PNNL-32969

Plan for Developing TRISO Fuel Processing Technologies

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Beric E Wells

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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Abstract

This Plan demonstrates the availability of technologies for processing TRISO used nuclear fuel for waste management and actinide recovery purposes. These technologies are judged to be at a very low level of technology readiness and as such they constitute a fertile research area for the DOE-NE's Office of Materials and Chemical Technologies. Strategies to mature the technologies to a point where they can reasonably be considered in engineering alternatives analyses typically involve laboratory-scale tests using fuel simulant to characterize process streams and demonstrate key engineering features. Several criteria are available to help selecting candidate technologies for further maturation.

Summary

The United States Department of Energy Office of Nuclear Energy (DOE-NE), Office of Materials and Chemical Technologies is leading development of technologies for processing Used Nuclear Fuel (UNF) to help inform future decisions regarding the nuclear fuel cycle. While Light Water Reactors have been deployed throughout the world for electricity production for many years, several advanced reactor concepts are currently being progressed with a view to deployment in the next decade. High Temperature Gas-cooled Reactors (HTGRs) hold promise in offering potentially wider applications in addition to electricity generation such as hydrogen production. These reactors achieve their high temperatures in part by the fuel's enhanced integrity in containing fission products and neutron moderation using relatively large quantities of graphite. The fuel's integrity is proffered by coating individual fuel particles in layers of pyrolytic carbon and silicon carbide. Such fuel is known as Tri-structural ISOtropic (TRISO). Breaching these layers, however, to access the used fuel to recover the actinides is not possible with the technologies currently deployed in the nuclear industry. Additionally, separation and separate disposal of the graphite moderator potentially presents benefits for waste management and represents a new technical challenge. Therefore, this task was initiated to establish a strategy to help guide DOE-NE in:

- identifying and maturing options for separating graphite from TRISO UNF so that this material can be recycled or disposed of as low-level waste; and,
- recovery of actinides from TRISO UNF for recycling into the nuclear fuel cycle to produce additional electrical power.

TRISO fuel consists of fuel kernels that are coated with pyrolytic carbon and silicon carbide to form the fuel particles. These particles are cast into cylindrical compacts or spheres with graphite. The compacts are inserted into channels formed in the graphite blocks. Neutron activation of carbon-13 and nitrogen-14 in the graphite leads to the formation of carbon-14. Therefore, the graphite moderator also becomes radioactive despite it being isolated from the fuel by the particle coatings.

Processing TRISO UNF has never been industrially undertaken, but various approaches have been evaluated up to pilot scale since the fuel was developed in the 1970s. Early approaches relied on burning the graphite and either releasing the carbon (contaminated with carbon-14) to the air as carbon dioxide or to the ocean as lithium carbonate precipitate formed from aqueous scrubbing of the combustor off-gas. Grinding and milling were then proposed for breaching the particle coatings to expose the fuel that could then be processed by established techniques to recover uranium and plutonium for recycling.

More recent research has focused on separating the graphite while containing it in solid form and non-mechanical means of breaching the particle coatings. With one exception, these approaches have not progressed beyond laboratory-scale tests demonstrating basic feasibility and typically are applicable either to graphite block deconsolidation or coating breach but not both. A pyrometallurgical approach has been developed to pilot scale at the Savannah River Site. The technologies and their published claims to applicability are summarized in the table below.

	Block and compact deconsolidation	Pyrolytic carbon breach	Silicon carbide breach
Acid Intercalation	✓		
Thermal Shock	✓	✓	✓
Acoustical		✓	✓
Hot Chlorine Gas		✓	✓
Pyrometallurgical		✓	✓
Combustion		✓	
Electrolytic – Constant Current	✓		
Electrolytic – Pulsed Current	✓		

Strategies to mature the technologies to a point where they could be reasonably considered in engineering alternatives evaluations largely involve laboratory-scale tests with appropriate simulated UNF. Simulant design is an important consideration and should account for the projected and desired processing characteristics of actual UNF with the specific technology being developed. The design of TRISO UNF simulants is an important topic by itself given the fuel's unique form and material integrity. Importantly, technologies need to be demonstrated that integrate solid-solid separation of graphite from fuel particles and kernels from coatings. Process streams including off-gas and liquid need to be characterized and tests should demonstrate key engineering features.

The applicable technologies being at a very early stage of maturation means evaluation criteria for selecting which to progress are helpful to target resources. Evaluation criteria include:

- Technology robustness (the extent to which performance varies with process conditions)
- Adaptability (considering ongoing improvements to TRISO fuel integrity)
- Integration with established processes for actinide recovery
- Hazard control
- Waste management
- Practicability of technology maturation for deployment
- Engineering for remote operations.

This Plan demonstrates the availability of technologies for processing TRISO UNF for waste management and actinide recovery purposes. These technologies are judged to be at a very low level of technology readiness and as such they constitute a fertile research area for the DOE-NE's Office of Materials and Chemical Technologies.

Acknowledgments

This work was sponsored by the U.S. Department of Energy Office of Nuclear Energy through the Nuclear Fuel Cycle and Supply Chain office. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC05-76RL01830.

Acronyms and Abbreviations

DOE-NE	Department of Energy Office of Nuclear Energy
GTCC	Greater Than Class C
LLW	Low Level Waste
LWR	Light Water Reactor
HTGR	High Temperature Gas-Cooled Reactor
LWR	Light Water Reactor
PUREX	Plutonium Uranium Reduction Extraction
TALSPEAK	Trivalent Actinide-Lanthanide Separations by Phosphorus Reagent Extraction from Aqueous ‘K’omplexes
SRNL	Savannah River National Laboratory
TRISO	Tri-structural ISOtropic
TRL	Technology Readiness Level
TRUEX	Transuranium Extraction
UNF	Used Nuclear Fuel

Contents

Figures

Tables

1.0 Introduction

1.1 Background

Aqueous separation technologies have been successfully used to recover and recycle uranium and plutonium from irradiated commercial Light Water Reactor (LWR) used nuclear fuel (UNF) most notably in Europe. Uranium and plutonium recycle results in increased power production from mined uranium resources and contributes to the national energy security of the country recycling their UNF. In addition, appropriately processing the UNF reduces the volume of high-level waste requiring geologic disposal and there are potential benefits in reducing the radiotoxicity of the disposed material. Processing the UNF to also separate the minor actinides for transmutation results in further improving the utilization of a geologic repository by reducing the long-term heat load. In the United States, the current approach to managing UNF is once-through, with it being stored at the reactor sites while a geological repository is established for its disposal. The United States Department of Energy Office of Nuclear Energy (DOE-NE), Office of Materials and Chemical Technologies is leading development of technologies for processing UNF to help inform future decisions regarding the nuclear fuel cycle.

While LWRs have been deployed throughout the world for electricity production for many years, several advanced reactor concepts are currently being progressed with a view to deployment in the next decade. High Temperature Gas-cooled Reactors (HTGRs) hold promise in offering potentially wider applications in addition to electricity generation such as hydrogen production. These reactors achieve their high temperatures in part by the fuel's enhanced integrity in containing fission products, which also allows for significantly higher burnup than achievable in LWRs, and neutron moderation using relatively large quantities of graphite. The fuel's integrity is proffered by coating individual fuel particles in layers of pyrolytic carbon and silicon carbide. Such fuel is known as Tri-structural ISOtropic (TRISO). Breaching these layers, however, to access the used fuel to recover the actinides is not possible with the reprocessing technologies currently deployed in the nuclear industry. Additionally, separation and separate disposal of the graphite moderator potentially presents benefits for waste management and represents a new technical challenge. Therefore, this task was initiated to establish a strategy to help guide DOE-NE in identifying and maturing options for recovery of actinides from TRISO UNF for recycling into the nuclear fuel cycle to produce additional electrical power.

1.2 Scope

This Plan is directed at providing DOE-NE with guidance on approaches for developing technologies for processing TRISO UNF within the context of its Office of Materials and Chemical Technologies. Therefore, the Plan focuses on maturing technologies to the point when commercial engineering organizations could consider them for industrial application. Maturation objectives beyond that preliminary level of maturity are typically driven by what is needed to underpin design and operations. Therefore, for DOE-NE to establish those objectives is considered unreasonably speculative at this time.

The Plan does not speculate on potential technologies beyond what's already been considered and reported. Additionally, the Plan does not explicitly judge between reported technologies given their low maturity although advantages and disadvantages are described for each when they are clear from available test results and expert opinion. Nonetheless, best practice criteria based on expert opinion are provided in the Plan to help with selecting and guiding technologies for maturation given DOE's limited resources.

While not specifically discussed, some of the technologies and criteria described in this Plan are also applicable to processing unirradiated TRISO fuel to recover High Assay Low Enriched Uranium, for example, from fresh fuel that has failed quality requirements.

2.0 The Technology Maturation Process

The DOE (2015) have established a guide for maturing technologies and integrating the maturation process into their standard processes for acquiring capital assets. Specifically, the Guide assists individuals and teams involved in conducting Technology Readiness Assessments and developing Technology Maturation Plans. Certain of the concepts outlined by DOE (2015) have been used by the authors to assess Technology Readiness Levels (TRLs) and then broadly develop strategies for initial maturation.

The readiness or maturity of a technology for a specific project life cycle phase is indicated by its TRL. There are nine TRLs indicative of increasing maturity as described in Table 2-1 below.

Table 2-1. Technology Readiness Levels

Relative Level of Technology Development	TRL	Definition
System Operations	9	Actual system operated over the full range of expected mission conditions.
System Commissioning	8	Actual system completed and qualified through test and demonstration.
	7	Full-scale, similar (prototypical) system demonstrated in relevant environment.
Technology Demonstration	6	Engineering/pilot-scale, similar (prototypical) system validation in relevant environment.
Technology Development	5	Laboratory scale, similar system validation in relevant environment.
	4	Component and/or system validation in laboratory environment.
Research to Prove Feasibility	3	Analytical and experimental critical function and/or characteristic proof of concept.
	2	Technology concept and/or application formulated.
Basic Technology Research	1	Basic principles observed and reported.

In terms of the capital asset life cycle, a TRL of 4 is required for it to be considered for the first Critical Decision of Alternative Selection. Therefore, maturing technologies to a TRL 4 is considered by the authors as a reasonable target for the types of programs currently funded by DOE-NE. At a TRL of 4, initial technology development, technologies could then be considered sufficiently mature for consideration for commercial or industrial application. At that point, a complete Technology Maturation Plan would be prepared to increase maturity to a TRL of 6, which is recommended for the third critical decision to complete design and start construction.

The descriptions provided by DOE (2015) for each TRL up to 4 are provided in Table 2-2.

Table 2-2. Descriptions of Initial TRLs

Relative Level of Technology Development	TRL	Description
Technology Development	4	The basic technological components are integrated to establish that the pieces will work together. This is relatively “low fidelity” compared with the eventual system. Examples include integration of ad hoc hardware in a laboratory and testing with a range of simulants and small-scale tests on actual feedstock. Supporting information includes the results of the integrated experiments and estimates of how the experimental components and experimental test results differ from the expected system performance goals. TRL 4-6 represent the bridge from scientific research to engineering. TRL 4 is the first step in determining whether the individual components will work together as a system. The laboratory system will probably be a mix of on hand equipment and a few special purpose components that may require special handling, calibration, or alignment to get them to function.
Research to Prove Feasibility	3	Active research and development is initiated. This includes analytical studies and laboratory-scale studies to physically validate the analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representatively tested with simulants. Supporting information includes results of laboratory tests performed to measure parameters of interest and comparison to analytical predictions for critical subsystems. At TRL 3 the work has moved beyond the paper phase to experimental work that verifies that the concept works as expected on simulants. Components of the technology are validated, but there is no attempt to integrate the components into a complete system. Modeling and simulation may be used to complement physical experiments.
	2	Once basic principles are observed, practical applications can be invented. Applications are speculative, and there may be no proof or detailed analysis to support the assumptions. Examples are still limited to analytic studies. Supporting information includes publications or other references that outline the application being considered and that provide analysis to support the concept. The step up from TRL 1 to TRL 2 moves the ideas from pure to applied research. Most of the work is analytical or paper studies with the emphasis on understanding the science better. Experimental work is designed to corroborate the basic scientific observations made during TRL 1 work.
Basic Technology Research	1	This is the lowest level of technology readiness. Scientific research begins to be translated into applied R&D. Examples might include paper studies of a technology’s basic properties or experimental work that consists mainly of observations of the physical world. Supporting information includes published research or other references that identify the principles that underlie the technology.

There is considerable subjectivity in assigning TRLs to maturing technologies, which is heavily influenced by a project’s risk tolerance, context and objectives. Nonetheless, the target TRL of 4 should be commensurate with the information needed to make informed technology selection decisions and complete initial conceptual design for industrial application.

DOE (2015) also define some of the specific terms used in their descriptions of each TRL. In terms of scale, the DOE (2015) suggest laboratory or bench scale systems, applicable to the lower TRLs, can be anything less than tenth scale but acknowledge engineering judgment should be applied in determining what is most appropriate. The fourth TRL represents the point when a scaled prototype should be demonstrated while lower TRLs use ‘pieces’ or components of the complete prototype. The fourth TRL also represents the point when the technology is demonstrated with actual feedstock but a limited range can be expected at this TRL. Otherwise, tests at lower TRLs use a range of simulants. The selection and formulation of simulants is important because testing, ultimately on a prototype at the fourth level, up to this point should prove the technology ‘works’ at an engineering level. What is meant by ‘works’ is again subjective but typically tests that advance a technology to the fourth TRL should at least inform understanding the technology’s capability to absorb process and feedstock variability or, colloquially, its ‘robustness’.

This Plan, therefore, represents an informed description of the approaches for advancing currently maturing technologies applicable to actinide recovery from TRISO UNF to the fourth level. This necessarily involves assigning initial TRLs to the currently maturing technologies identified in the published literature and identifying the types of tests needed to advance them to the fourth level. As already mentioned, simulant formulation is an important consideration and the significant factors affecting it are described in this plan.

3.0 Description of TRISO Fuel and Challenges to Actinide Recovery

Many descriptions of TRISO fuel already exist in the published literature and various websites but a summary is included here to provide the reader with immediate context for this work. The development of TRISO fuel was driven by the desire to increase burnup. More extensive fission of fissile plutonium and reducing the downtime for refueling reactors are two reasons to operate to higher burnup. The cladding of conventional LWR fuel is in-service life-limiting component and TRISO fuel looks to improve in-service life by more effective containment of fission products.

As shown in Figure 3-1, TRISO fuel consists of particles approximately 1 mm diameter that are formed into 'compacts' of either cylindrical shape (~12 mm diameter and ~25 mm long) or spheres ('pebbles') ~60 mm diameter. Compacts are fabricated by mixing graphite powder with a phenolic resin, then adding the TRISO particles and isostatically pressing the mixture. A heat treatment sometimes is applied. The cylindrical compacts are loaded into prismatic graphite blocks to fuel a HTGR and can be considered like the subassemblies of conventional LWR fuel. The pebbles are also coated with graphite (approximately 5 mm thick) and would be used to fuel a 'pebble-bed reactor'. In the HTGR, inert gas (e.g., helium) passes through channels in the block or around the pebbles to cool the fuel and provide heat transfer for power conversion.

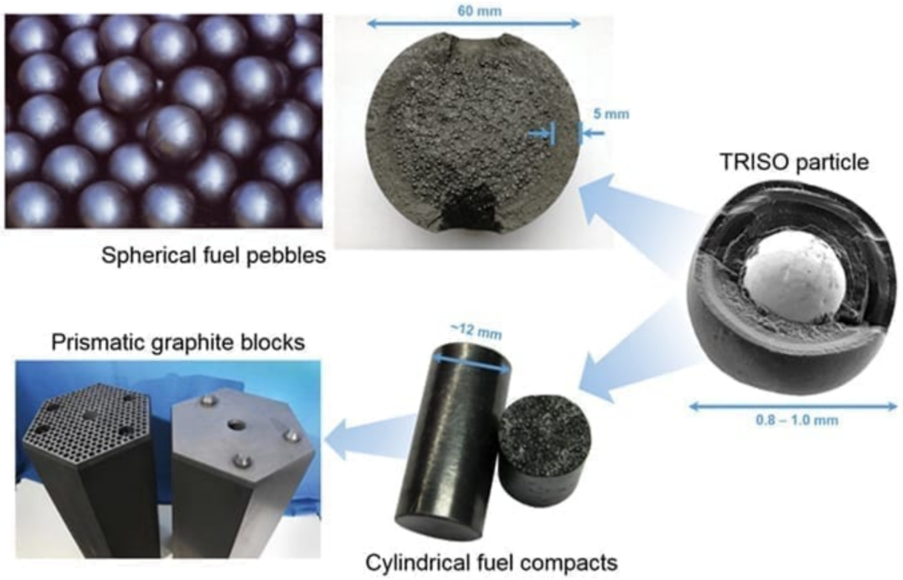

Figure 3-1. TRISO Fuel Assemblies (Source: US Department of Energy. Reproduced in POWER at https://www.powermag.com/the-allure-of-triso-nuclear-fuel-explained/)

Important to this plan is a consideration of the fuel particles further illustrated in Figure 3-2. The inner core or 'kernel' of the particle consists of uranium dioxide or uranium carbide between 350 and 500 μm in diameter. The kernels are successively coated with layers of silicon carbide and pyrolytic carbon:

- A 'buffer' approximately 100 μm thick of 50% dense pyrolytic carbon that provides space for gas accumulation.

- Another, more dense layer of pyrolytic carbon approximately 40 μm thick that protects the particle surface from chloride during the subsequent deposition of silicon carbide.
- The main structural layer of silicon carbide, approximately 35 μm thick, which is primarily for retaining non-gaseous fission products.
- A final layer of pyrolytic carbon approximately 40 μm thick that protects the silicon carbide during handling and provides a surface for bonding the particle into the compact or pebble.

Both the inner and outer layers of pyrolytic carbon also contribute to gas retention.

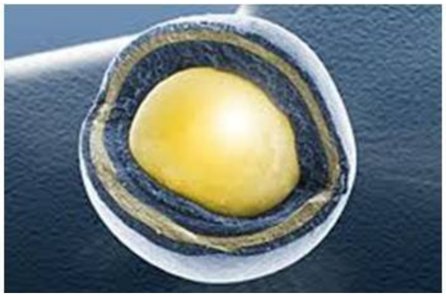

Figure 3-2. The TRISO fuel particle (Source: US Department of Energy)

There are two primary challenges to recovering the actinides from the TRISO fuel that differentiate it from LWR fuel:

- Clearly the superior structure in the successive coatings of the fuel to retain gas and non-gaseous fission products also present significant barriers to accessing the fuel kernel for actinide recovery. Pyrolytic carbon and silicon carbide are chemically inert by design (from the standpoint of in-service fuel performance) that would make industrially mature UNF treatment processes ineffective. That is, the nitric acid normally used to dissolve LWR fuel cannot penetrate through the pyrolytic carbon and silicon carbide layers.
- A relatively considerable quantity of graphite is used in HTGRs and other TRISO-fueled reactors that present a secondary waste challenge. For example, Lotts et al. (1992) have postulated the volume of HTGR UNF dispositioned as a whole block in a geologic repository would be approximately 25 times that of conventional LWR fuel for the same quantity of heavy metal. That and the combustible nature of the graphite are arguably reasons for processing the HTGR UNF. Nonetheless, if the fuel can be cleanly separated from the graphite blocks then the latter could conceivably be dispositioned as low level waste (LLW). However, notwithstanding the challenges in making a ‘clean’ separation by mechanical means to minimize contamination, another challenge is the carbon-14 content. Tzelepi et al. (2020) describe how nitrogen and oxygen impurities and the stable carbon, itself, in the graphite can all be neutron-activated to carbon-14, which is a limiting constituent for the LLW classification. Maintaining the carbon-14 concentration low enough for the de-fueled graphite blocks to be disposed of as LLW could be a significant factor in limiting the practical burnup achievable with TRISO fuel. Notwithstanding graphite’s combustibility, it is important to note that the graphite is already an ideal waste form for the carbon being insoluble with high carbon density.

4.0 Historical Approaches to Processing TRISO UNF

This section of the plan is intended to provide historical context to the description of the main outcomes of the study in the next section. The report by Del Cul et al. (2002) provides a convenient demarcation between historic and current approaches to recovering actinides from TRISO UNF.

Early approaches to reprocessing HTGR fuel are characterized by a reliance on mechanical handling to crush the fuel particles and combustion to remove the graphite. For example, Heath and Spaeth (1975) described work, federally funded but performed by General Atomic, in which industrially available mechanical crushers and fluidized bed systems were experimentally demonstrated with unirradiated TRISO fuel blocks. Exposed fuel particles could then be processed using conventional means by leaching in nitric acid and separating the actinides using a PUREX-type solvent extraction flowsheet.

Similar methods (crushing and combustion) were advocated by Hoogen and Merz (1982) nearly a decade later but carbon-14 capture and sequestration from the off-gas was acknowledged as a likely requirement. The authors recommended carbon-14 capture using a calcium hydroxide scrubber to form calcium carbonate that could then, reflective of accepted practice at the time, be dispositioned by controlled dumping on the ocean floor.

By the time Lotts et al. (1992) produced their report, combustion to separate the graphite and pyrolytic carbon had become considered likely unacceptable mainly because of the increase in waste volume arising from generating calcium carbonate and the need for land disposal. To minimize that waste volume, the authors described mechanical separation of the fuel compacts from the graphite blocks using special tools. The blocks could then be dispositioned as LLW assuming the carbon-14 content was sufficiently low.

As already mentioned, the work of Del Cul et al. (2002) represents a landmark in the approaches considered for reprocessing TRISO fuel. Because of the waste management challenges associated with combustion, these authors recommend separating the fuel compacts from the graphite blocks like Lotts et al. (1992) but then mechanical crushing and milling to breach the pyrolytic carbon and silicon carbide layers of the particles. Various mechanical crushing and milling machines were considered. Additionally, various solid-solid separation approaches were discussed to separate the exposed fuel and silicon carbide from the relatively light graphite fragments. The exposed fuel could then be leached in nitric acid and subsequently processed using a PUREX flowsheet. Crushing and milling of the fuel could likely be less intensive if a pyroprocess flowsheet using a molten salt bath is employed rather than the PUREX flowsheet.

Technologies explored subsequent to the study of Del Cul et al. (2002) have principally focused on non-mechanical means to breach the pyrolytic carbon and silicon carbide layers and expose the fuel. This trend is reasonable because it is usually the mechanical handling operations of UNF processing plants that determine its reliability and availability and its cost effectiveness. Additionally, mechanical handling equipment typically requires routine maintenance and repair that necessitates including capabilities for remote access to the equipment. These recent non-mechanical approaches are evaluated in the next section and are the focus of this plan.

5.0 Recent Approaches to Processing TRISO UNF and Maturation Recommendations

5.1 Mechanical and Physical Approaches

5.1.1 Acid Intercalation

Though using chemical reagents and graphite oxidation, this technology is categorized as a physical process here in that the graphite of compacts is exfoliated to expose the fuel particles. Guittonneau et al. (2010) used mixtures of concentrated sulfuric and nitric acids with microwave assistance at a power of 1400 W, a temperature of 200 ^{o}C and pressure of 55 bar. Only sulfuric acid at room temperature was tested without microwave assistance but preceded with oxidation of the graphite with hydrogen peroxide. The acid essentially infiltrates between the oxidized graphene layers and accumulation of gas causes those layers to exfoliate. Both approaches were successful in separating the TRISO particles from the graphite. The microwave treatment appeared to cause partial oxidation of the exterior pyrolytic carbon coating of the particles.

Guittonneau et al. (2010) evaluated a limited number of process conditions; the ratio of nitric and sulfuric acids and the volume of hydrogen peroxide. Other process conditions that could be evaluated include the microwave power, temperature, pressure and exposure duration. Their work was also limited to simulated TRISO compacts using zirconium instead of uranium. The authors highlight the need to test the approaches with irradiated compacts to study the effects of irradiation on the process. They also identify the need to understand the role of the amorphous carbon resulting from the phenolic resin used in fabricating the compacts.

There is a significant understanding of the fundamental graphite intercalation process as summarized by Guittonneau et al. (2010). The author's work did exhibit success albeit with simulated fuel compacts and so this technology is assigned to the low end of the second TRL. The recommended maturation strategy and objectives for each TRL are described in Table 5-1. Most of the work to advance from the second to fourth TRLs can be accomplished with single simulated compacts and aims to understand the effects of process variables on the separability of the fuel particles from the graphite. The strategic objective at the fourth TRL should be to demonstrate the potential of the technology for industrial application at a small scale using unirradiated compacts.

Table 5-1. Acid Intercalation Technology Maturation Strategy and Objectives

Relative Level of Technology Development	TRL	Maturation Strategy and Objectives
Basic Technology Research	1	Accomplished for this level.
Research to Prove Feasibility	2	The technology is considered to have a readiness at the low end of this level. The main objective to advance from this level is to improve understanding of the effects of the main process variables: acid concentrations and volumes, and exposure duration. The main effect would be the degree to which the fuel particles are separated from the graphite as observed in the bulk solids mixture. Tests would continue with simulated TRISO fuel compacts at laboratory scale (i.e., experiments using a single compact).
	3	Investigation of the effects of secondary process variables including microwave power, temperature and pressure at laboratory scale (i.e., experiments using a single compact). Physical separability of the fuel particles from the graphite should be assessed at given conditions of intercalation. Work continues with simulated fuel compacts.
Technology Development	4	The primary objective at this level is to demonstrate an integrated process that exfoliates the graphite and then separates the fuel particles. Process conditions are selected based on the results from experiments at the second and third TRLs. Most tests should again be undertaken at the laboratory scale with single compacts. However, initial multiple compact tests should be undertaken to demonstrate the scale-up of the technology and its potential industrial application. Tests at this level should be undertaken with actual non-irradiated compacts though integrated systems would be commissioned with simulated compacts.

5.1.2 Thermal Shock

Lee et al. (2008) evaluated a method of thermal shock to breach the silicon carbide layer. Graphite blocks coated with silicon layers approximately 30 μm thick were subject to cycles of heating in a furnace and then rapid cooling in a liquid nitrogen bath. The temperature difference ranged from 900 to 1300 ^{o}C and up to 30 cycles were applied. Thermal shock by itself was insufficient to breach the silicon carbide layer but the hardness was substantially reduced. Furthermore, scanning electron microscopy indicated the indentation caused in evaluating the hardness produced substantial fractures at 30 thermal cycles. As a result, the authors speculate that the fission gases accumulated in the particle should be sufficient to rupture it. However, they also point out the force needed to crush the particle is substantially reduced after the thermal shock if the pressure from fission gas is insufficient.

Guittonneau et al. (2008) investigated the effect of thermal cycling on compacts manufactured from simulated fuel in which zirconium oxide kernels replaced the fuel. Their initial experiments limited the temperature swing from hot to cold environments to approximately 500^{o}C to avoid oxidizing the graphite. These experiments were unsuccessful in damaging the compact.

Application of a larger temperature swing like that used by Lee at al. (2008) oxidized the graphite and outer pyrolytic carbon but the particles remaining coated with silicon carbide appeared undamaged. Had Guittoneau et al. (2008) measured the hardness or tested the strength of the remaining particles that they would have observed similar trends as Lee et al. (2008) seems likely. Guittoneau et al. (2008) also evaluated the effect of thermal shock by reversing the cycle. Compacts were immersed in liquid nitrogen and then in warm water or a temperature swing of approximately 280 ^{o}C. In this case, the compacts readily fragmented but produced few individual fuel particles free of adhering graphite. The authors speculate the liquid nitrogen enters into the graphite pores and then rapidly expands when the compact is placed in hot water with similar effect to the chemical intercalation technology described in section 5.1.1.

Thermal shock by itself appears inappropriate for processing TRISO compacts if the release of carbon dioxide is to be avoided unless the cold to hot thermal swing could be made to work. There appears to be some promise for the method to enable accumulated fission gases to breach the silicon carbide layer. However, applicability of the method would need demonstration with either irradiated fuel or simulated fuel that internally generated and accumulated gas by chemical means. A TRL of unity is applied to this technology given the basic concept has been identified and tested on a graphite block coated with silicon carbide but not yet with simulated or actual TRISO fuel particles.

There are two potential applications of this technology: compact graphite intercalation and weakening the silicon carbide layer with concomitant combustion of the outer pyrolytic carbon layer. Maturing the graphite intercalation technology would be broadly like that described in Table 5-1 for acid intercalation but with temperature, pressure and exposure time being the primary process variables. Maturation of the technology for weakening the silicon carbide coating, if selected as the only means of doing so, appears to be dependent on developing a suitable simulated irradiated fuel particle that exhibits internal gas pressurization. The recommended maturation strategy and objectives are described in Table 5-2 below. Alternatively, the technology could be combined with another such as acoustical (see section 5.1.3 below) that could then fully breach the silicon carbide coating using the weaknesses introduced by thermal cycling.

Table 5-2. Silicon Carbide Thermal Shock Technology Maturation Strategy and Objectives

Relative Level of Technology Development	TRL	Maturation Strategy and Objectives
Basic Technology Research	1	Accomplished for this level.
Research to Prove Feasibility	2	The main objective to advance from this level is to improve understanding of the effects of the main process variables: temperature range and number of cycles. The main effect would be the degree to which the silicon carbide layer is weakened. Tests would necessarily be performed using graphite blocks coated with silicon carbide to provide sufficient area for measurement of the resulting hardness or integrity of the coating. However, tests with simulated fuel particles would evaluate combustion of the outer pyrolytic carbon layer. Parallel efforts would focus on the supplementary technology for making the final breach of the silicon carbide coating. Alternatively, or additionally, the design of a simulated fuel particle that chemically simulates its pressurization from fission gas would be initiated here ready for testing at the third TRL.
	3	Work at this level should focus on testing the technology with simulated fuel particles at laboratory scale. Tests would include those using simulated particles with simulated fission gas pressurization. Alternatively, microscopic techniques could be employed to examine the silicon carbide coating surface deformation. Parallel efforts would focus on the supplementary technology for making the final breach of the silicon carbide coating.
Technology Development	4	The primary objective at this level is to demonstrate, for potential industrial application, an integrated process that completely breaches the silicon carbide coating. Process conditions are selected based on the results from experiments at the second and third TRLs. At this level, the thermal shock and selected supplementary technology would be integrated and the process conditions of each optimized to the benefit of the total system. If a supplementary technology was not selected, then tests should at least be performed with non-irradiated actual fuel particles chemically simulating the fission gas pressurization. Fabricating such a simulant that also provides confidence in the results to advance the TRL might be challenging. In that case, tests with actual irradiated fuel particles may be required to advance beyond the fourth TRL.

5.1.3 Acoustical

Guittonneau et al. (2010) conducted some preliminary experiments investigating the effect of ultrasound on graphite particles produced from crushing compacts and suspended in water. High resolution transmission electronic microscopy showed the particles reduced in size from several hundred microns to several tens. The authors speculated a process of cavitation bubble implosion tears apart the graphite sheets. Key process variables are the ultrasonic intensity and residence time; particle size decreases with increases in either variable. Furthermore, hydroxyl and hydrogen radicals produced from water sonolysis reacted with the carbon to form mainly aromatic organic compounds such as phenol. The pH also decreased from approximately neutral to plateau at ~4 with increasing residence time likely because of dissolved nitrogen being oxidized via sonolysis.

More recently at the DOE-sponsored workshop on innovative separations research and development needs for advanced fuel cycles (August 30th through September 21st, 2021), staff from the Idaho National Laboratory discussed the application of acoustic cavitation for penetrating the graphite and silicon carbide coatings of TRISO fuel particles (DOE, 2022). An internally funded effort by Idaho National Laboratory allowed the researchers to demonstrate penetration of the carbon and silicon carbide layers of simulated TRISO particles. An update on this work was presented by Grimes et al. (2022) and showed that sonication of unirradiated TRISO particles with a uranium carbide kernel allowed for leaching uranium (as uranyl) into dilute nitric acid, thus demonstrating that the silicon carbide layer could be breached with this method. Such penetration then enables the fuel to be dissolved and processed by conventional means. This work has thus far been preliminary in nature; the uniformity with which the particles were breached or the morphology of the breached layers post-sonication is unknown.

A TRL of 1 is applied to this technology given the basic concept has been identified and tested on graphite powder and in a single instance with simulated and actual TRISO fuel particles. Of note is the formation of organic material. This phenomenon deserves particular attention given the effect of organic material on the hydrodynamic and mass transfer performance of downstream liquid-liquid extraction processes for actinide separations. Key process variables are the ultrasonic density and residence time, the composition of the suspending medium and the role of dissolved gases. Guittonneau et al. (2010) also mention bubbling with hydrogen gas as a process variable.

The summary technology maturation approach is outlined in Table 5-3 below. Not clear is whether the acoustical approach is appropriate for deconsolidating fuel compacts or just for breaching the TRISO coatings. The ability to deconsolidate fuel compacts should be established early in the program. If not, then parallel efforts would be directed at maturing such an approach and demonstrating an integrated process to achieve the fourth TRL.

Table 5-3. Acoustic Technology Maturation Strategy and Objectives

Relative Level of Technology Development	TRL	Maturation Strategy and Objectives
Basic Technology Research	1	Accomplished for this level.
Research to Prove Feasibility	2	The main objective to advance from this level is to improve understanding of the effects of the main process variables: ultrasonic density and residence time. The main effect would be the degree to which the silicon carbide and carbon layers are breached. Tests would be performed using simulated fuel particles. Establish whether the technique is appropriate to deconsolidate compacts.
	3	Work at this level should focus on optimizing the composition of the suspending medium and further understanding the role of dissolved gases. Any organic compounds formed should be identified.
Technology Development	4	The primary objective at this level is to demonstrate, for potential industrial application, an integrated process incorporating any other compact deconsolidation technology that deconsolidates the compact and breaches the silicon carbide and carbon layers. Process conditions are selected based on the results from experiments at the second and third TRLs. At this level, the acoustic and selected supplementary technology would be integrated and the process conditions of each optimized to the benefit of the total system. Tests at this level should be undertaken with actual non-irradiated compacts though integrated systems would be commissioned with simulated compacts.

5.1.4 High Pressure Jet

As well as thermal shock, Guittonneau et al. (2008) also described their work investigating the use of high-pressure jets to break up TRISO compacts to separate the fuel from the graphite, which could be dispositioned as low-level waste if uncontaminated with fuel. A consideration of the fraction of damaged fuel particles is, therefore, key. A water jet at a pressure of 1670 bar (24,200 psi) was directed at a compact maintained in a filter to allow only graphite particles to pass. The technology was very effective at removing graphite but there were significant fractions of damaged fuel particles, which in some cases had lost all coatings to expose the zirconium oxide kernel. The authors speculate that at least some fuel particle damage was caused by high-speed collisions between each other and with the filter mesh. Jet orientation relative to the compact, water pressure and the distance between the nozzle and compact are all process variables needing to be optimized. Two of the three tests undertaken that could be considered duplicative showed significant variation in the fraction of damaged fuel particles, which indicates this technology may be challenging to control and optimize. The authors also speculate that liquid nitrogen instead of water may provide better performance.

Although the tests were performed with simulated compacts, a TRL of 1 is applied given only one of the three tests could be considered successful (in terms of leaving no exposed simulated fuel kernels) and there appears to be only the single publication. The key challenge for this approach is one of control to preserve the integrity of the fuel particles so that they can be cleanly separated from the graphite. Contamination of the compact deconsolidated graphite above LLW limits would not in itself prevent subsequent recovery of the actinides but would negate any benefit in reducing the HLW volume.

The authors of this report do not consider this approach as viable given the unsuccessful, albeit limited, tests completed to date, the apparent control issues already described and envisioned full-scale jet configuration challenges. A technology maturation approach was, therefore, not developed.

5.2 Chemical Approaches

5.2.1 Pyrometallurgical

A pyrometallurgical approach to breaching the silicon carbide and pyrolytic carbon coatings using a eutectic mixture of lithium, sodium and potassium carbonate salts was postulated by Masson et al. (2006) but not experimentally demonstrated. They go on to consider the feasibility of recovering the actinides from the exposed fuel particles by electrodeposition.

Lee et al. (2008) completed limited tests using a ‘glassy’ carbon rod and a graphite block coated with silicon carbide by a chemical vapor deposition process. A molten salt mixture of magnesium and lithium chlorides was used. The authors interpreted their results to suggest the electrochemically formed lithium ions intercalates the carbon structure and causes it to exfoliate. The magnesium ions react with silicon carbide to form magnesium silicide and carbon.

Pierce (2017) has described a patented technology that uses alkaline metal nitrate and hydroxide salts at between 400 and 700°C. The graphite is digested by the nitrate salt to produce carbon dioxide while the metal hydroxide reacts with the silicon carbide to yield the metal silicate. Note that this technology is combined in the patent with that described below in section 5.2.3 that uses nitric acid gas to digest the graphite. However, the metal salt approach appears not to be pursued for implementation.

This technology is assigned a TRL of 1 given it essentially exists in theory only albeit with some very limited experimental demonstration with relevant material (though not simulated TRISO fuel).

5.2.2 Hot Chlorine Gas Reaction

Masson et al. (2006) experimentally demonstrated the feasibility of reacting the silicon carbide coating with chlorine gas at 950°C to produce gaseous silicon tetrachloride. The silicon tetrachloride goes on to react with oxygen to produce silicon dioxide and chlorine gas. Furthermore, the pyrolytic carbon coating is oxidized to carbon dioxide and/or monoxide. Preliminary tests were completed with yttria-stabilized zirconia particles coated with one layer each of pyrolytic carbon and silicon carbide. This technology is assigned a partial TRL of 2 given the limited experimental work completed with simulated fuel particles.

This technology is only applicable to breaching the fuel particle coatings since complete combustion of the compacts would generate an undesirable volume of secondary LLW from scrubbing the off-gas. Although effective, the technology uses a high temperature and chlorine gas that constitute significant hazards needing to be controlled at industrial scale. An off-gas treatment system also requires consideration given the carbon will be combusted at high temperature with potential products of incomplete combustion, including chlorinated products, present. Nonetheless, the recommended technology maturation approach is outlined in Table 5-4.

Table 5-4. Hot Chlorine Gas Reaction Technology Maturation Strategy and Objectives

Relative Level of Technology Development	TRL	Maturation Strategy and Objectives
Basic Technology Research	1	Accomplished for this level.
Research to Prove Feasibility	2	Tests completed to date have been successful. The effects of residence time and temperature need to be evaluated on the rates at which the individual layers are breached. Tests should be completed using complete simulated fuel particles (i.e., two layers of pyrolytic carbon).
	3	Work at this level should investigate the extent of combustion of the carbon layers as a function of temperature and residence time. Products of incomplete combustion should be identified and any additional off-gas treatment beyond carbon monoxide/dioxide capture established.
Technology Development	4	The primary objective at this level is to demonstrate, for potential industrial application, an integrated process incorporating compact deconsolidation and off-gas treatment technologies. Process conditions are selected based on the results from experiments at the second and third TRLs. At this level, the technologies would be integrated and the process conditions of each optimized to the benefit of the total system. Tests at this level should be undertaken with actual non-irradiated compacts though integrated systems would be commissioned with simulated compacts.

5.2.3 Combustion

Once the bulk of the graphite (either the block or pebble) is separated from the fuel then combustion becomes practical to remove the outer pyrolytic carbon layer and residual graphite because the subsequent secondary waste is of comparatively small volume.

Masson et al. (2006) described some very initial tests in which a cold crucible melter was used under an oxygen atmosphere to combust graphite fragments. The authors state successive thermal cycles are being investigated for de-coating the fuel particles by combustion and oxidation of the graphite and pyrocarbon layers without ignition of the materials. The inference here is the initial tests proved problematic in controlling any tendency to ignition. No further work was found published and direct communication with one of the authors indicated the work was terminated.

Zhu et al. (2012) heat-treated unirradiated fuel particles with oxygen at 750°C. The fuel particles had previously been processed through a crusher designed to break open the particles to expose the intact uranium dioxide kernels. The primary reason for the heat treatment was actually to convert the uranium dioxide to triuranium octoxide (i.e., voloxidation) in preparation for conversion to uranyl nitrate with liquid dinitrogen tetraoxide and then supercritical extraction with tri-butyl phosphate.

Of a similar theme, work is ongoing at the Savannah River National Laboratory (SRNL) to mature a graphite digestion technology for implementation in the H-Canyon facility on Savannah River Site. The implemented process will treat irradiated HTGR pebbles from Germany to recover the uranium. Much of the work is not published due to export controls but Pierce (2017) describes the technology in which nitric acid gas at between 400 and 700°C is used to digest the graphite to produce primarily carbon dioxide gas. An independent Technology Readiness Assessment conducted in 2015 and described by Pierce (2022) provides TRLs of four for the digestion technology and its ancillary processes such as off-gas treatment and crushing to breach the silicon carbide layer. The same Assessment rated the integrated process at a TRL of three. Since the Assessment, Pierce (2022) indicates laboratory-scale tests with multiple unirradiated pebbles and engineering scale tests with graphite-only pebbles and simulated fission products have been completed. No fully integrated tests have been completed to date. The final disposed volume of carbon-14 precipitate is larger than what the graphite would be, as already described. While this technology is relatively advanced, it is being developed to treat a relatively small and defined quantity of TRISO UNF and the waste volume from off-gas carbon capture is not significant compared to the larger quantities arising from the plant and site operations. Therefore, for wider applicability to processing of TRISO UNF arising from future more widespread HTGR operations, the technology, as applied to graphite combustion, may not allow an economic operation because of the secondary waste volume.

Notwithstanding the uncertainty in using a cold crucible melter, combustion technology is comparatively mature and warrants a TRL of three given its demonstration with unirradiated actual fuel and its simplicity. However, it is only applicable to breaching the pyrolytic carbon layers and so must be combined with others to deconsolidate the compact and breach the silicon carbide. As shown in Table 5-5, it’s the integration of the combustion technology with the others that is required to achieve a TRL of four. This general assessment is consistent with that promulgated by Pierce (2022).

Table 5-5. Pyrolytic Carbon Combustion Technology Maturation Strategy and Objectives

Relative Level of Technology Development	TRL	Maturation Strategy and Objectives
Basic Technology Research	1	Accomplished for this level.
Research to Prove Feasibility	2	Accomplished for this level.
	3	Accomplished for this level.
Technology Development	4	The primary objective at this level is to demonstrate, for potential industrial application, an integrated process incorporating compact deconsolidation and silicon carbide breach technologies. Process conditions are selected based on the results from experiments at the second and third TRLs. At this level, the technologies would be integrated and the process conditions of each optimized to the benefit of the total system. Tests at this level should be undertaken with actual non-irradiated compacts though integrated systems would be commissioned with simulated compacts.

5.3 Electrolytic Approaches

Removal of graphite from TRISO cylindrical compacts or spheres is advantageous over chemical oxidation of the bulk graphite due to minimized production of $^{14}CO_2$ and ^{14}CO, and the potential to contain other gaseous fission products during the removal of the bulk graphite. Electrochemical decarbonization can be accomplished through one of two means: the pulsing of high currents and voltages through an aqueous solution containing the carbon matrix (Masson et al. 2006), or by coupling the compact/pebble to an electrical lead so it can serve as the anode in an electrochemical cell. The cell would then be run at a comparatively low current and voltage through the compact until disintegration is achieved. Under either scenario, the bulk graphite is reduced to rubble freeing the TRISO particles. The graphite rubble and TRISO particles can then be separated by physical means. Each of these two methods have advantages and drawbacks.

The low voltage/current method is amenable to fundamental studies and optimization in a laboratory setting during low TRL level studies as it can be easily accomplished with low-cost commercially available power supplies. With this method the cell geometry requires a uniform electric field across the entire anode to prevent deconsolidation at dissimilar rates across the TRISO compact/sphere. Uneven electrochemical reaction on an electrode surface due to nonuniform electric fields is often referred to as electrochemical shadowing. In severe cases, electrochemical shadowing could allow large pieces of the compact or sphere to break off prior to deconsolidation. If a single TRISO geometry is to be processed then challenges such as electrochemical shadowing could be overcome through engineering efforts such as designing highly symmetric electrochemical cells, rotation of the anode (TRISO compact), or gradual submersion of the anode in the electrolyte during deconsolidation.

The pulsed current technology does not need to have electrical leads attached, should allow for high throughput in a remote handled facility, will work with multiple (sphere vs compact) shaped materials, and alleviates concerns of electrochemical shadowing. Consequently, there are several advantages to this method for a remote handled facility, but it is more challenging to accomplish for preliminary fundamental settings in a laboratory setting.

5.3.1 Constant Current

During low voltage/current electrochemical deconsolidation where the graphite matrix is treated as the anode, anions from either acid or salt dissolved in solution will preferentially collect around the anode followed by penetration of the anions into the graphite along grain boundaries. The graphite will form intercalation compounds with these anions. Additionally, partial oxidation of the graphite to form hydroxyl, epoxide, ketone, and carboxylic acid functional groups along the grain boundaries cause internal stress that leads to fracturing of the graphite along grain boundaries. This technology is immature but is by far the more studied of the two approaches to electrochemical decarbonization of TRISO fuel. For application to irradiated fuel elements, there are multiple engineering challenges that would need to be overcome for a remote handled facility including attachment of the electrochemical leads, and prevention of electrochemical shadowing.

5.3.1.1 Spherical Compacts

Cyclic voltammetry has been employed in combination with Raman spectroscopy and X-ray diffraction to investigate the mechanism by which deconsolidation of the graphite occurs. (G. Zhang, Wen, and Wang 2016) The cause of graphite fragmentation is attributed to multiple mechanistic pathways including anion intercalation, gas evolution, and water electrolysis causing mechanical force along the graphite lattice. The electrooxidation process also produces various graphite oxide species which likely contribute to lattice strain. As such, these variables are likely to effect both the particle size, and disintegration rate.

The effect of electric current density on the deconsolidation rate of zirconium dioxide simulated spherical fuel elements has been studied.(Chen et al. 2016) In order to achieve uniform disintegration, the spherical fuel element was first processed by electrolyzing the element while it was partially submerged in electrolyte and rotating it. This produced a cylindrical element after partial deconsolidation which was then rotated to be orthogonal to the horizon and progressively submerged during the remaining electrolysis. The necessity of this type of manipulation shows the challenge associated with preventing electrochemical shadowing for spherical TRISO elements. Currents of 2 A (2.4 V), 7 A (6.4 V), 10 A (8.5 V), and 13A (10.7 V) were tested with nitric acid as electrolyte. The disintegration rate (gh^{-1}) was found to be linearly dependent on the applied current when the current is maintained below 20 A, which suggests the number of electrons passed is the determining factor in the carbon deconsolidation and not the applied voltage within the range of voltages tested. Graphite fragments gained 7-15 % mass with a minor portion of the additional mass being attributed to graphite nitrate compounds and the majority attributable to partial oxidation of the graphite based on elemental analysis and XPS results. In general, the particle size of the resulting rubble decreased with increasing current. A follow-up study from the same group examined the mechanism of decarbonization under similar conditions but varied the content of glassy carbon present in the sample.(C. Zhang et al. 2019) The study concludes that increased glassy carbon content increases the amount of graphene oxide compounds in the final rubble, and that the deconsolidation occurs as a result of expansion stress at the grain boundaries from both anion intercalation and the formation of graphene oxides. This demonstrates that changes in the graphite structure during irradiation will need to be understood in order to develop carbon-based waste forms after electrochemical deconsolidation.

The effect of electrolyte, both acid and salt forms have been examined for the deconsolidation rate of simulated spherical elements.(Tian et al. 2009) Of the tested anions, the rate of disintegration is higher for nitrate than for dihydrogen phosphate or sulfate. However, within nitrate-based electrolytes the disintegration rate varies minimally with cation identity. While nitric acid (2.4 $gA^{-1}h^{-1}$) shows a slightly faster disintegration rate than sodium nitrate (2.0 $gA^{-1}h^{-1}$) or ammonium nitrate (2.0 $gA^{-1}h^{-1}$) at the same current and concentration, the nitrate salts would be less corrosive to processing equipment in a shielded facility. A further consideration is that nitric acid and ammonium nitrate can both be decomposed to gaseous molecules (the 'CHON' principle), which reduces the burden of secondary waste disposal.

The temperature (15-40 °C, current density (0.1-0.3 A/cm^2), and electrolyte concentration (2-6 M sodium nitrate) effect on electrochemical disintegration was examined in 2013 with spherical elements which contained UO_2 TRISO particles. (Tian, Wen, and Chen 2013) They observed no obvious changes in the rate with respect to temperature or electrolyte concentration but there was a large dependance on the current density. This mostly agrees with a previous study from the same group which examined simulated spherical elements in ammonium nitrate electrolyte and found only a slight dependance on temperature and electrolyte concentration.(Tian, Wen, and Chen 2010)

5.3.1.2 Cylindrical Blocks and Compacts

Two low voltage DC graphite deconsolidation tests of cylindrical fuel blocks have been performed in nitric acid as part of the post irradiation examination (PIE) for AGR-1 ((Baldwin et al. 2014)) and AGR-2 fuel.(Hunn et al. 2018) The objective of the studies was not to optimize electrolytic disintegration conditions, but rather to separate the TRISO particles from the bulk graphite so that they could be analyzed for loss of fission products during irradiation. At the end of the electrolytic disintegration, all silicon carbide layers were found to be intact, which suggests that during operations of a plant, release of fission products into the bulk graphite stream will be minimal.

5.3.2 Pulsed Currents

The pulsed current technology described by Masson et al. (2006) is applicable to desegregation of the blocks and compacts to yield the fuel particles and removal of the outer pyrolytic carbon layer. The technology has apparently been used to clean equipment and involves exposing the target to high voltage, high intensity pulses between 200 and 500 kV and discharge currents between 10 and 20 kA. The target is immersed in water and the energy deposited into the block and compact to result in a local temperature of ~10,000 K and local pressure of ~10^{10} Pa, which fractures the solid. Alternatively, electrical energy deposited in the water creates a shock wave that has a similar effect. The technology has only been tested on graphite blocks 27 mm square and 40 mm thick. The blocks were completely reduced to small fragments after about a minute with about 90% of the fragments by mass up to 1000 μm in size. The number of pulses and their frequency, voltage and current are the important process variables. Process conditions would need to be optimized to first desegregate the compact to leave the fuel particles intact so they can be separated and then processed to remove the pyrolytic carbon coating. The control of hazards associated with the high energy intensity will be key to large-scale application of this technology.

5.3.3 Technology Readiness Evaluation and Maturation Approach

A TRL of unity is applied to the pulsed current technology given the limited tests and that the target material was not truly simulated TRISO compacts. However, this technology offers several promising features which make it attractive for further development. Particularly the ease of scale up and the likely facile adaptation to a remote handled facility. The constant current technology is somewhat more advanced, particularly for spherical compacts and TRL of two is applied. The maturation approaches are summarized in Table 5-6. Notable is the degree of commonality between the technologies and the need for appropriate simulated material that simulates irradiation effects.

Table 5-6. Constant and Pulsed Current Technology Maturation Strategy and Objectives

Relative Level of Technology Development	**TRL**	**Maturation Strategy and Objectives**	
		Constant Current	**Pulsed Current**
Basic Technology Research	1	Accomplished for this level.	This is the current state of the pulsed current method, with one demonstration being available in the literature. The technology would advance in this level by better understanding how the mechanism of the pulsed method varies from the low voltage and constant current method and the degree that the graphite is oxidized. Additionally, studies to determine the degree of graphite oxidation by comparison to the constant current methods could prove useful for subsequent waste form development for the graphite.
Research to Prove Feasibility	2	The constant current method is considered to be low within this level. To advance within this level, additional tests are needed with compacts containing TRISO particles in which the size of the rubble is analyzed. Further additional tests are needed with both cylindrical compacts and spherical compacts to determine cell geometry and rotation speeds to eliminate electrochemical shadowing.	At this level the particle size distribution of the deconsolidated graphite should be determined as a function of pulse width, current, voltage and the duration of the experiment using simulated compacts and pebbles.
		For both technologies, development of appropriate simulated material that, in particular, simulates the ‘glassy carbon’ generated from irradiation will be needed. Initial simulated material could simply be graphite blocks or spheres and ultimately progressing to full simulated fuel including simulated or unirradiated TRISO particles simulating irradiation effects.	
	3	At this level, the technology will need engineering design development and testing for feasibility with respect to scale up and throughput. A test at a scale appropriate for demonstrating the engineering concepts would be warranted using simulated compacts.	For the pulsed current technology, the ability to handle multiple fuel element designs within the same equipment should be demonstrated. Studies to determine the impacts of the imparted energy on the integrity (corrosion and fatigue) of vessel construction material will be important in demonstrating feasibility. These studies could be undertaken at small scale with coupons.
		For both constant current and pulsed methods, the ability to physically separate TRISO particles from electrolytically generated rubble needs to be developed. In general, the ability to separate particles by size and density by mechanical means is well developed but will need to be optimized for this process.	
Technology Development	4	The primary objective at this level for both technologies will be testing with unirradiated TRISO fuel compacts while monitoring the solution and off-gas for escape of fission products and integrated with TRISO particle separation from the graphite fragments. Some preliminary tests with irradiated TRISO fuel compacts would help to prove or calibrate the results from simulated material. The separated particles should be examined to determine relative proportions of exposed layers (pyrolytic carbon versus silicon carbide) for the irradiated fuel samples.	

5.4 Summary of Applicable Technologies

The previous sections have provided summaries of the technologies so far tested for processing TRISO UNF. Many of these technologies have application to more than one component of the fuel. Categorization of the technologies is summarized in Table 5-7, which shows thermal shock to be the most widely applicable and acoustical and hot chlorine gas reaction applicable to all the fuel particle's layers.

Table 5-7. Summary of Technology Applications

	Block and compact deconsolidation	Pyrolytic carbon breach	Silicon carbide breach
Acid Intercalation	✓		
Thermal Shock	✓	✓	✓
Acoustical		✓	✓
Hot Chlorine Gas		✓	✓
Pyrometallurgical		✓	✓
Combustion		✓	
Electrolytic – Constant Current	✓		
Electrolytic – Pulsed Current	✓		

5.5 Approaches to Separating Carbon-14 from Irradiated Graphite

This section describes two technologies at very early stages of development appropriate for separating carbon-14 from stable carbon. Both technologies are ranked at the very low end of the first TRL but are briefly described here given their applicability to processing TRISO UNF. Maturation strategies and objectives for these technologies are not provided given their extreme immaturity.

5.5.1 Microbial Treatment

Preliminary experiments described by Dunzik-Gougar et al. (2008) showed that unspecified microbes became enriched in carbon-14 when mixed with a suspension of natural graphite and carbon-14 diagnostic medical tablets. Further experiments were ongoing at the time of the publication, but nothing further was found published. A TRL of unity is assigned given the experimental work on the simulated, though not prototypic, graphite.

5.5.2 Plasma Chemical Reactions

Mori et al. (2006) described a model-based study whereby carbon-14 was separated through a cascade of plasma reactors. Irradiated graphite in the form of carbon monoxide is fed to the cascade and carbon is deposited on the walls through the disproportionation of vibrationally excited carbon monoxide molecules. The deposit is enriched in carbon-14 because the heavier molecules are preferentially excited. A TRL of unity is appropriate for the technology given theoretical nature of the studies so far.

6.0 Desirable Attributes of TRISO UNF Process Technologies

This section is intended to provide a guide to future technology maturation plans and criteria for selecting proposed new technologies. None of the attributes are intended to have precedence over any other though specific circumstances in a technology's application may warrant their ranking.

6.1 Technology 'Robustness'

This attribute is associated with ease of control and the extent performance varies with varying process conditions. Assuming performance is sufficient then it ideally should be invariant over a broad range of the relevant process conditions and feed composition; e.g., pH, concentration of reagents, temperature, flow rate. For example, very tight control on pH was required of the original Trivalent Actinide-Lanthanide Separations by Phosphorus Reagent Extraction from Aqueous 'K'omplexes (TALSPEAK) liquid-liquid extraction technology for separating lanthanide metals and minor actinides described by Nilsson and Nash (2007). Recognizing this undesirable attribute for industrial application then led to the Advanced TALSPEAK process described by Lumetta et al. (2017) that reduced the pH sensitivity of the technology's performance, thereby improving its robustness.

Key to assessing a technology's robustness is identification of the important process variables and evaluating their impact on performance. This aspect is one important focus of the early TRLs and can, in large part, be accomplished with simulated UNF with confirmatory tests using actual feedstock. The importance of the latter should never be underestimated. For example, Phillips (1989) has described how UNF separations tests with irradiated UNF identified previously unknown complexation between technetium and zirconium leading to undesirable quantities of the former metal appearing in the uranium-plutonium product. Zirconium had not been included in any simulated feeds used in previous tests. The separations flowsheet was subsequently adapted and successfully implemented in the Thermal Oxide Reprocessing Plant at Sellafield in the United Kingdom.

6.2 Technology Adaptability

This attribute refers to a technology's ability to adapt to developments in TRISO fuel. It acknowledges that the advantageous properties of TRISO in containing fission products to extend burn-up while maintaining fuel integrity also render it more challenging to process. There are ongoing programs that look to improve further still the performance of TRISO fuel in the reactor. For example, Porter et al. (2017) have described the effects of adding a zirconium carbide coating (in addition to the silicon carbide coating) while Seibert at al. (2019) showed cracks and crack propagation in the coatings can be reduced by incorporating multi-layered silicon carbide – pyrolytic carbon in place of the single silicon carbide coating. These developments all look to increase the mechanical strength of the silicon carbide coating and, thereby, the integrity of the fuel particle. Therefore, technologies that aim to breach the silicon carbide layer should be adaptable to these improvements and probably not wholly reliant on exploiting cracks, for example. Mechanical crushing, in particular, will require attention in implementation to ensure the techniques and equipment are sufficiently tunable to improvements in the coating strength. In this regard, non-mechanical technologies of breaching the metal carbide coatings probably offer greater advantage in that the process variables are intuitively easier to manipulate.

6.3 Integration with Technologies for Actinide Recovery

At least initially, the quantity of TRISO UNF will likely be quite small compared to that from Light Water Reactors (LWRs). Actinide recovery from TRISO UNF will, therefore, likely be integrated into a facility that would also be recovering actinides from LWR UNF. A variety of technologies are available for actinide recovery although a modified Plutonium Uranium Reduction Extraction (PUREX) coupled with Transuranium Extraction (TRUEX) and TALSPEAK could be considered the ‘state of the art’. A pyrometallurgical approach to deconsolidating the graphite and breaching the particle coatings would ostensibly be challenging from a plant perspective to integrate with liquid-liquid extraction processes for recovering the actinides because the former uses high temperatures and reagents not used in the latter. Alternative head-end technologies for processing LWR UNF should not be discounted. For example, electrolytically assisted dissolution of UNF in nitric acid has been promulgated for several decades and would be compatible with electrolytic graphite deconsolidation.

The graphite digestion technology being developed at SRNL and described by Pierce (2022) is expected to be implemented in H-Canyon on the Savannah River Site. Although a relatively high temperature is used, the nitric acid reagent is also used in H-Canyon, which employs the PUREX technology to recover actinides. The off-gas treatment system proposed for the technology also replicates that in the Defense Waste Processing Facility so that technology maturation is ostensibly minimized.

6.4 Hazard Control

The intentional significant integrity of the TRISO particles almost exclusively requires application of a high-energy or highly chemically reactive technology to access the fuel. In maturing technologies for processing TRISO UNF, therefore, early consideration of hazard control is important since a significant portion of the cost of operating a plant processing nuclear and hazardous material is associated with controlling hazards (i.e., making the plant acceptably safe). In this regard, following are some specific hazard control considerations:

- Technologies demanding or generating low energy or benign chemicals are advantageous. For example, and as already mentioned, the hot chlorine gas reaction technology is arguably unattractive because it requires managing a hazardous chemical (chlorine) and is performed at high temperature.
- Hazard control, especially of chemical by-products, can be accomplished by operating within an envelope that minimize generation of hazardous by-products. For example, important for electrolytic technologies will be managing the hydrogen gas by-product and identifying a preferably broad operating envelope that minimize gas generation.
- The means to shut down the process automatically and instantaneously is advantageous. For example, electrolytic processes terminate upon termination of the power supply.

6.5 Waste Management

The most immediate waste management concern with processing TRISO UNF has already been acknowledged and resolved. Simply burning the graphite, although cleanly separating it from the fuel particles, creates a larger waste volume because the carbon dioxide gas containing carbon-14 must be captured and immobilized for disposal. Such capture and immobilization technologies are already industrially mature but they create a larger waste volume than initially presented by the graphite. This recognition has led to a number of technologies such as those electrolytically based, that deconsolidate the graphite in a solid form.

One of the motives for processing TRISO UNF is to reduce the volume of waste, specifically graphite, that must be dispositioned in a geologic repository. In this regard, many of the technologies reviewed in this Plan aim at deconsolidating the graphite blocks and compacts so the material can be separated from the TRISO fuel particles (which primarily constitute the high-level waste requiring geological disposal). Key for a deconsolidation technology is to ensure the fuel particles remain intact so the graphite does not become contaminated with the used fuel. As an aside, and notwithstanding the potential for fuel contamination, attention must be paid to the carbon-14 content of the graphite since the radionuclide is a determinator for low level waste (LLW) classification. If the carbon-14 concentration is higher than allowed for near-surface disposal as LLW then it would be classified as Greater Than Class C (GTCC). There needs to be a disposal pathway (or pathway to recycle) more straightforward than exists for UNF for GTCC LLW graphite to make processing TRISO UNF attractive unless burnup is constrained to limit the carbon-14 concentration.

Finally, as with any technology processing hazardous or radioactive material, the quantity of reagent that must be added to the process should be minimized to minimize the effluent treatment burden. Furthermore, reagents that create solid wastes should be minimized and preferably consistent with the CHON principle.

6.6 Technology Maturation Beyond TRL 4

Progressing through TRLs from 4 to 6 (when the technology is sufficiently mature for plant start-up) rely increasingly on pilot plants to prove the functionality of the process in prototypic equipment. However, pilot plants intended to process UNF are unattractive to construct and operate due to the expense involved particularly in waste management and hazard control. As described by Phillips (1989), plants like THORP were piloted using full-scale prototypic equipment processing uranium-active simulated UNF, large scale (1:250) prototypic equipment processing plutonium-active simulated UNF and much smaller scale (1:6,250) near-prototypic equipment with actual UNF. The liquid extraction equipment used on THORP (pulsed columns) proved scale-able with confidence without the need to demonstrate them with actual or highly active simulated UNF. Although this Plan is limited to the early TRLs, developing a maturation approach beyond TRL 4 that relies on equipment scale-up using low active simulated UNF and limiting chemistry development at small-scale is important. In part, this attribute implies technologies with performance that can be scientifically understood in their fundamental chemical and physical aspects are desirable to minimize engineering ‘surprises’.

Associated with this attribute is the need for appropriate simulated UNF. A chemical or physical simulated may not be sufficient in itself to mature a technology and developing and qualifying performance-based simulants then becomes important. One example already provided is the technology relying on fission product gas pressure to help breach the coatings. Such a simulant might be difficult to develop without introducing other non-representative features. Other features potentially challenging to simulate might be the effects of irradiation; formation of ‘glassy’ carbon be one example. Technologies that can use ‘simple’ simulants to mature them especially at larger scale are then more attractive.

6.7 Engineering for Remote Operations

Finally, TRISO UNF must be processed using remotely operated and maintained equipment. Chemical technologies are preferred over electromechanical technologies because the latter necessarily require routine maintenance and replacement for which space and remote handling capabilities must be included in the plant. In this regard, technologies that grind TRISO fuel particles to breach the coatings are least desirable.

7.0 Considerations for Used Nuclear Fuel Simulant Design

As discussed, this Plan represents an informed description of the approaches for advancing currently maturing technologies applicable to actinide recovery from TRISO UNF to the fourth TRL. To progress to TRL 4 (Technology Development), Research to Prove Feasibility, which includes analytical studies (TRL 2) and experimental work that verifies that the concept works as expected on simulants (TRL 3), must be completed. Simulant formulation is a key consideration because of the expense and hazards associated with the radioactive TRISO UNF and its availability.

While non-radioactive simulants make handling far easier, the risks and benefits of developing accurate and reliable simulants are discussed in NRC (2009):

> “The absence of adequate understanding of the behavior of process streams can necessitate overly conservative and costly process designs to minimize the risk of a process failure or the risk of unrecognized safety issues, which as a worst case can render a facility inoperable with the actual radioactive waste it was intended to process.”

The American Society for Testing and Materials (ASTM) Method C1750-21 provides general considerations for the development, verification, validation, and documentation of high-level waste sludge simulants. However, the underpinning concepts are equally applicable to UNF. As described by that standard, the first step should be to determine the purpose of the simulant, whereby the key processing properties required for development of the simulant can then be identified. Simulant requirements relative to those properties are then specified, and simulant design and preparation methodology follow. Finalization of the simulant design is achieved once verification and validation that the simulant meets the requirements throughout the testing duration is completed.

Section 5.4 provides a summary of the applicable technologies for actinide recovery from TRISO UNF. The applicable technologies include acid intercalation, thermal shock, acoustical, hot chlorine gas, pyrometallurgical, electrolytic, and pulsed current. Thermal shock is noted to be the most widely applicable technology, and acoustical and hot chlorine gas reaction are noted as applicable to all the fuel particle’s layers. From the descriptions provided for these technologies, the key processing properties required for development of a TRISO UNF simulant can vary significantly depending on the technology or technologies selected. For example, the acid intercalation technology uses chemical reagents and graphite oxidation to exfoliate the graphite of compacts to expose the fuel particles, whereas the use of the thermal shock technology can be dependent on fission gases accumulated in the particle. The former technology therefore can require the UNF simulant to have the same chemical interaction characteristics while the latter technology can require the UNF simulant to have the same off-gas production response.

The current application of simulants for TRISO kernel fabrication, TRISO particle fabrication and development, accident condition evaluations, degradation testing, separate effects testing, and for consolidation process development provides examples of the different kernel simulants that may be selected depending on the key processing properties of interest. For a TRISO fuel kernel fabrication process alternative evaluation, Vasudevamurthy et al. (2015) selected tungsten carbide to simulate uranium carbide on account of its economical availability, lack of contamination risks, and the similarities of its melting point with uranium carbide. Kim et al. (2020) selected zirconium dioxide for the fuel kernel for TRISO particle coating process development as they note it has “similar physical and thermal properties” to a uranium dioxide fuel kernel. Jolly et al. (2016) likewise selected zirconium dioxide for the fuel kernel simulant for use in separate effects testing and for consolidation process development. They noted that characterization of the produced TRISO particles met the desired coating property specifications.

With respect to accident condition evaluation, Cho and Lu (2021) also employed zirconium dioxide for the fuel kernel simulant. They investigated oxidation behaviors of the simulant TRISO fuel particles under accident conditions for HTGRs wherein the silicon carbide layer can be exposed to water vapor. Lowe et al. (2015) used zirconium dioxide fuel kernel simulant TRISO particles to illustrate how recent advances in laboratory - based X-ray computed tomography instruments allow the examination of the particles at the nano and micro-scales in three dimensions for both the characterization of individual TRISO layers with variations in thickness as well as their subsequent interactions to allow manufacturing validation as well as assisting in working towards a mechanistic understanding of fabrication and in-service issues.

As a final example with an alternate actual fuel kernel, Bhattacharya et al. (2021) found particles of tungsten carbide cobalt cemented carbide were an ideal simulant to test coating mechanical and thermal stability when exposed to different temperatures for the development of a robust metal diffusion barrier coating for TRISO particles with $UC_{1-x}N_x$ fuel kernels. Similar dimensions and thermal expansion properties, thermal conductivity and “most importantly” surface chemistry were noted as key performance parameters.

The effects the TRISO fuel is exposed during irradiation must also be accounted for with respect to the key processing properties for the selected technology. That is, the kernel and coating layers must have properties germane for actinide recovery from TRISO UNF. For example, the thermal conductivity of the fuel kernel is a function of the burnup (e.g., Geelhood et al. 2020), and the strength and Weibull modulus of the pyrolytic carbon and silicon carbon layers is affected by irradiation (e.g., IAEA 2012).

While simulants should be designed for the specific technology under consideration, this subject deserves some particular attention in a general sense to identify appropriate material, forms and fabrication techniques. Laboratory-scale studies can be performed with simulants and unirradiated fuel and then verified with irradiated fuel. A source of irradiated fuel needs to be identified but fuel may not have to be irradiated in a reactor to induce the key irradiation effects important to the technology under consideration. For large scale tests of a technology’s engineering features, simulants and unirradiated fuel are typically used understanding they are qualified with irradiated fuel at laboratory-scale. Therefore, while not important through TRL 4 *per se*, development and qualification of simulants at the low TRLs is certainly desirable and, arguably, needed in preparing for further technology maturation.

8.0 Conclusions

This Plan has demonstrated the availability of technologies for processing TRISO UNF for waste management and actinide recovery purposes. These technologies are judged to be at a very low level of technology readiness and as such they constitute a fertile research area for the DOE-NE's Office of Materials and Chemical Technologies. Specific conclusions for the aspects addressed in this Plan are outlined below.

- Application of TRISO fuel for power generation presents clear advantages over established metal-clad fuels because they can remain in the reactor longer. However, the large quantities of graphite moderator containing carbon-14 present a waste disposal challenge while the robust coatings applied to the fuel kernels present physical barriers to actinide recovery by established approaches.

- Technologies and approaches for processing TRISO UNF have been under development since the advent of the fuel in the 1960s. In general, the technologies and approaches of the 20th century relied on mechanical means, mainly grinding, to access the fuel kernels and were predicated on waste disposal and environmental emissions socially or legally unacceptable today. Mechanical operations in a UNF process plant are generally undesirable because the remote operations leads to a large footprint and special facilities for maintenance. Therefore, these historical approaches are generally not recommended for further development.

- Several physical, chemical and electrolytic technologies have been investigated this century that are consistent with the desirable social and legal attributes of a UNF process plant and show promise for application. Most of these technologies have undergone very limited development and mainly focused on testing for preliminary conceptual feasibility. Therefore, there is considerable work that can be pursued to mature them further for DOE-NE's Office of Materials and Chemical Technologies. Most technologies are applicable to either, but not both, graphite moderator block deconsolidation and particle coating breach. Therefore, some integration of technologies is required if actinide recovery is desired.

- The development and use of simulants in the early technology maturation for DOE-NE's Office of Materials and Chemical Technologies is important notwithstanding actual TRISO UNF being unavailable. Simulant design is an important consideration and should account for the projected and desired processing characteristics of actual UNF with the specific technology being developed. A systematic approach to simulant design is available and recommended.

- There are several criteria that can be used to judge a proposed technologies' potential for application to processing TRISO UNF, including technology 'robustness', technology adaptability, integration with technologies for actinide recovery, hazard control, waste management, technology maturation to demonstration and practicability for remote operations.

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