\frac{1}{2}O_2 + CO_2 + 2e^- \longrightarrow CO_3^{2-}$$
$$H_2 + CO_3^{2-} \longrightarrow CO_2 + H_2O + 2e^-$$

reactions at the cathode and anode, respectively, with a mass transfer of CO_2 through the cell from the cathode to the anode. The combustion reactions are:

$$2C + O_2 \longrightarrow 2CO$$
$$C + O_2 \longrightarrow CO_2$$

with the first reaction being kinetically preferred. The relative rate of reaction for the two reactions for refined graphite (<100 ppm impurities) is given by:

$$\frac{k_3}{k_4} = 14.1e^{(-6240/T)}$$

and approximated an oxidation rate of:

$$-\frac{dm_c}{dt} = 3.55x10^{-6}p_{O_2}^{0.32}e^{(-1812/T)}\, g/cm^2 - s$$

where $\frac{dm_c}{dt}$ is the carbon oxidation rate, p_{O_2} is the oxygen pressure in kPa and T in Kelvin. The actual oxidation rate is dependent on graphite type as impurities can act as catalysts and surface modification due to radiation damage.

Another experiment from Brookhaven National Laboratory from 1958-1966 looked at the use of fluidized beds of inert granular material for the volatilization of fuel cladding or matrix material and the reaction with fluorine at temperatures as high as 550 °C for the recovery of fissile material as hexafluorides. (S.J. Wachtel, 1966) Graphite was burned in the bed fluidized with pure oxygen at ~750 °C and then fluorinated. Other combustion-fluorination experiments from 1963 from ORNL are described for the Rover project, although there may be some overlap. (F.L. Culler, 1963)

There has been substantial research of the various reactions of NOx and carbon, primarily focusing on carbon black and soot particles. (B.R. Stanmore, 2008) For temperatures <700 °C the primary reactions are:

$$2NO_2 + C \rightarrow 2NO + CO_2$$
$$NO_2 + C \rightarrow \frac{1}{2}N_2 + CO_2$$

It was noted that the C-NO_2 reaction is enhanced in the presence of water vapor. At 300 °C the carbon consumption was three times faster than dry NO_2 but there is a negative dependence with higher temperature. The increase was attributed to the formation of nitric and nitrous acids:

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$
$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

Above 600 °C the C-NO reaction begins to occur with similar rates to oxygen but much lower than NO_2 following the reaction:

$$C + 2NO \rightarrow CO_2 + N_2$$

And the reaction with N_2O:

$$C + 2N_2O \rightarrow CO_2 + 2N_2$$

The reviewers also noted that the soots, activated carbons and carbon blacks studied are more reactive than graphite.

Phosphoric acid (H_3PO_4) reactions with carbon have been researched indicating a formation of a surface oxide and the evolution of CO_2. (A. Guenbour, 2006) The electrochemical corrosion of carbon proceeds with the formation of carbon surface oxides on preferred sites such as edges, dislocations and discontinuities and in some studies oxide formation only occurs after the acid has been intercalated into the graphite.

A recent report from ORNL, (B.B. Spencer, 2004), investigated the head end processing of the TRISO kernels. The approach described removing the fuel compacts from the prisimatic block and then crushing and milling the compact to remove the fuel particles with a fluid-energy milling device for potential separation of heavy fines from lower-density fines. The fuel particles were then treated with a pyrochemical process based on carbochlorination with a molten alkali chloride salt. A second process of leaching with nitric acid was investigated as a proof-of-principle experiment. The report references the Dragon Project fuel (UC_2-ThC_2) ground to <125 µm with a swing-hammer mill where the wear rates were "untenably high for a machine that uses a screen to control product size" and indicated a double-roll crusher might be more robust. Some concerns from the previous grind-leach studies were the production of by-product soluble organic species from leaching and the use of large volumes of leach and wash solutions resulting in low uranium concentrations. During the experiment, a manual method for crushing TRISO surrogates used an alumina ceramic mortar and pestle and noted wear of the components "rapidly became apparent." The work was continued in a stainless steel beaker and the material was pounded with a stainless steel rod.

5.5 Potential Methods

Potential methods for the separation or reprocessing of graphite fuel components discussed here are novel applications of existing technology or other techniques that historically have not been investigated for nuclear graphite waste applications. For any given technique or technology there can be substantial barriers to adoption such as incumbent resistance, scalability concerns, validation and verification, technical limitations, or incompatibilities with processing nuclear materials. The potential methods mostly remain under the basic mechanical or chemical designation; however, the application and results of the methods are of interest to this review.

One potential method for graphite separation is fragmentation. The fundamental aspect of fragmentation is a resulting fracture of the material under the application of stress that fragments or separates from the main material. With respect to nuclear graphite concerns, the application of stress has traditionally been achieved through physical or mechanical means of crushing or grinding the graphite material into smaller sections. However, using a technology developed for mining and mineral extraction, the stresses have been applied with shockwaves: a large amplitude compression wave that has nearly discontinuous change in pressure, temperature, and density of the medium. The large pressure differentials that can be in excess of 1 GPa (10 kbar) can be produced by several methods; in general a large or rapid volume displacement in a fluid is required. This displacement can be generated through rapid thermal expansion, sonic, cavitation, or physical volumetric displacement. One technique referred to as electrohydraulic fragmentation (among other names) generates a shockwave through the formation of a plasma channel from an electrical discharge. This process is similar to lightning producing thunder through a massive electrical discharge forming a plasma channel that rapidly displaces a volume of fluid, in this case air, creating a shockwave, thunder. Electrohydraulic fragmentation similarly uses an electrical discharge to form a plasma channel in either a fluid or material that causes a shockwave that impinges on or travels through the material causing high levels of stress.

A novel application of high voltage discharges has generated a promising technology for head-end processing of high temperature reactor type graphite pebbles. (Michael A. Futterer F. v., 2010) (Michael A. Futterer P. H., 2013) This technique has been previously used and developed for fragmenting rock and other applications. The premise is an electrically insulated container filled with water with a high voltage spark discharged through the volume of the water using the device shown in Figure 5-9. The discharge creates a cavitation shockwave or electro-hydraulic shockwave and the resulting pressure differential facilitates the fragmentation of material in the water volume that can then be separated using a sieve located at the bottom of the vessel. The power supply is operated from 200-400 kV and a maximum current of ~10 kA over a pulse time of ~500 ns for a total max power of 4GW and energy of ~2 kJ per discharge (using rough estimations for values and $P(W) = V * I(A)$ and $E(J) = \frac{P(W)}{t(s)}$). The researchers give an estimate of 0.23 kWhe to fragment all particles of a pebble compared to the energy produced by the pebble of 540 kWhe and 2,000-5,000 kWh/t to fragment the graphite matrix liberating the kernels and 8,000 kWh/t for the fragmentation of the kernel coatings. The researchers also indicate the possibility that through controlling the voltage, current electrode distance, water volume, and sieve size, the liberation of coated kernels from the graphite matrix, Figure 5-10, and subsequent fragmentation, Figure 5-11, of the kernels coatings is feasible.

Figure 5-9: Commercially available fragmentation machine from selFrag lab that stands about 2 m high from (Michael A. Futterer F. v., 2010)

Figure 5-10: Fragmented fuel pebble after 15 pulses over 3 seconds and liberated representative fuel kernels after 300 pulses in 60 seconds, from Ref (Michael A. Futterer F. v., 2010).

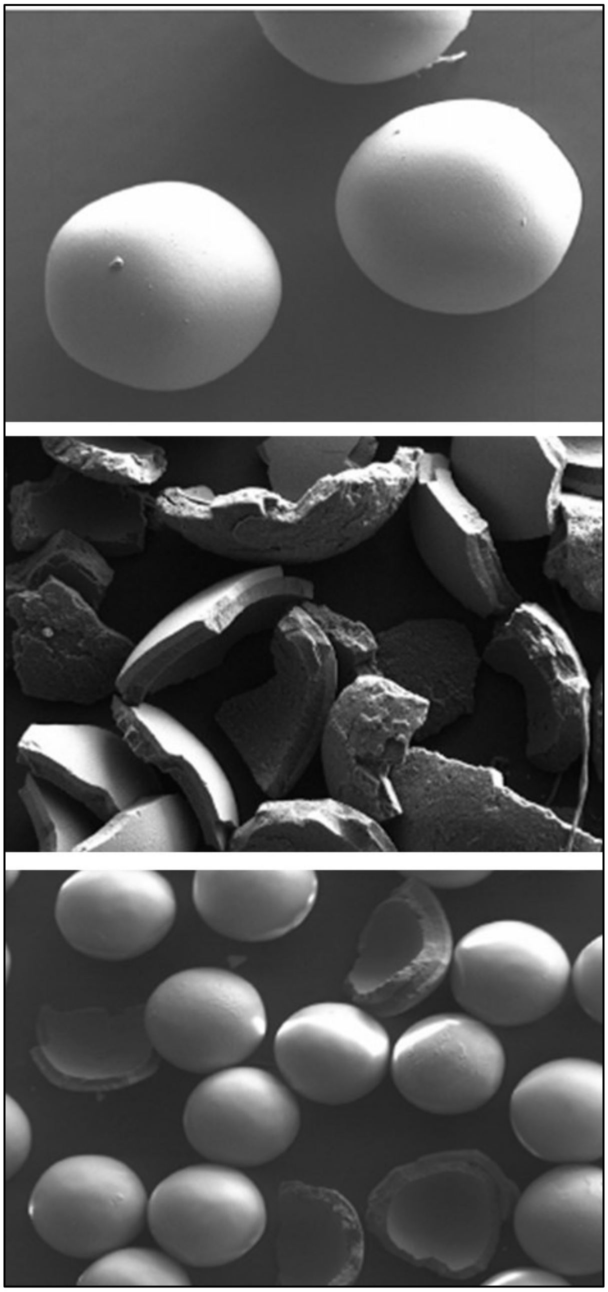


Figure 5-11: Intact particles, separated coating shells, kernels separated from their shells, from Ref (Michael A. Futterer F. v., 2010)

A similar patent describes a high voltage (HV) fragmentation system with the addition of a solid/fluid separation and return device and a method for keeping the particulates suspended in the fluid to achieve a more effective fragmentation, saving time and energy. (Wolfgang Frey, 2011) However, the gasless fluid suspension method and separation equipment would add complexity and exposed mechanical parts that may become difficult to maintain during extended processing of fuel components.

A plasma blasting method is described for boring and tunneling through rock as a replacement for high explosives through the mechanical drilling of a borehole and then inserting a coaxial electrode assembly with an electrolyte fluid. While this method is not directly applicable to fragmenting pebbles, it does offer relevant information. The inventors determined that a delivery rate of ≥100 MWe/μs to a power of ≥3 GW produces shockwaves sufficient (>1 GPa) to fracture hard rock with the delivery rate being critical. (Frank Kitzinger, 1992) Also referenced is a report by the U.S. Bureau of Mines in 1969 and several other electrohydraulic patents. The report mentions that the main disadvantage of electrohydraulic fracturing is the pressure pulse spreading out and dissipating a large fraction of energy to the fluid.

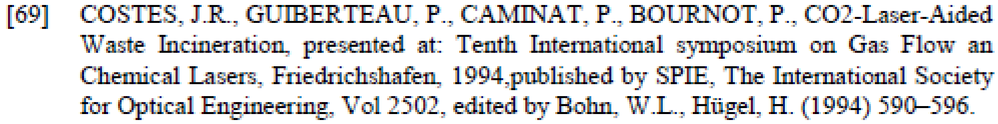
Another fragmentation method, the plasma channel drilling process, is detailed for drilling through material without heating the material to the melting point. Rather than generating shockwaves in a fluid and dissipating energy as the wave propagates, the coaxial electrodes generates a repetitive discharge across the surface or within the material itself. Powers of 1-100 MW are generated at 10-50 kV, delivering 10-500 J with a rise time of 100 ns and duration of 1-50 μs. A drilling rate of 2.5 cm/min was given for hard sandstone. The pulse can be negative or positive; however, the positive polarity pulsed discharge extinguishes more rapidly allowing for a higher pulse rate. (MacGregor, 2007) As such a limiting factor is the time it takes for the plasma channel to deplete or extinguish before the next discharge is initiated, otherwise if the channel is still ionized to a significant level then the subsequent current pulse will propagate through a relatively conductive medium and not generate a large pressure differential. As the method does not require the propagation of a shockwave through a fluid it can be operated either in a fluid or in a dry setup. While it might not be desirable to bore a hole through pebbles, the technology might be adapted to selectively remove the first 5 mm of kernel-free graphite to separate out the higher level ^{14}C-graphite if it is deemed an issue.

A parallel use of electrical fragmentation is for refining quartz through the liberation of fine grained trace minerals. (E. Dal Martello, 2012) After treatment, the quartz is described as having ‘dense networks of fractures throughout the grain’. If the same occurs in graphite, this could be useful or detrimental in releasing entrained fission products. Other conclusions are increased liberated quartz particles with higher energy and the trace mineral grains were liberated mostly along the grain boundaries and not cleavage planes. Conditions used were 125 kV, a rise time of <500 ns, and 1-10 kg batches of quartz. As the shockwave propagates through the material, the wave reflects and refracts along physical boundaries concentrating the stress and weakening the interfaces. This aspect could beneficial to the fracturing pebbles given the large number of interfaces between the outer layer and matrix, kernel and matrix, and the individual kernel layers.

A paper was presented at the 41st US symposium on Rock Mechanics and published by the American Rock Mechanics Association that describes two methods of HV fragmentation of rock. The first is generation of a shockwave in a fluid and fragmentation results by the impact of the wave on the material. The second method is the passage of current through the material separating the mineral contents from the preferential current flow along boundary interfaces, which requires substantially less energy than the first method. [A third method could be the passage of current through the material causing breakdown and plasma formation and subsequent pressure shock internal to material.] Several steps of the fragmentation are listed: 1) formation of channel in rock with voltage increase, 2) flow of current with rapid decrease in voltage and increase in current, 3) generation of mechanical stress from expanding channel, 4) propagation of crack, and 5) dispersion of fragments. Also mentioned is that the fracture pattern is determined by the applied pressure loading rate.

Modifications to the current technology include using a different fluid either for better discharge properties and/or low dissolution of fuel and matrix components. One point of concern is the possible ‘ionization’ or increase in ion content (through both plasma formation and dissolution of fragments) of the water resulting in more conductive solution changing the discharge parameters, although that could be addressed with the filtration and separation methods employed for the fragmentation waste stream. Another problem with generating the shockwaves with electrical discharges is the erosion of electrodes and internal components due to spark formation and the replacement of those components. Repeated discharges in fluid would fragment/dissociate the fluid components. Benefits to this process include the equipment could be made into a relatively closed system with a limited number of parts coming in contact with the fuel components, the use of non-hazardous fluids, minimal generation of additional waste streams, the capability to controllably separate the kernels from the graphite matrix and then separate the fuel kernels from the kernel shell layers, and a majority of the waste would be solid graphite fragments that could have easier disposal conditions than a liquid or gas waste product. There would remain the possible release, into the closed-system, of fission products through both shockwave and plasma generation from the matrix, kernel shells, or kernels. Fracturing through other non-mechanical cracking could be caused with alternate sources of shockwaves from laser, ultrasound, transducers, piezoelectric, or other. Some of the plasma drilling and fracturing techniques described could be adapted in a manner that would allow controllable removal of the outer layer of the pebbles before separating the inner region to create a separate waste stream of ^{14}C concentrated graphite. It could be possible to design a system for ‘dry’ fragmentation where the electrical discharge only contacts the material and not a transfer fluid. While most fragmentation applications use some derivation of pulsed arc electrohydraulic discharges to form the shockwaves, there could be other shockwave generation sources that might be considered. Other sources could include pulsed laser discharges akin to a scaled up Laser Induced Breakdown Spectroscopy (LIBS) system, energy deliver through pulsed electromagnetic (EM) radiation such as Radio Frequency (RF) or Microwave (MW) could heat to a greater depth than laser causing larger fragmentation, or other method.

Laser incineration was investigated at CEA, France using a CO_2 laser with 5-22 kW power and a beam diameter of 35 mm. The graphite reaches 1,100-1,200 °C in areas irradiated with laser light and combustion raising temperature further easily attaining 14 kg h^{-1} rates. (Characterization, Treatment and Conditioning of Radioactive Graphite from Decommissioning of Nuclear Reactors, 2006) The benefits of this technique include no prior mechanical fragmentation is required, temperature control, localized high temperature to the combustion area and not the entire system, and remote IR process monitoring. The referenced information was presented at a symposium:


[69] COSTES, J.R., GUIBERTEAU, P., CAMINAT, P., BOURNOT, P., CO2-Laser-Aided Waste Incineration, presented at: Tenth International symposium on Gas Flow an Chemical Lasers, Friedrichshafen, 1994,published by SPIE, The International Society for Optical Engineering, Vol 2502, edited by Bohn, W.L., Hügel, H. (1994) 590–596.

This research was reported in 1994 and since that time there has been substantial research and development in high power lasers including gas and solid state varieties that can offer higher power levels, greater frequency options, and higher efficiencies. Revisiting this approach with current technology might yield better results.

Heat flux experiments on A-3 graphite were conducted and reported in 1991 with a ruby laser with output of 6.4 J and a pulse length of 1 ms. These conditions were able to deliver calculated heat loads up to 4,200 MW/m^2, increasing temperature to >3,000 °C, which cooled to 600 °C after 3 ms. (H. Kamezaki, 1991) This work was investigating gas release and sublimation under vacuum and did not give mass change data. The long pulse length would not likely cause a shockwave for fragmentation, and no mention of such was given in article. Recent advances in lasers for higher power and quicker pulse lengths could generate high enough power densities for ablation and fragmentation.

Application of MWs in non-plasma generating capacities could be used to enhance reaction rates for either direct oxidation or digestion for the removal of graphite. There is some evidence of selective and enhanced chemical reactions for organic synthesis; however, it has been met with some skepticism. Even if that is not the intention or mechanism, it could effectively ‘catalyze’ the reaction by providing selective or localized heating, formation of hotspots, and reduce the overall temperature of the reaction system.

This could enhance the reaction of the graphite with air, oxygen, acid solutions or vapors, molten salts, or other to be determined reactants.

There have been at least two research projects investigating the use of RF induction for the disposal of nuclear graphite. Westinghouse Idaho developed a pilot scale incineration process using radio frequency induction heating under inert atmosphere followed by the introduction of a thermal lance providing oxygen to the combustion zone, although no reference material was given. (Characterization, Treatment and Conditioning of Radioactive Graphite from Decommissioning of Nuclear Reactors, 2006) An induction furnace was developed by CEA operating at 400 kHz in an oxygen environment with 10-20 kW maintaining a combustion temperature of 1,100 °C and a graphite combustion capacity of 3 kg h^{-1} with further modifications and enhancements being investigated. (Michel Masson, 2006)

Benefits of both the MW and RF scenarios include being ‘electrode-less’ and selectively applying additional energy to the reaction. Both MW and induction RF could be operated to enhance the efficiency or rate of a standard reaction. While the overall process might not conclude with a net gain in energy or electricity, the application of EM might allow the overall process to occur under more favorable conditions or rates compared to a non-enhanced process that would offset any incurred energy penalties. These methods could be viewed as enhancements or add-ons to an existing set of reaction chemistries, such as oxidation, but could have significantly different outcomes.

Another set of potential methods for graphite removal that have been utilized in a wide variety of industrial applications are plasma enhanced oxidation, fluorination, and thermal vaporization. Plasma can be extremely useful regarding chemistry as it can in many cases enhance reaction rates, allow reactions to occur at substantially lower temperatures or pressures, achieve substantially higher temperatures, negate the need for traditional catalysts, and allow for novel chemistries to be realized. Often described as the ‘fourth state of mater’, plasma is in general a gas with excited or ionized molecules and in most cases charge neutral. Energy can exist in multiple forms in plasma. It can populate higher levels of molecular and atomic electronic, vibrational, and rotational levels. These levels can be excited to the point of dissociation or ionization. The ionized electrons and ions can then gain energy at different rates represented by temperatures, T_e and T_i. These unique energy states are what allow for the exotic chemistries to occur. It is possible to reach energy distributions only found at much higher temperatures with a plasma as the energy can be stored or added in non-thermal modes or methods.

Thermal or equilibrium plasmas are usually high energy and high density with electron temperatures and ion temperatures being in equilibrium. Electrons gain energy quicker than ions given the large mass difference and higher mobility, then transfer to ions through collisions. Atmospheric pressure is highly collisional and plasma temperatures will quickly equilibrate. Examples are DC/AC cutting and welding torches. Non-thermal or non-equilibrium plasmas have lower energy, lower temperatures even to room temperature, and electron temperature is much greater than ion temperature. These plasmas are useful for low-temperature chemistry.

Related to graphite removal, plasma could be generated in a chamber containing graphite with the reactants as the working gas or in remote system and introduced into the chamber. The plasma could contain oxygen or other reactive components, such as halogens, for an enhanced chemical reaction. Additionally, a higher temperature or energetic plasma could be used for thermal vaporization transitioning into the gasification technique. Plasma enhanced volatilization could offer increased reaction rates as the oxidation is ‘catalyzed’ through the excited reactant species. Setups could include negative, atmospheric, or positive pressures. As there are numerous methods for generating plasma, there are several methods for controlling the plasma energetics from mildly ionizing low temperature to highly ionized and thermal plasma.

Plasma assisted burners have been investigated to enhance combustion of low grade coal fuels. (E.I. Karpenko, 2007) (Han Sup Uhm, 2012)

Thermal plasma has several advantages over conventional burning such as 1) high throughput and low reactor geometry, 2) high quench rates of $>10^6$ K/s, and 3) low gas flow rates reducing off-gas treatment. (E. Gomez, 2009) Arc torches can have currents up to 1E5 A with lengths of cm to m and an energy density of 2800 MJ/m^3. Depending on the electrode and torch configuration (electrode-less designs for RF and MW), contamination from electrode wear can be reduced for high purity applications. Graphite electrodes made of a rod with a through hole for gas deliver are a simple and inexpensive alternative and would not contaminate pebble processing and have low wear rates of ~<5kg/MWh. Electrode-less plasma generation from RF induction or MW can allow for processing gases that can be highly reducing or oxidizing and have commercially available powers of more than 100 kW. For waste processing, plasma offers high-energy density, fast reaction times, steep thermal gradients, treatment of solids, liquids, and gases, high heat flux relevant to graphite reactions, use of chemically reactive gases or oxidants is not needed to produce heat, and the incorporation of steam plasma for increased reaction rates. Additionally plasma reactors can be utilized to form a vitrified slag of non-volatilized components.

Another industrial scale process is gasification. This term is mostly applied to non-combustion methods although it can utilize the controlled addition of oxygen or steam. Using similar technology to solid municipal waste gasification, the technology has been shown to work for a variety of municipal wastes, biomass, and even explosives. Some designs utilize plasma or other heat sources and are already designed for the capture of off gas usually intended for the production of syngas and/or energy production. The Biomass Cogeneration Facility, Figure 5-12, located at SRS is a gasification method using fluidized bed combustors, Figure 5-13, that are capable of producing 240,000 lbs/hr of steam at 825 °F and 20 MWe. (Bulgarino, 2013) The facility is capable of processing timber, wood products, and used tires with the exhaust treated by several pollution abatement controls meeting South Carolina Department of Health and Environmental Control, SCDHEC, and Federal Environmental Protection Agency, EPA, regulations.

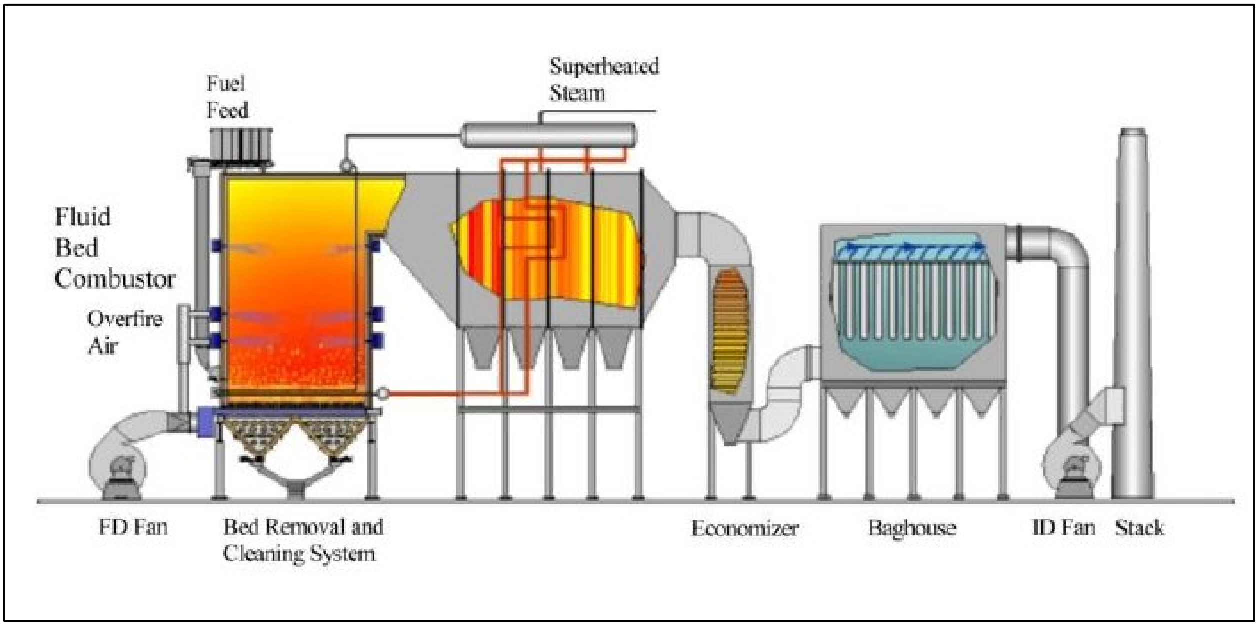


Figure 5-12. Biomass Cogeneration Facility from (Bulgarino, 2013).

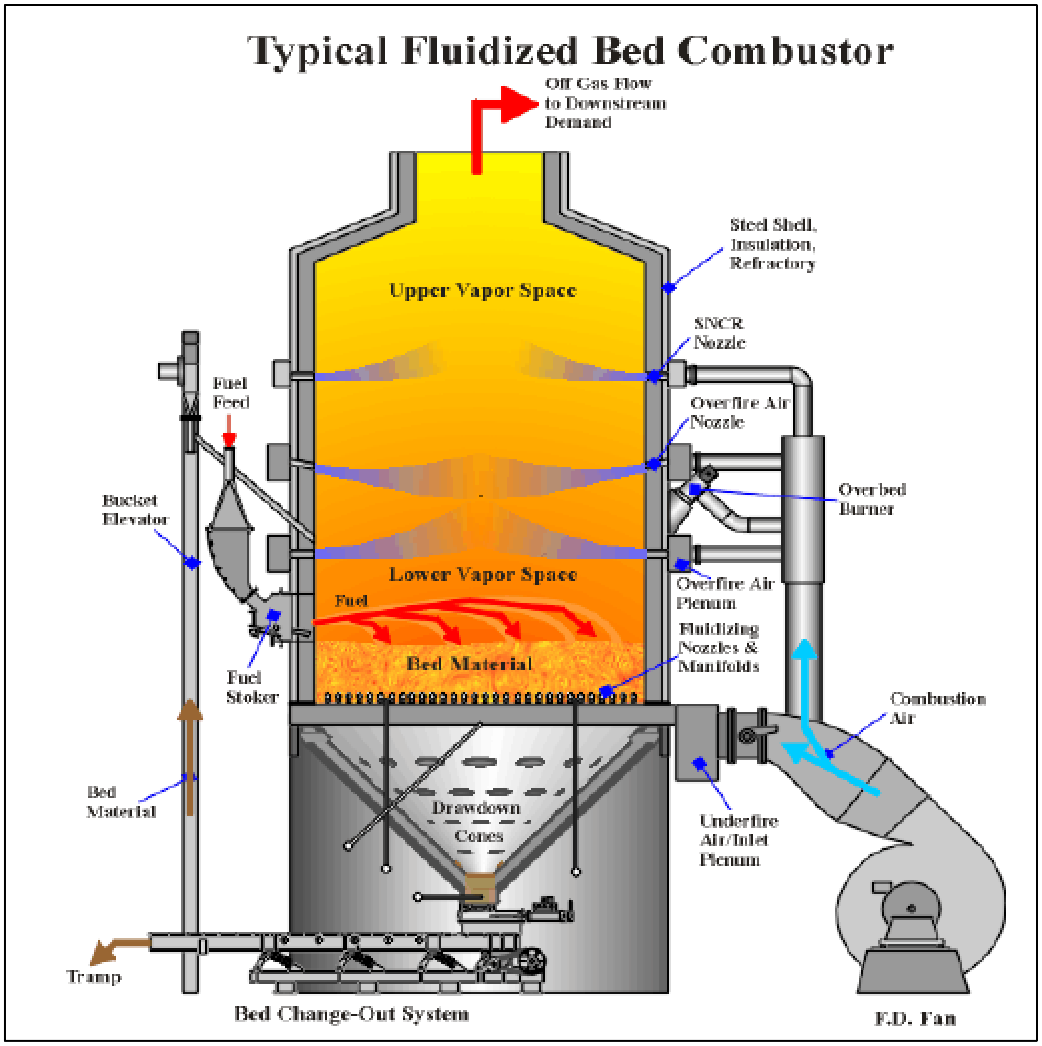


Figure 5-13. Biomass Cogeneration Facility fluidized bed combustor from (Bulgarino, 2013).

The U.S. Army has developed a Plasma Ordnance Demilitarization System (PODS), Figure 5-14, for the destruction of pyrotechnic ordnance items including smoke canisters, incendiaries, and high explosives. (Flynn, 2007) This system is capable of processing over 1,300 lbs/hr of smoke canisters with pollution abatement for exhaust and produces a low-leachable non-hazardous vitrified slag.

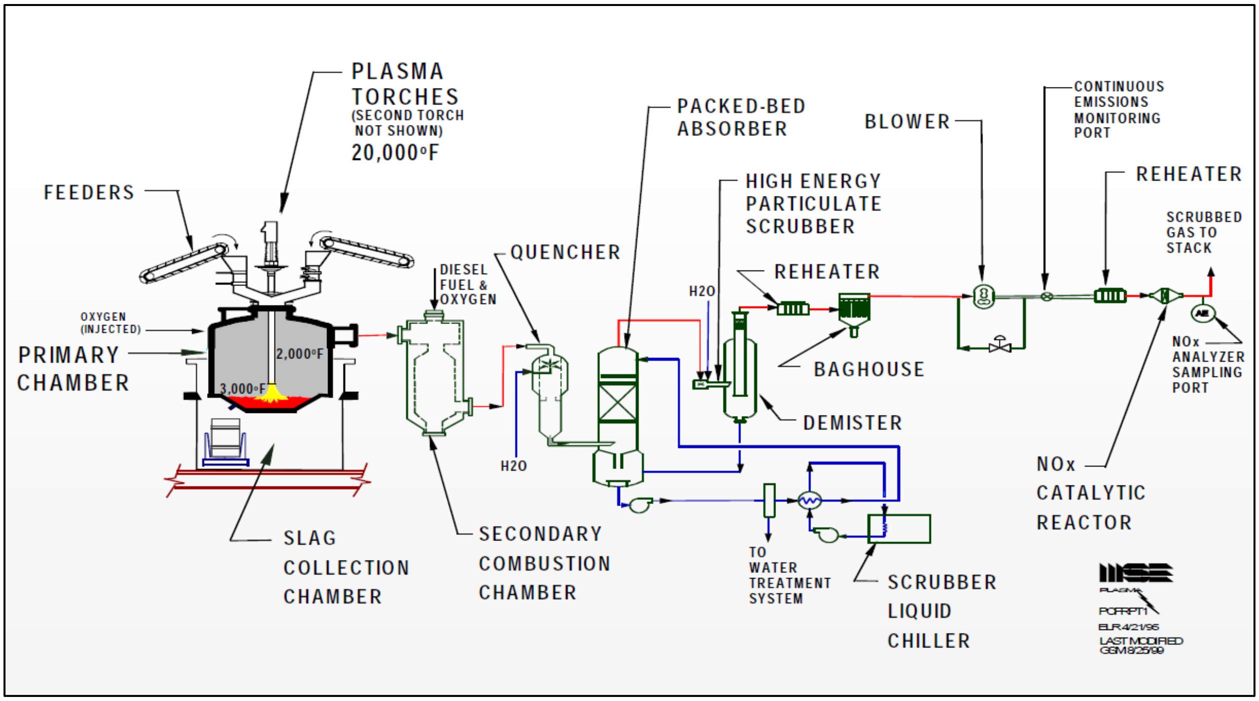


Figure 5-14: Plasma Ordnance Demilitarization System from (Flynn, 2007).

The U.S. Navy is planning to employ the Plasma Arc Waste Destruction System (PAWDS), Figure 5-15, on the new Gerald R. Ford-class aircraft carrier to process all combustible solid waste generated on the ship. It has been tested for processing at a rate of 430 lbs/hr or 6,800 lbs/day surrogate Navy waste mixtures into synthesis gas (syngas).

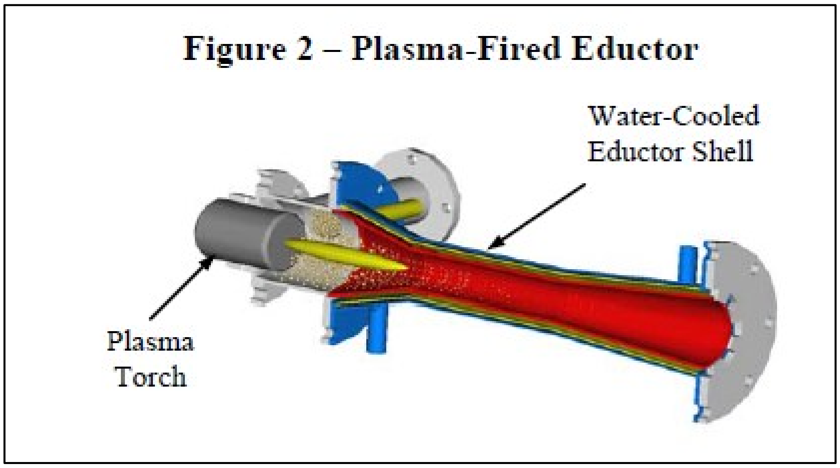


Figure 5-15: Plasma Arc Waste Destruction System (PAWDS) Ref (Aida Kaldas, 2008)

Several research groups are investigating the use of microwave heating for the gasification and vitrification of a variety of waste forms including sewage sludge, tires, plastic packaging, and medical wastes. (J.A. Menendez, 2005) (T.J. Appleton, 2005) Work by Westinghouse Savannah River Company was referenced for the disposition of electronic circuitry and components, medical wastes, radioactive materials and tires. (T.J. Appleton, 2005).

The gasification method has several benefits that include industrial scale projects have treated hazardous wastes, explosives, and carbonaceous materials with pollution abatement controls and it has the capability to vitrify the remaining non-volatile components. While the science and technology for gasification might be sound for several applications, there certainly would need to be more development of the process for processing of nuclear grade graphite and components. This will be true with any method or combination selected to address the issue.

Another approach to the remediation of nuclear graphite is through a combination of electrochemical techniques conducted in molten salts such as Li_2CO_3, K_2CO_3, Na_2CO_3, and Li_2O. Direct carbon fuel cell technology developed for electrical power generation is capable of electrochemically oxidizing solid carbon into CO_2 in molten carbonates. (Dianxue Cao, 2007) (K. Hemmes, 2013) The basic oxidation reaction proceeds as:

$$C + 2CO_3^{2-} \longrightarrow 3CO_2 + 4e^-$$

Similar to gaseous oxidation, coal was identified to be more reactive than pyrolytic graphite due to the significant factors of poor crystallinity and high lattice disorder.

Conversely, CO_2 has been introduced into molten salts and electrochemically reduced to carbon and oxygen for the processing of industrial exhaust streams. (Koya Otake, 2013) (Huayi Yin, 2013) The basic decomposition reaction proceeds as:

$$CO_2 + O^{2-} = CO_3^{2-}$$
$$CO_3^{2-} + 4e^- = C + 3O^{2-}$$

The reduced carbon is deposited as nanometer sized aggregates of amorphous carbon and rod shaped graphite crystals. (Koya Otake, 2013) The use of electrochemical methods could be configured to allow for the oxidation of graphite, isolating the fuel particles followed by the reduction of the CO_2 into a solid carbon form to sequester the ^{14}C. Additional research would be needed to determine the viability of this approach.

It might be prudent to use a combination of methods to maximize efficiency at the various steps from graphite matrix removal to cracking the kernels and finally processing the kernels into a manageable form.

6.0 Summary

Depending on the goals of the project there are several existing and potential methods for the removal of the graphite matrix and processing of fuel kernels that should be investigated. There are some methods that will require more testing and development before pilot-scale or full-scale implementation is possible. Other methods are capable of rapid implementation even if they are not the optimal methods. Simple tests could be developed and executed for the potential methods for either elimination or further development.

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