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Chemical Process Safety at TRISO-Based, Metal-Based, and Salt-Based Fuel Fabrication Facilities: Technical Assessment and Guidance Assessment

Final Report

August 2025

Ricardo D. Torres William J. Ivans Steven M. Short Gregg J. Lumetta Ron P. Omberg Kenneth M. Thomas Mike Y. Toyooka Jake Dorin



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Pacific Northwest National Laboratory Richland, Washington 99354

Executive Summary

As part of efforts to prepare for potential and ongoing safety reviews for licensing of advanced non-light-water reactor fuel cycles, the U.S. Nuclear Regulatory Commission (NRC) tasked Pacific Northwest National Laboratory to prepare an assessment on the state of knowledge of potential chemical processes at fuel cycle facilities supporting the front end of these fuel cycles, and to assess the associated regulatory guidance.

This report provides a technical assessment of chemical process safety considerations to support NRC licensing reviews of fabrication processes for tri-structural isotropic (TRISO) based, metallic-based, and salt-based fuels. The assessments involved collecting publicly available information on the fuel fabrication processes to (i) identify the operational process steps, characteristics and chemicals involved, (ii) identify the physical safety considerations and health safety considerations during licensing reviews of the various process steps, and (iii) collect information to support assessments of severity of accidents and potential mitigative measures to be implemented.

The assessment provides a foundational basis on chemical process safety considerations for advanced fuel fabrication activities, although it is recognized that licensing reviews may necessitate design-specific considerations. The specific conditions under which chemical hazards emerge will require process-specific considerations, highlighting the importance of process-informed interpretation. The assessment also determined that exposure guidelines and limits to assess the consequences of acute exposures are limited for some chemicals, although alternative limits and supplementary information from databases or safety data sheets provide sufficient information to evaluate consequences of acute exposures. In addition, it was identified that metallic and salt fuel fabrication processes may involve beryllium, which is an exposure hazard.

The regulatory framework for the licensing of advanced fuel cycle facilities, per 10 CFR Part 70 Domestic Licensing of Special Nuclear Material, is deemed robust and flexible to address the chemical safety considerations in this report. A review was conducted on various regulatory guidance and technical basis documents. This included reviewing NUREG-1520, Revision 2, Standard Review Plan for Fuel Cycle Facilities License Applications – Final Report and the process descriptions in Appendix A of NUREG/CR-6410, Nuclear Fuel Cycle Facility Accident Analysis Handbook, to address advanced fuel types. As new fuels will involve process-specific chemical uses, process-specific considerations are provided in this report. Additionally, it is noted that the U.S. Department of Energy protective action criteria database includes Temporary Emergency Exposure Limits (TEELs) for process-specific chemicals.

This report provides technical information to support chemical safety assessments of new advanced fuel cycle facilities and identifies technical and safety information to support licensing reviews. No regulatory barriers were identified for the licensing of advanced fuel cycle facilities.

Executive Summary i

Acronyms, Abbreviations and Symbols

°C degree Celsius

% percent μm micrometer

A3-3 graphite binder matrix A3-27 graphite binder matrix

ADUN acid-deficient uranyl nitrate

AEGL Acute Exposure Guideline Level

AGR Advanced Gas Reactor

Al aluminum
Ar argon

atm atmosphere

AVR Arbeitsgemeinschaft Versuchsreaktor

ASME American Society of Mechanical Engineers

Be beryllium

BeF₂ beryllium fluoride BeO beryllium oxide

C carbon

 $(CH_2)_6N_4$ hexamethylenetetramine

CH₂CHCH₃ propylene CH₂O formaldehyde

(CH₃CH₂CH₂CH₂O)₃PO tributyl phosphate

CH₃COOH acetic acid

CH₃SiCl₃ methyltrichlorosilane

CH₄ methane

CCl₄ carbon tetrachloride
CO carbon monoxide
COCl₂ carbonyl dichloride

CO(NH₂)₂ urea

CO₂ carbon dioxide C₂H₂ acetylene

C₂Cl₄ perchloroethylene, tetrachloroethylene

C₃H₆ propylene

C₃Cl₆ hexachloropropene (Cl₂C=CCICCl₃)

C₆H₅OH phenol

 $(C_6H_5OH)_x\cdot(CH_2O)_y$ phenol-formaldehyde polymer / binder

C₈H₁₅NaO₈ Sodium carboxymethyl cellulose

C₈H₁₈O 2-ethyl-1-hexanol

Ca calcium

CFR Code of Federal Regulations

Cl₂ chlorine gas
Cr chromium

CVD chemical vapor deposition

DOE U.S. Department of Energy

EBR Experimental Breeder Reactor

EPA U.S. Environmental Protection Agency
ERPG Emergency Response Planning Guideline

F₂ fluorine gas

Fe iron

FeCl₂ iron (II) chloride

FCM® Fully Ceramic Micro Encapsulated

FHR fluoride salt-cooled high temperature reactor

FMEA Failure Mode and Effects Analysis

Fs fissium g gram

GHS Globally Harmonized System

HALEU high-assay low-enriched uranium

HAZOP Hazard and Operability

H* hydrogen ion, proton

HCI hydrogen chloride

HF hydrogen fluoride, hydrofluoric acid HMTA hexamethylenetetramine, (CH₂)₆N₄

 HNO_3 nitric acid H_2 hydrogen gas

H₂O water

H₂S hydrogen sulfide H₂SO₄ sulfuric acid

HT9 ferritic-martensitic steel

HTGR high temperature gas-cooled reactor

HTR High Temperature Reactor

IDLH Immediately Dangerous to Life or Health

 $\begin{array}{ll} \text{IPyC} & \text{inner pyrolytic carbon} \\ \text{ISA} & \text{Integrated Safety Analysis} \\ \text{K}_2\text{CO}_3 & \text{potassium carbonate} \\ \end{array}$

Kairos Power, LLC

kcal kilocalorie kg kilogram

KMgF₃ parascandolaiteL/D length-to-diameterLEL lower explosive limitLEU low-enriched uranium

Mg magnesium

 $\begin{array}{ll} \text{MgF}_2 & \text{magnesium fluoride} \\ \text{MgO} & \text{magnesium oxide} \\ \text{MgO}_2 & \text{magnesium peroxide} \\ \text{Mg}_3 \text{N}_2 & \text{magnesium nitride} \end{array}$

MgZrO₃ magnesium zirconium oxide

mm millimeter

MMR[®] Micro-Modular Reactor

Mo molybdenum

mol mole

mol% mole percent

MOU Memorandum of Understanding

MPa megapascal

MSR Molten Salt Reactor

MSRE Molten Salt Reactor Experiment

Na sodium

NaCl sodium chloride

NH₃ ammonia

NH₄⁺ ammonium ion

 NH_4CI ammonium chloride $NH_4 \cdot HF_2$ ammonium bifluoride NH_4NO_3 ammonium nitrate NH_4OH ammonium hydroxide

Ni nickel

NIOSH National Institute for Occupational Safety and Health

NNSA National Nuclear Security Administration

NO₃- nitrate

NO_x nitrogen oxide

NQA-1 Nuclear Quality Assurance – 1

NRC U.S. Nuclear Regulatory Commission

OPyC outer pyrolytic carbon

OSHA Occupational Safety and Health Administration

PAC protective action criteria
PERC perchloroethylene, C₂Cl₄

PNNL Pacific Northwest National Laboratory

ppm parts per million

ppm-wt parts per million by weight

Pu plutonium S^{2-} sulfide ion

SDS Safety Data Sheet
SiC silicon carbide
Si(CH₃)₄ tetramethylsilane
SFR sodium fast reactor
SnCl₂ stannous chloride

SO₄²- sulfate

SRP Standard Review Plan

Sv sievert

TBP tributylphosphate TCE trichloroethylene

TDIS thermal diffusion isotopic separation
TEEL Temporary Emergency Exposure Limit
THTR Thorium High Temperature Reactor

TMS tetramethylsilane, Si(CH₃)₄

TRISO tri-structural isotropic

U uranium
²³⁵U uranium-235

UCl₃ uranium trichloride
UCl₄ uranium tetrachloride
UCl₅ uranium pentachloride
UCO uranium oxycarbide

UF₃(OH) uranium trifluoride hydroxide

 $\begin{array}{lll} \text{UF}_4 & & \text{uranium tetrafluoride} \\ \text{UF}_6 & & \text{uranium hexafluoride} \\ \text{UOF}_2 & & \text{uranium oxyfluoride} \\ \text{UO}_2 & & \text{uranium dioxide} \\ \end{array}$

UO₂²⁺ uranyl ion

UO₂(CH₃CO₂)₂ uranyl acetate

 $UO_2[CO(NH_2)_2]_2^{2+}$ uranyl urea complex

 UO_2CI_2 uranyl chloride UO_2F_2 uranyl difluoride

UO₂(NO₃)·6H₂O uranyl nitrate hexahydate

 $UO_2(OH)_2$ uranyl hydroxide UO_3 uranium trioxide

UO₃·2H₂O hydrated uranium trioxide

U₃O₈ triuranium octoxide

USNC Ultra Safe Nuclear Corporation

V volt

wt% weight percent zirconium

 Y_2O_3 yttria, yttrium oxide ZrC zirconium carbide ZrF $_4$ zirconium tetrafluoride ZrO $_2$ zirconium dioxide

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1.0 Introduction

As part of efforts to prepare for potential and ongoing safety reviews for licensing of advanced non-light-water reactor fuel cycles, the U.S. Nuclear Regulatory Commission (NRC) tasked Pacific Northwest National Laboratory (PNNL) to prepare an assessment on the state of knowledge, safety, and regulatory considerations for potential chemical processes at advanced fuel cycle facilities supporting the front end of these fuel cycles. This report discusses chemical processes related to the fabrication of advanced fuel forms, including tri-structural isotropic (TRISO) based fuels, metallic-based fuels, and salt-based fuels. The information is used to assess the safety considerations and hazards from pertinent chemical processes and to identify potential mitigative measures. Various safety review guidance and technical basis documents were also reviewed to identify where new chemicals and new processes are involved for chemical process safety at advanced fuel cycle facilities. Within this report, process-specific considerations and descriptions are provided. Additionally, it is noted that the U.S. Department of Energy (DOE) protective action criteria database includes Temporary Emergency Exposure Limits (TEELs) for process-specific chemicals. The information provided will support efficient licensing reviews. The report was developed in fulfillment of Task Order 31310024S0024, Task 1. Technical Assessment for Advanced Fuel Facilities' Chemical Process Safety and Identification of Potential Regulatory Guide Updates.

1.1 Regulatory Considerations

The regulations in Title 10 of *Code of Federal Regulations* (10 CFR) Part 70, *Domestic Licensing of Special Nuclear Material*, establish procedures and criteria for the issuance of licenses to receive title to, own, acquire, deliver, receive, possess, use, and transfer special nuclear material, as well as establish and provide for the terms and conditions upon which the NRC will issue such licenses (see 10 CFR 70.1(a)). The NRC has issued NUREG-1520, Revision 2 (NRC 2015), which provides guidance to the NRC staff for the safety reviews of fuel cycle facilities to be licensed per the requirements in 10 CFR Part 70, Subpart H, *Additional Requirements for Certain Licensees Authorized to Possess a Critical Mass of Special Nuclear Material*, as applicable (NRC 2024c).

Chemical processes at fuel cycle facilities may involve occupational safety under the purview of both the NRC and the Occupational Safety and Health Administration (OSHA). Accordingly, the NRC and OSHA signed a Memorandum of Understanding (MOU) (NRC-OSHA 2013), which delineates the general areas of responsibility of each agency, describes generally the efforts of the agencies to achieve worker protection at facilities licensed by the NRC, and provides guidelines for coordination of activities regarding occupational safety and health between the two agencies.

The MOU identifies four main types of safety considerations that may be associated with NRC-licensed facilities:

- a. Radiation hazards produced by radioactive materials.
- b. Chemical hazards produced by radioactive materials.
- c. Facility conditions that affect the safety of radioactive materials and thus present an increased radiation risk to workers. For example, conditions that might produce a fire or an explosion and thereby cause a release of radioactive materials or an unsafe condition.

Introduction 1

d. Facility conditions that result in occupational hazards that do not involve the use of licensed radioactive materials (i.e., industrial safety and health hazards). Industrial safety and health hazards may include employee exposure to toxic nonradioactive materials such as beryllium and hazards such as electrical, fall, confined space, and equipment energization hazards.

As indicated in the MOU: "The NRC has broad statutory authority to protect against radiation hazards produced by radioactive materials, chemical hazards produced by radioactive materials, and facility conditions that affect the safety of radioactive materials and thus present an increased radiation risk to workers and the general public." and "NRC does not conduct industrial safety and health inspections at NRC-licensed facilities. However, in the course of inspections of radiological and nuclear safety at such facilities, NRC inspectors may observe industrial safety and health hazards or receive complaints from employees that are within OSHA's authority and responsibility. In such instances, the NRC will bring the matter to the attention of licensee management."

The MOU clarifies that, generally, the NRC has authority and responsibility for occupational health and safety under (a) to (c), while OSHA has authority and responsibility for health and safety under (d).

The safety review of fuel cycle facilities to be licensed per the requirements in 10 CFR Part 70 includes consideration of *hazardous chemicals produced from licensed materials*, which is defined by 10 CFR 70.4 (NRC 2024c), as "substances having licensed material as precursor compound(s) or substances that physically or chemically interact with licensed materials and that are toxic, explosive, flammable, corrosive, or reactive to the extent that they can endanger life or health if not adequately controlled. This includes substances commingled with licensed material such as hydrogen fluoride, which is produced by the reaction of uranium hexafluoride (UF₆) and water. However, it does not include substances that are not yet part of a process with licensed material, such as substances from prior to process addition to licensed material or substances from after process separation from licensed material."

Per NUREG-1520, Revision 2 (NRC 2015), the NRC staff conducts a chemical safety review per 10 CFR Part 70, Subpart H, which includes a requirement for each licensee or applicant to establish and maintain a safety program that demonstrates compliance with the performance requirements of 10 CFR 70.61 (see 10 CFR 70.62(a)), and for each licensee or applicant to conduct and maintain an integrated safety analysis (see 10 CFR 70.62(c)).

As part of the review process, the NRC staff reviews whether the applicant's proposed facility design and chemical process operations adequately protect the health and safety of workers and the public. These chemical process safety considerations apply during the storage, handling, and processing of licensed materials that are within the NRC's regulatory jurisdiction. The facility design and chemical process safety operations are to provide adequate protection to the health and safety of workers as well as the public during both normal operations and credible accident conditions. Further, the facility is also to adequately protect against conditions that could affect the safety of licensed materials as a result of radiation or chemical exposures. For example, a facility would have appropriate controls and protections for any chemical that could incapacitate operators and prevent their entry into an area of the facility where licensed materials are handled.

Introduction 2

1.2 Report Scope and Structure

This report provides a structured technical assessment and regulatory guidance assessment of chemical processes related to the fabrication of new fuel forms, particularly TRISO-based, metallic-based, and salt-based fuels. The report is structured as follows:

- Section 2.0 provides a review of open and publicly available literature to identify and
 describe the new fuels and summarize chemical processes associated with their
 fabrication. For TRISO-based fuels, consideration is given to the production of TRISO
 fuel particles, TRISO fuel compacts (graphite and ceramic-based) and graphite prismatic
 blocks. For metallic-based fuels, consideration is given to the production of uranium
 metal, sodium-bonded metallic fuel and dry metallic fuel. For salt-based fuels,
 consideration is given to fluoride- and chloride-based salts. The production of industrial
 carrier salts is also discussed.
- Section 3.0 provides a structured chemical process safety assessment of the fabrication
 of each fuel type. The evaluation focuses on the chemical process safety by considering
 the inherent properties of materials and the specific physical and health-related hazards
 that may arise under fabrication conditions. The assessment framework was applied and
 documented in a consistent manner across the fuel types, to support facile evaluation of
 chemical risks.

Section 3.1 describes the assessment used to identify chemical process safety considerations for each fuel type. This involved identifying and evaluating key materials, including inputs, intermediates, and byproducts, within the context of the chemical processes.

Section 3.2 presents the assessment findings, including fuel type-specific summaries of chemical process safety considerations, as well as cross-cutting considerations relevant to safety reviews. The compiled information supports a consistent and ordered basis for evaluating safety measures and the associated controls in advanced fuel cycle applications.

- Section 4.0 provides a review of various safety review guidance and technical basis documents to identify new chemicals and new processes associated with new fuels.
 Within this section, process-specific considerations and descriptions are provided.
 Additionally, it is noted that the DOE protective action criteria database includes TEELs for process-specific chemicals.
- Section 5.0 provides a summary of conclusions and findings per the report's contents.
- Appendix A provides comprehensive descriptions of the fabrication processes for each fuel type, which were used to support the summaries in Section 2.0.
- Appendix B provides details from the assessments on chemical safety for each fuel type.
 These details include tables outlining the physical and health safety considerations
 associated with the process chemicals for fabrication of each fuel type. Additional tables
 summarize threshold limit values for the process chemicals. Standard mitigative
 measures are also outlined, with particular attention to identifying any unique measures
 pertinent to the specific fuel types.

Introduction 3

2.0 Fabrication Processes for Advanced Fuel Cycle Facilities

This section provides descriptions of the characteristics of TRISO-based, metallic-based, and salt-based fuel forms, and summaries of their fabrication processes, per information available in open public sources. Appendix A provides additional detailed descriptions on the chemical processes and operational parameters for fabrication.

The fabrications of each of the new fuels covered in this report will utilize feedstock of uranium in the form of 235 U-enriched UF₆ or uranium tetrafluoride (UF₄), or uranium oxides (UO₂, UO₃ or U₃O₈) prepared by deconversion and oxidation/calcination, if needed. For each of the new fuels, the preparation of feedstock from ore or from recycled fuel, as well as deconversion to stable oxides, are expected to follow similar, already-demonstrated processes; the preparation of feedstock is therefore not described in this report. In addition, fabrication processes may involve support operations such as waste processing or scrap processing/uranium recovery. The chemical hazards for those operations are generally expected to be similar to those already reviewed as part of previous licensing actions for fuel cycle facilities in support of light-water reactors. Thus, these hazards are not described in this report.

This section thus covers fuel type-specific aspects of the fabrication processes. The fabrication processes described in license applications for NRC review are expected to be generally similar to those described in this report. However, the chemicals and operational parameters may be different for fabrication of specific fuel designs in those applications.

2.1 Fabrication of TRISO-Based Fuels

Coated particle fuel types were developed in the United Kingdom as part of the Dragon project, an experimental high temperature gas-cooled reactor (HTGR) and have since been used in various reactors, including the Peach Bottom Atomic Power Station Unit 1 (United States), the Fort Saint Vrain HTGR (United States), the Thorium High-Temperature Reactor (THTR-300, Germany), the High Temperature Reactor (HTR)-10 (China), and the High Temperature Engineering Test Reactor (Japan) (Kingrey 2003; Fisher 1998; Demkowicz et al. 2019; Liu et al. 2020).

In early gas-cooled reactors, the coated particles consisted of one layer (termed "mono") or two layers (termed "BISO", for buffer-isotropic or bistructural-isotropic) of pyrocarbon surrounding spherical fuel kernels. Highly enriched uranium and thorium carbides and oxides were used as fissile and fertile kernels, respectively. Ultimately, these early carbon layer coating systems were abandoned because they did not sufficiently retain fission products, leading to the development of the current three-layer coating system termed TRISO (Petti et al. 2004).

TRISO is the coated particle fuel form being used in contemporary designs for modular HTGRs and very high temperature reactors. This fuel form, and high level information about its fabrication, are further described below.

2.1.1 Fabrication of TRISO Fuel Particles

TRISO fuel particles are comprised of a spherical inner ceramic fuel kernel containing fissile or fertile material surrounded by high temperature coatings. One of the main benefits of the coatings being applied to the fuel kernel is to prevent fission products from escaping during irradiation under normal operating conditions as well as during accident conditions. A representative configuration of a TRISO particle is shown in Figure 1 Figure 1 (INL 2014).

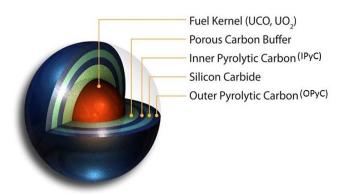


Figure 1. Configuration of TRISO Particle (INL 2014).

As shown in Figure 1 Figure 1, the TRISO particle coatings include an inner low-density carbon buffer layer, a high-density inner pyrolytic carbon (IPyC) layer, a silicon carbide (SiC) layer, and a high-density outer pyrolytic carbon (OPyC) layer. These coatings are designed to work together to make each fuel particle a pressure vessel that will maintain its integrity and retain fission products during normal reactor operation and potential accident conditions. Their design functions are described below.

- The inner porous carbon buffer layer is composed of low-density pyrolytic carbon with ~50 percent porosity (Liu et al. 2020). The buffer layer provides a reservoir for fission product gases, serves to accommodate the irradiation-induced swelling of the fuel kernel (including fission product recoil) and protects the other layers from damage due to these effects. Major purposes of the buffer are to absorb the kinetic energy of fission fragments ejected from the fuel kernel surface and to provide space for the accumulation of gaseous fission products and carbon monoxide. The buffer serves these functions by mechanically decoupling the kernel from the IPyC layer, which also accommodates kernel swelling.
- The IPyC layer retains most of the fission products, fixes the inner porous buffer layer, protects (seals) the next SiC layer from chemical attack by the fuel kernel fission products, acts as a support for the SiC layer, and prevents hydrogen chloride (HCI) and chlorine gases generated during the formation of the SiC layer from entering the fuel kernel.
- The SiC layer is the principal structural layer as it provides the largest contribution to the mechanical strength of the coated particle and also functions as a pressure boundary.
 The SiC layer serves as an impervious barrier, preventing the escape of gaseous or

- solid fission products (except ^{110m}Ag) from the coated particles. Zirconium carbide (ZrC) has also been considered as an alternative material for this layer (IAEA 1997).
- The high-density OPyC layer serves to protect the SiC layer from chemical attack from
 outside the particle and adds mechanical strength to the SiC layer. In addition, because
 the matrix material of the fuel compact will not bond to the SiC layer, the OPyC layer is
 necessary to provide a bonding surface between the TRISO particles and the
 carbonaceous matrix material of the pebble or prismatic compact.

The DOE has established the Advanced Gas Reactor (AGR) Fuel Program to support the qualification of TRISO-coated uranium oxycarbide (UCO) fuel particles for modern advanced non-light-water reactors (Petti et al. 2010; Demkowicz 2021). UCO-based TRISO particles have demonstrated superior high temperature performance and high burnup capabilities relative to uranium dioxide (UO₂) particles used in the designs of earlier pebble bed modular HTGRs. The AGR Fuel Program has focused on qualifying UCO TRISO-coated particles in cylindrical fuel compacts that are characteristic of prismatic fuel elements, following the characteristics of the ones which were exposed to irradiation in the Advanced Test Reactor at Idaho National Laboratory. Table 1 describes the scale of TRISO fuel fabrication activities per the AGR Fuel Program per (Demkowicz 2021).

Table 1. Scale of TRISO Fuel Fabrication Activities Under the DOE AGR Fuel Program.

| Fabrication Step | AGR-1 | AGR-2 | AGR-3/4 | AGR-5/6/7 |
|---------------------------------------|-------------|-------------|-------------|-------------|
| Kernel fabrication | Engineering | Engineering | Engineering | Engineering |
| TRISO coating | Laboratory | Engineering | Laboratory | Engineering |
| Resinated graphite powder fabrication | Laboratory | Laboratory | Laboratory | Engineering |
| Particle overcoating | Laboratory | Laboratory | Laboratory | Engineering |
| Compact fabrication | Laboratory | Laboratory | Laboratory | Engineering |
| AOD 1 1 1 | DOF 110 D 1 | · (= TD:00 | | • |

AGR = advanced gas reactor; DOE = U.S. Department of Energy; TRISO = tri-structural isotropic.

The DOE AGR Fuel Program is being conducted under a quality assurance program that meets Nuclear Quality Assurance (NQA-1) requirements (ASME [American Society of Mechanical Engineers] 2013), which was previously reviewed and found by the NRC to be acceptable for use during the technology development phase of the Next Generation Nuclear Plant Project (NRC 2012a), a DOE-sponsored activity from 2005 to 2011. The NRC has not explicitly defined quality assurance expectations for its fuel qualification assessment framework; however, it is expected that fuel qualification activities be controlled consistent with the fuel's importance to safety (NRC 2022).

The TRISO fuel particle specification for the AGR-5/6/7 test experiment (INL 2017; Collin 2018) has been referenced as the basis for the fuel design of the X-Energy LLC (X-Energy) Xe-100, whereas particle design for the Kairos Power LLC (Kairos Power) fluoride salt-cooled high temperature reactor (FHR) is similar to the specification for the AGR 2 test experiment (X-Energy LLC 2022; Kairos Power LLC 2022). Table 2Table 2 lists the TRISO fuel particle specification for the AGR-5/6/7 test, which accounts for advancements in the fabrication process by the AGR Fuel Program (INL 2017; Collin 2018).

Table 2. TRISO Fuel Particle Specification for DOE AGR-5/6/7 Test.

| TRISO Particle Component | Property | Specified Range for Mean Value | | |
|--|--|-----------------------------------|--|--|
| | Diameter (µm) | 425 ± 10 | | |
| | Density (g/cm³) | ≥ 10.4 | | |
| | ²³⁵ U Enrichment | 15.5 ± 0.1 | | |
| | Carbon/uranium (atomic ratio) | 0.40 ± 0.10 | | |
| | Oxygen/uranium (atomic ratio) | 1.50 ± 0.20 | | |
| Fuel kernel | [Carbon + oxygen]/uranium atomic ratio | ≤ 2.0 | | |
| | Total uranium (wt%) | ≥ 88.5 | | |
| | Sulfur impurity (ppm-wt) | ≤ 1,500 | | |
| | Phosphorous impurity (ppm-wt) | ≤ 1,500 | | |
| | Other impurities | ≤ 100 each | | |
| Dereye earbon buffer lever | Thickness (µm) | 100 ± 15 | | |
| Porous carbon buffer layer | Density (g/cm³) | 1.05 ± 0.10 | | |
| Inner pyrelytic carbon layer | Thickness (µm) | 40 ± 4 | | |
| Inner pyrolytic carbon layer | Density (g/cm³) | 1.90 ± 0.05 | | |
| Ciliaan aashida lawas | Thickness (µm) | 35 ± 3 | | |
| Silicon carbide layer | Density (g/cm³) | ≥ 3.19 | | |
| Outer purelytic carbon layer | Thickness (µm) | 40 ± 4 | | |
| Outer pyrolytic carbon layer | Density (g/cm³) | 1.90 ± 0.05 | | |
| AGR = advanced gas reactor; DOE = U.S. Department of Energy; TRISO = tri-structural isotropic. | | | | |

Section A.1 provides detailed descriptions on the fabrication process steps and conditions for TRISO fuel particles. Briefly, fuel kernels are synthesized from a colloidal solution ("sol" or "broth"), followed by gelation to form semirigid spheres of a controlled size distribution, washing, drying, calcination, and sintering to increase density.

The AGR Fuel Program selected the internal gelation process developed by BWX Technologies for TRISO particles with high-assay low-enriched uranium UCO kernels, focusing on improvements in kernel density and carbon dispersion. The process utilizes an acid-deficient uranyl nitrate (ADUN) solution mixed with an ammonia-donor solution to achieve optimal composition and stability. Therefore, gelation in the fabrication of modern fuel kernels is most likely to be accomplished by internal ammonia gelation. Figure 2 provides a process flowsheet of the internal gelation process for fabrication of TRISO fuel kernels, per AGR Fuel Program references (Phillips et al. 2012; Marshall 2019).

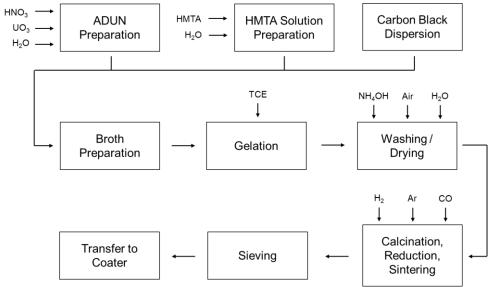


Figure 2. Process Flowsheet for Fabrication of TRISO Fuel Kernels by Internal Gelation per the AGR Fuel Program.

Specific methods for preparing ADUN solutions include adding various uranium compounds to nitric acid (HNO₃), leading to exothermic reactions requiring management of nitrogen oxide (NO_x) gases. The process also incorporates washing and drying of the gel particles with specific agents, followed by thermal treatments in furnaces for calcination, carbothermic reduction, and sintering, ultimately shrinking fuel kernels by about 50%.

The fuel kernel is coated by several protective layers to yield the TRISO particles: an inner low-density carbon buffer, an inner pyrolytic carbon (IPyC) layer, a silicon carbide (SiC) layer, and an outer pyrolytic carbon (OPyC) layer. These layers are engineered to maintain the structural integrity of the fuel particle and prevent the release of fission products during normal and accident conditions. The coatings are applied sequentially via chemical vapor deposition (CVD) in a fluidized bed reactor, using various gases at specific temperatures to deposit each layer. This complex process involves handling flammable and toxic gases, such as acetylene and propylene, and managing byproducts like hydrogen and hydrogen chloride, emphasizing the need for safety protocols in manufacturing.

A detailed review of public information on fabrication of TRISO fuel particles is provided in Section A.1, which includes the specific chemicals and process characteristics. The information in Appendix A was utilized for the chemical process safety assessment discussed in Section 3.0 of this report. The physical safety considerations associated with fabrication of TRISO fuel particles include flammability, thermal or reactive instability, physical corrosivity, pressurization and oxidation. The health safety considerations associated with fabrication of TRISO fuel particles include acute toxicity, skin/eye damage and irritation, chronic/systemic toxicity, and aspiration hazards.

2.1.2 Fabrication of TRISO Fuel Compacts

TRISO particles are overcoated and physically bonded into graphite or ceramic compact forms for utilization in pebble bed or prismatic core reactors. Pebble bed reactors utilize graphite pebble spheres (Figure 3 Figure 3 and Figure 4 b) that are typically approximately 6 cm in

diameter (IAEA 1997). Prismatic core reactors utilize cylindrical-type compacts designed to fit into hexagonal graphite blocks (<u>Figure 5</u>Figure 5), which are referred to as prismatic blocks.

By convention, pebbles which contain fuel as well as blocks which contain fuel compacts are both referred to as fuel elements (IAEA 1997). Pebbles remain as geometrically separate in a reactor rather than being incorporated into any larger 'structured group', and each fuel-containing pebble is thus referred to as a separate fuel element. In contrast, cylindrical fuel compacts are designed to be inserted into a hexagonal block to create a 'structured group', and this hierarchical structure of a block containing fuel compacts is then called a fuel element. Designating the fuel-containing block as a fuel element (rather than the individual compacts) is somewhat analogous to the terminology of today's light-water reactor (LWR) fuels, for which multiple fuel rods are fastened into a 'structured group' within a fuel assembly, and the full fuel assembly is then called a fuel element (NRC 2021).

In the United States, the design compacts for prismatic blocks are generally 12 mm in diameter and 49 mm long (IAEA 1997). The compact matrix provides a homogenous envelopment with significant mechanical strength to protect the particles against external forces. The matrix materials are chosen to provide good thermal conductivity, good corrosion resistance, and high dimensional stability to support proper functioning of the fuel element.

Figure 3Figure 3 illustrates the pebble fuel element and TRISO particle design for the Xe-100, a small modular pebble bed HTGR design being developed by X-Energy (Mulder and Boyes 2020; Mulder 2021a, 2021b). The 60 mm diameter fuel pebble consists of a ~50 mm diameter inner fuel zone with TRISO-coated particles (diameter of ~855 μm) embedded in a matrix material and surrounded by a fuel-free shell of graphite (~5 mm thick) molded over the fuel zone (Mulder 2021b). The pebble matrix material includes a carbonized organic binder material (A3-3 binder resin) and nuclear-grade graphite, which acts as a neutron moderator and heat transfer medium for the nuclear heat produced and provides protection to the TRISO particles against external forces.

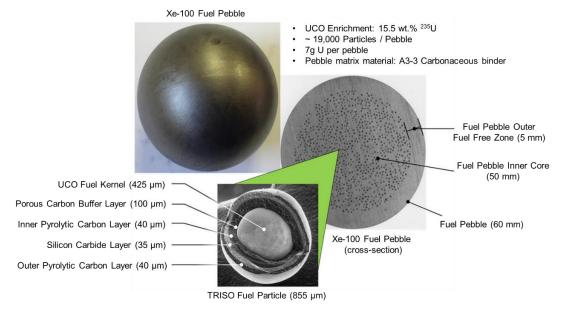


Figure 3. Design of Xe-100 Fuel Pebble and TRISO Particles. Image courtesy of X-Energy (Mulder and Boyes 2020; Mulder 2021a, 2021b).

Figure 4Figure 4 illustrates the fuel pebble and TRISO particle design for the FHR design, a thermal spectrum solid-fueled modular molten salt reactor design being developed by Kairos Power. The pebble design (4 cm diameter) contains a central sub-dense inner core surrounded by an annular layer of ~16,000 TRISO particles packed into a partially graphitized matrix material (fuel pebble annulus) and covered by an outer shell of fuel-free matrix material (Kairos Power LLC 2022). The TRISO particles used for the FHR have a fuel specification similar to those of the DOE AGR Fuel Program (Kairos Power LLC 2022).

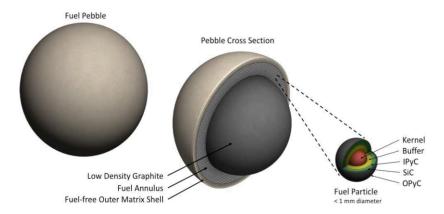


Figure 4. Design of FHR Fuel Pebble and TRISO Particles (Kairos Power LLC 2022).

<u>Figure 5</u> illustrates the cylindrical compacts for use in prismatic fuel blocks for an HTGR concept reactor (IAEA, 2019). TRISO particles are embedded into the graphite cylindrical compacts, which are structured in hexagonal prismatic fuel blocks formed with nuclear-grade graphite.

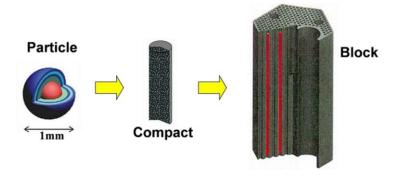


Figure 5. Illustration of HTGR Cylindrical Fuel Compact and Prismatic Block (IAEA 2019).

Ceramic compact elements, a more recent approach to TRISO fuel compacts, are the fuel form specified in the Ultra Safe Nuclear Corporation (USNC) Micro-Modular Reactor (MMR®) HTGR design.¹ The MMR® core utilizes hexagonal graphite blocks containing stacks of Fully Ceramic Micro Encapsulated (FCM®) pellet compacts with TRISO fuel particles. In contrast to traditional HTGR designs incorporating TRISO particles in a carbonaceous material or graphite matrix, the FCM® fuel pellet uses a dense SiC matrix to provide an additional barrier to fission product release and improve each TRISO particle's structural and containment characteristics. The

¹ Nano Nuclear Energy has recently acquired USNC's intellectual property rights on the MMR[®] fuel system (NANO Nuclear Energy Inc. 2024).

implementation of SiC is expected to provide improved irradiation stability and thermal characteristics compared to graphite (Terrani et al. 2012).

Section A.2 provides details on the fabrication process steps and conditions for TRISO fuel compacts. Graphite compacts may be fabricated from thermoplastic or thermosetting resin matrices (Demkowicz et al. 2019; Heit et al. 2017; IAEA 2015). Two graphitic resin matrix materials are primarily used in fabrication of pebble compacts for modular HTGRs, namely A3-3 and A3-27 (INL 2017; Collin 2018). The two matrix materials exhibit differences with respect to resin binder composition, cross-linking approach and resulting microstructure.

Pebble compact fabrication requires overcoating of the TRISO particles via a warm-mixing process with graphite powder and the same resin binders used for pebble fabrication. The overcoating (in the range of 200 μm) aides binding of the TRISO particles with the pebble's graphite matrix and prevents any undesired mechanical damage of the particles during pressing/compaction. The overcoated particles are then mixed with additional graphite powder-resin material and are pre-molded in silicone rubber molds at pressures between 5–30 MPa and room temperature to form the fuel zone for the pebble design. An outer protective fuel-free zone is then formed by isostatic pressing at 300 MPa and room temperature. The pebbles are then lathed to design specifications followed by carbonization and heat treatment to extract residual gases and impurities.

The process conditions for fabrication of graphite pebble compacts are different from those for graphite cylindrical compacts. In particular, a two-step overcoating process for TRISO particles is implemented to ensure good adhesion of the overcoating to the cylindrical compact matrix and mitigate contact between particles (Minato et al. 1997). Further, the pressures for molding cylindrical fuel compacts are lower than for pressing pebble spheres (typically, less than 20 MPa vs. 300 MPa). In addition, pebbles have a lower volumetric packing fraction of TRISO particles in a sphere matrix (~10 to 30 percent) relative to that of particles in a cylindrical compact (~35 to 45 percent). The lower packing fraction for pebbles reduces the likelihood of contact between the outer surfaces of TRISO particles (Demkowicz 2021).

Public information on the fabrication of ceramic fuel compacts (FCM® fuel pellets) is more limited than that of graphite compacts (Terrani et al. 2019; UIUC 2023). The USNC processes for fabrication of SiC matrix fuel pellets are based on prior efforts under the DOE's Transformational Challenge Reactor Program (Van den Akker 2022). The approach involves the design of a pellet shell, which is reproduced by layering resinated SiC powder using a binder jet printer. The resulting 'green shell' is then heated to cure the binder resin. The shells are then loaded with TRISO particles and additional SiC powder for filling interstitials within the shell. Chemical vapor infiltration is then used to deposit SiC in the residual void volume.

The review of public information, as discussed in Section A.2, provided sufficient information on the specific chemicals and process characteristics for fabrication of graphite and ceramic compacts. The information supported the chemical process safety assessment discussed in Section 3.0 of this report. The physical safety considerations associated with fabrication of TRISO fuel compacts include flammability and pressurization. The health safety considerations associated with fabrication of TRISO fuel compacts include acute toxicity, skin/eye damage and irritation, sensitization, and chronic/systemic toxicity.

2.1.3 Fabrication of Graphite Prismatic Blocks

Prismatic hexagonal blocks are a core design component used in HTGRs. The fabrication of these graphite blocks does not involve fissile or fertile radioactive materials. As shown in Figure 5, the blocks are loaded with cylindrical graphite compacts and are designed to form a tightly-packed hexagonal lattice within the reactor core to support efficient moderation and heat transfer from the fuel to the reactor gas coolant.

Section A.3 provides a description of the fabrication process for graphite prismatic blocks. Since the process does not involve radioactive material, it is assumed that fabrication will occur at an industrial facility. Therefore, a chemical process safety assessment for the graphite prismatic block fabrication was not conducted in this report.

2.2 Fabrication of Metallic-Based Fuels

Sodium fast reactors (SFRs) utilize fuel in the form of metal alloys due to their high thermal conductivity, compatibility with liquid sodium coolant, and their potential to achieve very high burnups, allowing for efficient use of the fuel. Metallic fuel alloys are designed to achieve properties for improved performance in reactor operations, including phase stability, adequate corrosion performance and structural stability per the specific reactor design needs.

Various binary and ternary alloys have been explored, including uranium-zirconium (U-Zr), uranium-molybdenum (U-Mo),¹ uranium-plutonium-zirconium (U-Pu-Zr) and uranium-fissium (U-Fs) (Porter and Crawford 2021).² Section A.4.1 provides descriptions on different approaches for the production of uranium metal. The most common industrial approach for uranium metal preparation involves the high temperature chemical reduction of the feedstock UF₄ by Group II metals (Jang et al. 2022). Two metallothermic reduction processes may be implemented, namely magnesiothermic or calciothermic reduction, although the first is the most likely approach for implementation at an advanced fuel cycle facility.

Two general types of metallic fuel designs were considered in this report: sodium-bonded and 'dry' designs. In sodium-bonded metallic fuel designs, sodium metal is an integral part of the fuel pins. The sodium acts as a coolant and a bonding material for the fuel slugs, facilitating improved heat transfer to the reactor coolant system. Section A.4.2 describes the fabrication process for sodium-bonded metallic fuel. TerraPower's Natrium reactor is expected to implement a sodium-bonded metallic fuel design for its demonstration, also referred to as Type 1 fuel. Figure 6 illustrates the general design of sodium-bonded metallic fuel pins, which include the sodium-bonded fuel slugs, shield plugs, and a plenum for retention of fission gases. TerraPower's Natrium design is expected to utilize U-10 wt% Zr fuel slugs cladded in HT9, a ferritic-martensitic alloy steel (NRC 2024c; TerraPower 2022).

¹ U-Mo alloys of 10 wt% Mo improves dimensional stability and anisotropic behavior during irradiation.

² Fissium (Fs) is an equilibrium concentration of fission product elements left by the pyrometallurgical reprocessing cycle designed for EBR-II. An alloy with 5 wt% Fs (i.e., 5Fs) would contain 2.4 wt% Mo, 1.9 wt% Ru, 0.3 wt% Rh, 0.2 wt% Pd, 0.1 wt% Zr, and 0.01 wt% Nb.

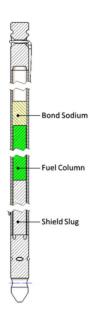


Figure 6. TerraPower Natrium Type 1 Fuel Pin Design (TerraPower 2022).

In contrast, dry metallic fuel refers to fuel element designs for use in SFRs, which do not incorporate sodium metal inside the pins. In dry metallic fuel designs, the design relies on direct contact between the fuel and the cladding to achieve sufficient thermal conduction. The annular fuel pins (tubes) are fabricated through coextrusion, a high-pressure and high-strain bonding process, which results in a very high-quality metallurgical bond between the metallic fuel, interdiffusional metallic layer barriers (if part of the fuel design), and the cladding. The typical process uses a metallic uranium core (machined billet) sleeved by the cladding (inner, outer) and encapsulated with an outer can (Wood et al. 2020). The outer can is normally evacuated and sealed to prevent ingress of air during preheat and extrusion. Dry metallic fuel has been proposed for use in the TerraPower Natrium SFR as their second generation, Type 1B, fuel design (TerraPower 2022). Figure 7Figure 7 illustrates the general design of dry metallic fuel pins, which include the annular fuel column, helium fill gas, shield plugs, and a plenum for retention of fission gases. No information was identified on potential fabrication processes to be implemented for fabrication of modern dry metallic fuel designs. Instead, Section A.4.3.1 provides a discussion on prior experience on the fabrication of similar type fuel for the N-Reactor, previously operated at the DOE Hanford Site from 1963 to 1987. Section A.4.3.2 also discusses recent advancements on annular coextrusion for dry metallic fuel, per a more recent PNNL development program.

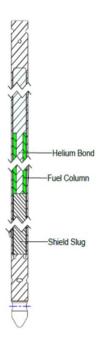


Figure 7. TerraPower Natrium Type 1B Fuel Pin Design (TerraPower 2022).

The review of public information, as discussed in Section A.4, provided sufficient information on the specific chemicals and process characteristics for fabrication of metallic uranium and sodium-bonded fuel designs, with more limited information available for dry metallic fuel designs. The information supported the chemical process safety assessment discussed in Section 3.0 of this report.

Regarding fabrication of metallic uranium, the associated physical safety considerations include flammability, thermal or reactive instability, physical corrosivity, pressurization and oxidation. Health safety considerations include acute toxicity, skin/eye damage and irritation, sensitization, and chronic/systemic toxicity.

Regarding fabrication of sodium-bonded metallic fuel designs, the associated physical safety considerations include flammability, thermal or reactive instability, physical corrosivity, pressurization and oxidizing hazards. Health safety considerations include acute toxicity, skin/eye damage and irritation, chronic/systemic toxicity and aspiration.

Regarding fabrication of dry metallic fuel designs, the associated physical safety considerations include thermal or reactive instability, physical corrosivity and oxidation. Health safety considerations include acute toxicity, skin/eye damage and irritation, sensitization, chronic/systemic toxicity and aspiration.

2.3 Fabrication of Salt-Based Fuels

Salt-fueled molten salt reactors (MSRs) utilize mixtures of fissile and possibly fertile halide salts with carrier salts. The primary purposes for carrier salts are (a) to lower the melting point of the mixture, as the melting temperatures of the fissile and fertile halide salts can be too high for practical or economical use and (b) to be able to adjust the concentration of fissionable material to control criticality. Section A.5 provides detailed descriptions on the synthesis of both fluoride-and chloride-based fissile salts, their purification and isotopic enrichment.

UF₄, commonly referred to as 'green salt', is the predominant fluoride-based fuel salt considered for modern liquid-fueled MSRs, including the Lithium Fluoride Thorium Reactor under development by Flibe Energy and the Molten Salt Research Reactor to be operated at Abilene Christian University (Torres et al. 2022). UF₄ enriched to 32 percent ²³⁵U was also utilized for operation of the Molten Salt Reactor Experiment (MSRE) at Oak Ridge National Laboratory (Shaffer 1971).

Section A.5.1 provides detailed descriptions on different approaches for UF $_4$ production and purification. The most common process currently used involves fluorination of UO $_2$ with hydrogen fluoride (HF) gas (Grenthe et al. 2006a; Souček et al. 2017). An alternative approach involves direct reduction of UF $_6$ to UF $_4$ with hydrogen (H $_2$) (Smiley and Brater 1959), which can be conducted via either "hot wall" or "cold wall" methods (International Nuclear Fuel Cycle Evaluation Working Group 7 1979); (Smiley et al. 1956; Bester et al. 1993). Other approaches have been studied for UF $_4$ production, although unlikely to be implemented at this time (McFarlane et al. 2019; Torres et al. 2022).

The two primary uranium chloride-based fuel salts being considered for MSRs are UCl₃ and UCl₄. (Mausolff et al. 2021). UCl₃ is much less corrosive than UCl₄; however, UCl₄ is more chemically stable and has a much lower melting temperature than UCl₃, so an MSR using UCl₄ can operate at a much lower temperature (Scatchard et al. 1952).

Section A.5.2 provides detailed descriptions on different approaches for chloride-based fuel salt production and purification. The discussion also addresses processes for ³⁷Cl enrichment and to reduce the ³⁵Cl content due to its high neutron cross-section and in-reactor production of ³⁶Cl. However, the use of any of those processes does not involve radioactive materials.

The present day most expected process for producing UCl₃ involves reduction of precursor UCl₄ with H₂ (Suttle and Hoekstra 1957; Patterson et al. 1967). Various other approaches may be used for UCl₃ production, including reduction of UCl₄ using metals, reaction of metallic uranium with HCl, reaction of uranium metal with transition metal chlorides, electrochemical processing, and chlorination of uranium metal with NH₄Cl. However, these processes are currently not expected to be implemented.

The reaction of uranium oxides with CCl₄ in the gas phase, referred to as carbochlorination, is the most expected approach for UCl₄ production (Wagner 1946; McFarlane et al. 2019). Other chlorinating agents including C₃Cl₆, Cl₂, COCl₂, or mixtures of CO with Cl₂ have been studied for UCl₄ production (McFarlane et al. 2019). However, there is no current expectation of these processes being implemented commercially.

Section B.3.4 discusses additional considerations for industrial carrier salt fabrication. The primary carrier salt for use in liquid-fueled MSRs with UF₄ or, potentially thorium fluoride (ThF₄) fuel, as well as solid-fueled MSRs with TRISO-based fuel, is commonly referred to as "FLiBe" or "Flibe". Flibe is a mixture of lithium fluoride (LiF) and beryllium fluoride (BeF₂) at a nominal 2:1 mole ratio. This is the same salt mixture used as the intermediate coolant in the MSRE. Flibe is prepared by blending high purity BeF₂ and LiF powders in inert environments to mitigate oxidation. The mixture is then treated by hydrofluorination to reduce residual oxides. It is likely that a separate industrial facility will be used for Flibe preparation, which would not be operated under a license per 10 CFR Part 70. However, recognizing the uncertainties on where blending of fuel and carrier salts will be conducted (i.e., 10 CFR Part 50 or 52 license vs. a 10 CFR Part 70 license), the assessment in this report considers the chemical process safety associated with carrier salt production and blending.

The review of public information, as discussed in Section A.5 and Section B.3.4, provided sufficient information on the specific chemicals and process characteristics for fabrication of fluoride-based and chloride-based fuel salts, as well as industrial carrier salts. The information supported the chemical process safety assessment discussed in Section 3.0 of this report.

Regarding fabrication of fluoride-based salt fuel, the associated physical safety considerations include flammability, physical corrosivity, and pressurization hazards. Health safety considerations include acute toxicity, skin/eye damage and irritation, and chronic/systemic toxicity.

Regarding fabrication of chloride-based salt fuel, the associated physical safety considerations include flammability, physical corrosivity, pressurization and oxidation. Health safety considerations include acute toxicity, skin/eye damage and irritation, chronic/systemic toxicity and aspiration.

3.0 Chemical Hazards Identification and Chemical Process Safety Assessment for Advanced Fuel Cycle Facilities

Structured assessments of three primary topics critical to the safety of advanced fuel cycle facilities were conducted, the three topics being: (i) Chemical Process Safety, (ii) Exposure Guidelines and Limits for Consequence Severity Categorization, (iii) and Considerations on Mitigative Measures. For each fuel type under consideration, chemical process safety and operational hazards were reviewed to summarize key risks associated with the chemicals and processes involved. Exposure guidelines were evaluated to categorize potential consequence severities and support alignment with regulatory performance requirements. Standard mitigative measures are also outlined, with particular attention to identifying any unique measures required for specific fuel types. This systematic approach supports a consistent review of safety considerations while addressing the specific characteristics and challenges of each fuel type. The following discussion provides context for the information provided on these three topics for advanced fuel cycles facilities for TRISO-based fuels (Section B.1), metallic fuels (Section B.2) and salt fuels (Section B.3).

3.1 Assessment Methodology

This section describes the methodologies used to assess each of the following three topics for each fuel type: (i) Chemical Process Safety, (ii) Exposure Guidelines and Limits for Consequence Severity Categorization, (iii) and Considerations on Mitigative Measures.

3.1.1 Chemical Process Safety and Operational Hazards for TRISO-Based Fuels, Metallic-Based Fuels, and Salt-Based Fuels

A general framework was developed to assess the chemical process safety associated with the materials and operations involved in fuel fabrication. The purpose of this framework is to facilitate a consistent evaluation across all fuel types discussed in the report, ensuring that safety considerations are appropriately identified, reviewed, and communicated.

The hazards associated with key materials used in fuel fabrication, including primary chemical inputs, intermediates, and byproducts, were summarized to the extent they could be identified, per the detailed chemical process descriptions in Appendix A. The full details on *Chemical Safety Considerations* are provided in Appendix B, specifically in Sections B.1.1 (TRISO-based fuels), B.2.1 (metallic-based fuels), B.3.1 (salt-based fuels). The approach used integrates chemical safety considerations, which address the intrinsic properties of materials, with process safety considerations, which reflect how these materials behave under operational conditions. By maintaining a consistent structure, the tables aim to summarize, at a high level, risks across the fuel types in a systematic and transparent manner.

Regarding chemical safety considerations, the associated tables are structured into three key columns, each providing a distinct aspect of the assessment. The first column, *Chemical Composition*, lists the specific chemicals relevant to fuel fabrication. It includes both the names and molecular formulas of the materials involved. Chemicals are selected based on their criticality to the processes and their potential for introducing safety risks, including those that may be substantially present as byproducts or intermediates.

The second and third columns, *Physical Hazards* and *Health Hazards*, respectively, focus on the inherent properties of the materials that may pose risks during handling, storage, or use. Physical hazards describe characteristics such as flammability, combustibility, reactivity, and corrosiveness. For example, strong oxidizers or flammable gases are identified in this category. Health hazards address potential effects on workers and the public, such as toxicity, irritation, and sensitization.

Regarding chemical process safety considerations, the chemical composition is again supplied, along with additional details in a *Process Environment* column, which describes the conditions under which the chemical is present. *Process Hazards*, the final column, considers risks arising from the operational context in which the chemical is used, stored, or processed. This includes scenarios such as uncontrolled reactions, loss of containment, spills, vapor releases, or exposure to abnormal conditions like elevated temperatures or pressures. Process safety also encompasses the potential for inadvertent interactions, such as the introduction of incompatible materials, loss of inert environments, or system failures that could amplify the inherent risks of a chemical.

The hazard assessment reflects a consideration of normal and abnormal process conditions, as well as accidental scenarios that may exacerbate chemical risks. Examples include uncontrolled conditions such as over pressurization, thermal runaway, or unintended reactions; abnormal conditions such as fire, leaks, or system malfunctions, which may amplify hazards; and inadvertent interactions including the introduction of air, water, or incompatible process chemicals, which may heighten the hazardous nature of a material. By considering these factors, the tables aim to capture a representative view of safety risks associated with the materials and processes across the fuel types.

3.1.2 Exposure Guidelines and Limits for Consequence Severity Categorization

For this effort, information on chemical exposure guidelines and limits is provided for process chemicals relevant to fabrication of each fuel type, including AEGLs (Acute Exposure Guideline Limits), ERPGs (Emergency Response Planning Guidelines), TEELs (Temporary Emergency Exposure Limits), IDLH (Immediately Dangerous to Life or Health) concentrations, and NIOSH (National Institute for Occupational Safety and Health) skin notations (if available), as well as their sources and relevance.

The full details on *Exposure Guidelines and Limits for Consequence Severity Categorization* are provided in Appendix B, specifically in Sections B.1.2 (TRISO-based fuels), B.2.2 (metallic-based fuels), and B.3.2 (salt-based fuels). The discussions identify thresholds to inform safety evaluations of chemical hazards and consequence severity for fuel fabrication processes.

Both the NRC and DOE implement frameworks aimed to address safety at fuel fabrication facilities by assessing and mitigating chemical hazards, but their approaches differ in how exposure guidelines are applied. The DOE framework explicitly establishes thresholds for chemical hazard evaluation, requiring adherence to defined criteria, including AEGLs, ERPGs, and TEELs, to support consistent application across facilities. In contrast, the NRC, through 10 CFR 70.61 (NRC 2024c) and NUREG-1520, Revision 2 (NRC 2015), requires applicants to select appropriate acute chemical exposure data, such as AEGLs and ERPGs, and relate them to performance requirements in 10 CFR 70.61(b)(4) and (c)(4). TEELs are not explicitly mentioned in NRC guidance. This highlights the variation in how each organization incorporates exposure guidelines and limits into their safety evaluations.

- AEGLs, ERPGs, and TEELs are essential protective action criteria (PAC) used to
 evaluate and manage chemical exposure risks during emergencies. As detailed in
 Table 2.1 of the DOE Handbook, *Temporary Emergency Exposure Limits for*Chemicals (DOE 2016), replicated in <u>Table B-1</u>Table B-1, these levels represent
 thresholds for increasing severity of exposure effects.
- AEGLs are developed by the U.S. Environmental Protection Agency (EPA) and provide guideline levels for the general population, including sensitive groups. AEGL-1 through AEGL-3 describe increasing exposure severity, ranging from transient discomfort to life-threatening effects or death.
- ERPGs, created by the American Industrial Hygiene Association, outline exposure levels at which nearly all individuals could avoid adverse effects or take protective action. These levels are used primarily for emergency planning and response for 60minute exposure durations.
- TEELs are developed by the DOE for chemicals lacking AEGL or ERPG values. They
 serve as interim limits to address operational emergencies, with TEEL-1 through TEEL3 mirroring the progression of effects described in AEGLs and ERPGs.

Together, these frameworks support comprehensive emergency planning in identifying exposure limits, enabling tailored protective measures based on the severity of potential chemical exposures. Appendix B provides additional details on the frameworks for assessing consequence severity categorization.

Sections 0 (TRISO-based fuels), 0 (metallic-based fuels) and B.3.2 (salt-based fuels) on Exposure Guidelines and Limits for Consequence Severity Categorization offer a comprehensive summary of threshold guideline and limit values for process chemicals relevant to fabrication of each fuel type. The Element or Compound column of the tables identifies chemicals by name and molecular formula, based on a review of the associated fabrication processes. The Limit Threshold Values column of the tables includes all three levels of PAC: PAC-1, PAC-2, and PAC-3, hierarchically derived from AEGLs, ERPGs, and TEELs, with values sourced from the DOE PAC database; TEELs are used when AEGLs and ERPGs are not available. The IDLH Concentration column of the table, sourced from NIOSH, provides additional references for evaluating acute exposure risks. The Skin Notation column highlights chemicals with dermal or ocular exposure risks, referencing NIOSH notations where available. Furthermore, the Health Hazard column in the chemical safety considerations tables from the Chemical Safety Considerations sections qualitatively assesses skin and eye risks, offering insights when formal skin notations are absent. This synthesized information establishes other organization's exposure limits for chemicals involved in various fabrication processes across different fuel types, providing a structured framework for assessing chemical hazards and recognizing the limitations of available data.

3.1.3 Considerations on Mitigative Measures

Fuel fabrication facilities employ a range of mitigative measures to address chemicals, many of which are standard and broadly applicable across different fuel types. These measures are well-documented in the *Nuclear Fuel Cycle Facility Accident Analysis Handbook* (NUREG/CR-6410) (NRC 1998) and the *Standard Review Plan for Fuel Cycle Facilities License Applications – Final Report* (NUREG-1520, Revision 2) (NRC 2015). These measures are typically integrated into the facility's design, operational procedures, and safety systems as part of the Integrated Safety Analysis (ISA) framework. Common mitigative measures include:

- <u>Containment Systems</u>: Engineered barriers, such as gloveboxes and sealed processing equipment, minimize the release of hazardous materials.
- <u>Ventilation and Filtration</u>: High-efficiency particulate air (HEPA) filtration and dedicated exhaust systems control airborne contaminants.
- <u>Inert Atmosphere and Fire Suppression</u>: Use of inert gases to prevent flammable mixtures and fire suppression systems for rapid response.
- <u>Leak Detection and Monitoring</u>: Continuous monitoring for chemical releases or spills supports quick detection and response.
- <u>Administrative Controls</u>: Procedures, training, and access restrictions reduce human error and improve hazard management.
- <u>Emergency Preparedness</u>: Plans aligned with PAC support readiness to address chemical release scenarios.

These measures are foundational to mitigating hazards and ensuring compliance with safety performance requirements. Sections B.1.3 (TRISO-based fuels), B.2.3 (metallic-based fuels) and B.3.3 (salt-based fuels) on *Considerations on Mitigative Measures* discuss potential mitigative measures that may be implemented for fabrication of each fuel type. Those discussions focus on fuel-specific considerations, highlighting where deviations or additional mitigative strategies may be necessary beyond those already contemplated in NUREG/CR-6410 (NRC 1998) and NUREG-1520, Revision 2 (NRC 2015). This approach avoids redundancy while ensuring that unique aspects of each fuel type are adequately addressed.

3.2 Assessment Findings

This section presents a synthesis of the chemical hazard findings derived per the assessment methodology described in Section 3.1 and the detailed chemical-specific information provided in Appendix B. The objective is to summarize the types of chemical hazards identified across fuel fabrication processes and organize them in a format that supports comparative analysis and cross-cutting insights. The information aims to support safety reviews per NUREG-1520, Revision 2 (NRC 2015), for compliance with 10 CFR Part 70, Subpart H, including 10 CFR 70.61, 70.62, 70.64 and 70.65, as applicable (NRC 2024c).

3.2.1 Summary of Chemical Safety Considerations

To enable consistency and clarity, the Globally Harmonized System (GHS) framework was used for organizing hazard information. GHS classifies chemical hazards according to standardized criteria and assigns hazard statement codes to reflect the severity and nature of the hazard. In this section, the GHS framework serves as a basis for categorizing the identified hazards into two overarching groups: physical safety considerations and health safety considerations. Each hazard type in the summary corresponds to one or more GHS hazard classes and is associated with the relevant hazard statement codes. These mappings, presented in Table 3 Table 4 Table 4, provide the foundation for the structured hazard summaries that follow.

The subsections under this section summarize chemical hazard types for the following fuel fabrication categories:

TRISO-based fuels

- Metallic-based fuels, which are evaluated across three subcategories: uranium metal fuel, sodium-bonded metallic fuel, and dry (non-sodium-bonded) metallic fuel
- Salt-based fuels

For each fuel type (or subtype), a high level overview of the fabrication process steps was developed to help bound the hazard evaluation. The analysis for each fuel type includes two summary tables: one for physical safety considerations and one for health safety considerations. These tables list:

- The applicable hazard type:
- The fabrication process steps in which the hazard may be introduced or becomes relevant;
- The chemicals associated with the hazard and process step; and
- Hazard context and considerations, which provides insight into process-specific factors that influence how a hazard may arise or be exacerbated.

Inclusion of a chemical under a given hazard type required a defined basis. Specifically, chemicals were included when a relevant GHS hazard statement code could be identified (typically sourced from safety data sheets (SDS) or chemical hazard classification databases). These statements are assigned according to established criteria that reflect the intrinsic properties of a substance under standardized conditions. However, not all hazards relevant to fuel fabrication processes are fully captured through GHS codes alone. In such cases, the Hazard Context and Considerations field was used to document additional contributing factors or conditional hazard scenarios (such as interactions, byproducts, or abnormal process conditions) that warranted recognition despite the absence of a codified GHS statement. This approach ensured that the chemical listings remained grounded in a recognized classification system, while still allowing space to acknowledge complex or process-specific hazard dynamics. All insights presented here were derived from the detailed material compiled in Appendix B, which includes supporting data, classification references, and explanatory rationale.

Table 3. Mapping of Physical-Related Safety Topics to GHS Hazard Classes.

| Physical Hazard Type | GHS Hazard Classes Included | GHS Hazard Statement Codes |
|---------------------------------|--|---|
| Flammability | Flammable Gases, Flammable Aerosols, Flammable Liquids, Flammable Solids | H220–H223, H224–H226, H228 |
| Explosivity | Explosives, Organic Peroxides | H200–H205, H240–H242 ¹ |
| Thermal or Reactive Instability | Self-Reactive Substances, Pyrophoric Substances, Substances that emit flammable gases when in contact with water | H240–H242 ¹ , H250–H252, H260– H261 |
| Physical Corrosivity | Corrosive to Metals | H290 |
| Pressurization Hazards | Gases Under Pressure, Self-Heating Substances | H280–H281, H251–H252, H282–H283 |
| Oxidizing Hazards | Oxidizing Gases, Oxidizing Liquids, Oxidizing Solids | H270–H272 |

GHS = Globally Harmonized System.

¹H240–H242 apply to both explosives and thermally unstable substances (e.g., self-reactives and organic peroxides) and are therefore listed under both Explosivity and Thermal or Reactive Instability.

Table 4. Mapping of Health-Related Safety Topics to GHS Hazard Classes.

| Health Hazard Type | GHS Hazard Classes Included | GHS Hazard Statement Codes | | | |
|-----------------------------------|--|--|--|--|--|
| Acute Toxicity | Acute Toxicity (oral, dermal, inhalation) | H300-H302, H310-H312, H330-H332 | | | |
| Skin and Eye Damage/Irritation | Skin Corrosion/Irritation, Serious Eye Damage/Eye Irritation | H314–H315, H318–H319 | | | |
| Sensitization | Respiratory or Skin Sensitization | H317, H334 | | | |
| Chronic/Systemic Toxicity | Germ Cell Mutagenicity, Carcinogenicity, Reproductive Toxicity, Specific Target Organ Toxicity (single/repeated exposure) | H340–H341, H350–H351, H360– H361, H370–H373 | | | |
| Aspiration Hazard | Aspiration Toxicity | H304 | | | |
| GHS = Globally Harmonize | GHS = Globally Harmonized System. | | | | |

3.2.1.1 Chemical Process Step Assessments for TRISO-Based Fuels

This subsection presents a summary of chemical safety considerations identified across the major process steps associated with TRISO-based fuel fabrication. The process summary, per Table 5, reflects typical steps used in coated particle fuel production, including kernel preparation, high temperature treatment, particle coating, fuel matrix formation, and final conditioning. Table 6 and Table 7 present a synthesis of relevant physical and health safety considerations for the chemicals involved in each process step, based on GHS hazard classifications.

Table 5. TRISO-Based Fuel Fabrication Process Summary.

| Fabrication Process Step | Description |
|-----------------------------------|--|
| Kernel Preparation | A uranyl nitrate solution is combined with stabilizers such as hexamethylenetetramine (HMTA) and urea to form the precursor mix. Controlled gelation occurs via ammonia release, followed by gel sphere washing to remove residual reactants including nitric acid, ammonium nitrate, and byproducts. Washing may involve use of mineral or silicone oils, and 2-ethyl-1-hexanol. The microspheres are then dried and stabilized for further processing. |
| Kernel Heat Treatment | Dried microspheres undergo calcination and sintering in high temperature furnaces under inert or reducing atmospheres. This converts chemical precursors into dense uranium oxide ceramic kernels. Process gases include hydrogen, argon, and carbon dioxide to control atmosphere composition. |
| Particle Coating and Pre-Forming | Microspheres are coated with a sequence of layers via chemical vapor deposition at high temperatures. These include a porous carbon buffer, inner and outer pyrolytic carbon, and a silicon carbide (SiC) barrier layer. Precursors like methane, acetylene, and methyltrichlorosilane are introduced with hydrogen and argon as carrier gases. Hydrochloric acid (HCI) may be generated as a byproduct. |
| Fuel Matrix Formation | Coated particles are embedded in either a graphite-based matrix (e.g., phenolic resin and graphite powder) or a ceramic matrix (e.g., SiC or carbon-rich preceramic polymer). The mixture is blended with binders such as phenol-HMTA resin or phenol-formaldehyde, then compacted into cylindrical or pebble-shaped fuel forms. Graphite powders may be overcoated to improve moldability. |
| Final Conditioning | Formed fuel compacts are heat treated through carbonization or high temperature curing to remove volatiles and solidify structure. Volatile decomposition products from binders are vented through inert gas systems. |
| TRISO = tri-structural isotropic. | |

Table 6. Physical Safety Considerations – Summary for TRISO-Based Fuel Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|--------------|-------------------------------------|--|--|
| Flammability | Kernel Preparation | Hexane (C_6H_{14}) Isopropanol (C_3H_8O) HMTA ($C_6H_{12}N_4$) 2-Ethyl-1-hexanol ($C_8H_{18}O$) | Flammable vapors may accumulate during solvent use. Graphite powder and other organics are present in nearby operations but are not classified as flammable under the Globally Harmonize System (GHS). Heated mineral oils and silicone oils used in adjacent washing steps may emit combustible vapors under certain conditions, though they are not GHS-classified as flammable. |
| | Kernel Heat Treatment | None identified | Inert and reducing atmospheres are used. Any residual volatiles must be fully purged to avoid ignition in hot zones. |
| | Particle Coating and Pre-Forming | Methane (CH ₄) Hydrogen (H ₂) Acetylene (C ₂ H ₂) Propylene (C ₃ H ₆) Methyltrichlorosilane (CH ₃ SiCl ₃) | Failure of inerting or flow control could lead to flammable gas accumulation. Residual particulates or coating intermediates could exacerbate ignition risk. |
| | Fuel Matrix Formation | HMTA(C ₆ H ₁₂ N ₄ | Graphite powder is not GHS-flammable but may enhance fire propagation or serve as a combustible dust in abnormal conditions. Phenolic resins are not GHS-classified as flammable but may emit flammable decomposition gases under severe heating. |
| | Final Conditioning | None identified | Off-gassing from incomplete binder breakdown may pose a transient flare risk if not managed by purge and exhaust. |
| Explosivity | Kernel Preparation | None identified | Nitric acid reactions with uranium oxides generate heat and nitrogen oxides (NO, NO ₂), which may result in pressure buildup if confined. These reactions are managed through thermal and off-gas control systems. |
| | Kernel Heat Treatment | None identified | Furnace operations use inert or reducing gases with no energetic substances. Explosive conditions are not anticipated, even under upset scenarios. |
| | Particle Coating and Pre-Forming | None identified | Flammable gases used in coating may form explosive mixtures with air if inerting fails. These risks are addressed through gas interlocks and purge control systems. |
| | Fuel Matrix Formation | None identified | Fine graphite powder and resin binders may present deflagration or dust explosion hazards if dispersed and ignited in confined spaces. Additional dust-forming materials such as raw coke and calcined coke may present similar behaviors during processing. |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|---------------------------------------|-------------------------------------|--|---|
| | Final Conditioning | None identified | Volatile residues may evolve during heating but do not present explosive risk under controlled purge and ramp rates. |
| Thermal or Reactive Instability | Kernel Preparation | Nitric acid (HNO₃) | Reaction of nitric acid with uranium oxides is exothermic and evolves nitrogen oxides (NO, NO ₂). Pressurization may occur if gas is not safely vented. These reactions are managed through thermal and off-gas control systems. |
| | Kernel Heat Treatment | None identified | Thermal treatment under inert or reducing gas conditions. Controlled heating rates are used to avoid runaway decomposition of any residuals. |
| | Particle Coating and Pre-Forming | Methyltrichlorosilane (CH ₃ SiCl ₃) | Reacts exothermically with water or humid air, potentially releasing HCl gas. Moisture intrusion or purge failure could cause localized thermal instability. |
| | Fuel Matrix Formation | None identified | Phenol-formaldehyde and phenol-hexamethylenetetramine (HMTA) resins may evolve gases during curing or pyrolysis. Decomposition under abnormal heating is possible but not classified as thermally unstable. Heated mineral oils and silicone oils used earlier in the process also pose low-level decomposition risks but are not GHS-classified. |
| | Final Conditioning | None identified | High temperature inert or reducing atmosphere is maintained. Volatile release is controlled by process timing and exhaust handling. |
| Physical Corrosivity | Kernel Preparation | Nitric acid (HNO₃) | Corrosive to common structural metals such as stainless steel and aluminum. Elevated temperatures or acid concentration may increase material degradation. |
| | Kernel Heat Treatment | None identified | Furnace operations are conducted under inert/reducing atmospheres using corrosion-resistant alloys or ceramics. |
| | Particle Coating and Pre-Forming | Hydrogen chloride (HCI) | HCl gas is produced by hydrolysis or decomposition of methyltrichlorosilane. It is highly corrosive to process equipment and requires gas handling and scrubbing systems. |
| | Fuel Matrix Formation | None identified | Materials such as phenol, graphite, and HMTA are not corrosive to metals under GHS and do not pose compatibility concerns with typical processing materials. |
| | Final Conditioning | None identified | Final high temperature processing is conducted in corrosion-resistant equipment. No new corrosive substances are introduced. |
| Pressurization Hazards | Kernel Preparation | None identified | Exothermic reactions between nitric acid and uranium oxides release nitrogen oxides (NO, NO ₂), which may cause localized pressure buildup if |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|----------------------|-------------------------------------|--|---|
| | | | not adequately vented. These gases are not added as input materials and do not qualify as gases under pressure under GHS. |
| | Kernel Heat Treatment | Argon (Ar) Hydrogen (H ₂) Carbon dioxide (CO ₂) | Inert or reducing gases are supplied from compressed cylinders. Pressurization hazards are managed via pressure regulators, purge control, and flow interlocks. |
| | Particle Coating and Pre-Forming | Hydrogen (H_2) Methane (CH_4) Acetylene (C_2H_2) Argon (Ar) | These gases are introduced into high temperature furnaces for chemical vapor deposition. Cylinder pressure, flow control failure, or backflow could result in localized overpressurization. |
| | Fuel Matrix Formation | None identified | No gases under pressure are introduced. Binder decomposition may evolve gases, but this is not related to compressed gas systems. |
| | Final Conditioning | Argon (Ar) Hydrogen (H ₂) | Furnace atmospheres rely on compressed gas supplies. Overpressure risks are mitigated by controlled heating and gas delivery systems with relief and monitoring. |
| Oxidizing Hazards | Kernel Preparation | Uranyl nitrate (UO ₂ (NO ₃) ₂) Nitric acid (HNO ₃) Nitrogen oxides (NO, NO ₂) | Uranyl nitrate, nitric acid, and evolved nitrogen oxides are strong oxidizers. In the presence of organics or flammables, these can intensify combustion reactions. |
| | Kernel Heat Treatment | None identified | Carried out under inert or reducing atmospheres (e.g., Ar , H_2). No oxidizers present or expected to persist from earlier steps. |
| | Particle Coating and Pre-Forming | None identified | Reducing conditions dominate (e.g., CH ₄ , H ₂), and no oxidizers are introduced. Presence of oxidizers would be incompatible with deposition processes. |
| | Fuel Matrix Formation | None identified | Phenol, HMTA, and graphite are reducing or combustible materials; no oxidizers are introduced. |
| | Final Conditioning | None identified | Final heating occurs under inert gas. No oxidizers are present; conditions are controlled to avoid unwanted reactions. |
| TRISO = tri-structur | al isotropic. | | |

Table 7. Health Safety Considerations – Summary for TRISO-Based Fuel Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|-----------------------------------|-------------------------------------|--|--|
| Acute Toxicity | Kernel Preparation | Uranyl nitrate (UO ₂ (NO ₃) ₂) Nitric acid (HNO ₃) Ammonium hydroxide (NH ₄ OH) HMTA (C ₆ H ₁₂ N ₄) 2-Ethyl-1-hexanol (C ₈ H ₁₈ O) Ammonium nitrate (NH ₄ NO ₃) Nitrogen oxides (NO and NO ₂) | Toxic vapors or droplets may form during weighing, dissolution, or ammonia release events. These risks are mitigated by fume hoods, slow addition, and operator personal protective equipment. |
| | Kernel Heat Treatment | None identified | N/A |
| | Particle Coating and Pre-Forming | Methyltrichlorosilane (CH ₃ SiCl ₃) Hydrochloric acid (HCl) | Toxic vapors such as HCl and chlorosilane may escape from thermal decomposition or leaks in high temperature furnaces if purge systems fail. |
| | Fuel Matrix Formation | HMTA (C ₆ H ₁₂ N ₄) | Airborne particulates from dry binder material may pose inhalation risk during blending or compaction without adequate dust capture. |
| | Final Conditioning | None identified | N/A |
| Skin and Eye Damage/Irritation | Kernel Preparation | Nitric acid (HNO ₃) Ammonium hydroxide (NH ₄ OH) Ammonium nitrate (NH ₄ NO ₃) | Splash potential during reagent handling or ammonia addition may result in corrosive effects on skin or eyes without proper personal protective equipment or shielding. Trace residues of ammonium nitrate may irritate eyes during washing or transfer steps. |
| | Kernel Heat Treatment | None identified | N/A |
| | Particle Coating and Pre-Forming | Methyltrichlorosilane (CH ₃ SiCl ₃) Hydrochloric acid (HCl) | High temperature gas streams and leaked vapors may contact exposed skin or eyes during coating furnace startup, leaks, or maintenance. |
| | Fuel Matrix Formation | Phenol-HMTA resin Phenol polymer with formaldehyde ((C ₆ H ₅ OH)x·(CH ₂ O)y) | Exposure to uncured binder during mixing, overcoating, or compaction may result in localized skin irritation or allergic response. |
| | Final Conditioning | None identified | N/A |
| Sensitization | Kernel Preparation | None identified | N/A |
| | Kernel Heat Treatment | None identified | N/A |
| | Particle Coating and Pre-Forming | None identified | N/A |
| | Fuel Matrix Formation | HMTA (C ₆ H ₁₂ N ₄) Phenol-HMTA resin | Direct skin contact with uncured binder or residual monomer may lead to sensitization over repeated exposure. Exposure risk is highest during hand-mixing or when gloves are not changed regularly. |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|------------------------------|-------------------------------------|--|---|
| | | Phenol polymer with formaldehyde ((C ₆ H ₅ OH)x·(CH ₂ O)y) | |
| | Final Conditioning | None identified | N/A |
| Chronic/Systemic Toxicity | Kernel Preparation | Uranyl nitrate (UO ₂ (NO ₃) ₂) | Prolonged dermal or inhalation exposure to uranyl nitrate may cause kidney or bone toxicity. Chronic exposure is unlikely with appropriate PPE and ventilation. |
| | Kernel Heat Treatment | None identified | N/A |
| | Particle Coating and Pre-Forming | Methyltrichlorosilane (CH ₃ SiCl ₃) | Although primarily an acute inhalation hazard, repeated exposure to unreacted vapor during coating cycles may cause cumulative systemic effects. |
| | Fuel Matrix Formation | HMTA (C ₆ H ₁₂ N ₄) Trichloroethylene (TCE) Perchloroethylene (PERC) | HMTA may cause genotoxicity or organ toxicity with prolonged binder handling. TCE and PERC vapors from adjacent cleaning steps may accumulate near matrix preparation stations if ventilation is insufficient. |
| | Final Conditioning | None identified | N/A |
| Aspiration Hazard | Kernel Preparation | Mineral oils Silicone oils | Oil residue from washing or gel sphere separation may pose aspiration risk if accidentally ingested during transfer or container draining. Some silicone oils used in degreasing may present aspiration hazards depending on viscosity and formulation. |
| | Kernel Heat Treatment | None identified | N/A |
| | Particle Coating and Pre-Forming | None identified | N/A |
| | Fuel Matrix Formation | None identified | N/A |
| | Final Conditioning | None identified | N/A |
| N/A = not applicable; | ; TRISO = tri-structural isotr | opic. | |

3.2.1.2 Chemical Process Step Assessments for Uranium Metal Fuels (General)

This subsection summarizes the chemical hazards associated with uranium metal fuel fabrication for use in both sodium-bonded metal fuels and dry metal fuels. The subsection focuses on the magnesiothermic reduction of uranium tetrafluoride (UF₄) using magnesium (Mg) under high temperature, inert atmosphere conditions. This assumption was selected as the representative baseline for uranium metal production. <u>Table 8 Table 8</u> provides a summary of process steps for uranium metal fabrication. <u>Table 9 Table 9</u> and <u>Table 10 Table 10</u> present a synthesis of relevant physical and health safety considerations for the chemicals involved in each process step, based on GHS hazard classifications.

Table 8. Uranium Metal Fuel Fabrication Process Summary.

| Fabrication Process Step | Description |
|--|--|
| Precursor Preparation and Charging | UF ₄ and Mg are batched and loaded together as the reactive charge. The charge is placed into sealed reduction vessels. Argon is introduced to displace oxygen and maintain an inert atmosphere before heating. |
| Magnesiothermic Reduction and Slag Removal | During the high temperature reaction between UF $_4$ and Mg, uranium metal and MgF $_2$ slag are produced. Magnesium continues to react as excess reagent. The resulting slag is removed mechanically, and cleaning may involve immersion in nitric acid (HNO $_3$). Use of a molten salt bath (typically a eutectic mixture of Li $_2$ CO $_3$ and K $_2$ CO $_3$) helps dissolve MgF $_2$ residues. The chemical interactions during this step may evolve HF, NO $_x$, and yield LiF and KMgF $_3$ as byproducts. |
| Casting and Final Conditioning | Uranium metal is melted and cast into molds, requiring high temperature crucibles. Coatings such as Y ₂ O ₃ , ZrO ₂ , and MgZrO ₃ are applied to prevent mold-metal interactions. BeO may be used in mold or joint coatings. Post-casting surface cleaning involves chemical treatments with HNO ₃ and HF. Sodium carboxymethyl cellulose can be used as a binder or coating additive during processing or post-casting cleaning. |

Table 9. Physical Safety Considerations – Summary for Uranium Metal Fuel Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|---------------------------------------|--|--|---|
| Flammability | Precursor Preparation and Charging | Magnesium (Mg) | Magnesium is a flammable and pyrophoric solid that can ignite when finely divided and exposed to air. Although inert gas purging is used, any delay in establishing an inert atmosphere during charging may permit ignition of airborne Mg particulates. |
| | Magnesiothermic Reduction and Slag Removal | Magnesium (Mg) | Residual magnesium may persist in slag or as surface deposits. Upon exposure to air during slag removal, these residues could ignite, especially if still hot. Magnesium's flammability remains a risk in scenarios involving premature vessel opening or loss of inerting. |
| | Casting and Final Conditioning | None identified | While no flammable reagents are added, off-gassing from thermal degradation of coatings or binders (e.g., sodium carboxymethyl cellulose) could generate flammable vapors under high heat and poor ventilation. |
| Explosivity | Precursor Preparation and Charging | None identified | While not Globally Harmonized System (GHS)-classified, magnesium fines or residual particulates may pose a combustible dust hazard if dried, dispersed, and ignited under abnormal ventilation or maintenance scenarios. |
| | Magnesiothermic Reduction and Slag Removal | None identified | Rapid pressurization from gas evolution or slag—water contact during process upset may resemble an explosive release. Also, while not GHS-classified, magnesium fines or residual particulates may pose a combustible dust hazard if dried, dispersed, and ignited under abnormal ventilation or maintenance scenarios. |
| | Casting and Final Conditioning | None identified | Residual moisture in mold coatings or joint materials may undergo flash boiling when in contact with molten uranium, potentially causing violent spattering or pressure ejection, a physical hazard resembling a localized explosive event. |
| Thermal or Reactive Instability | Precursor Preparation and Charging | Magnesium (Mg) | Contact with moisture may initiate self-heating and hydrogen evolution from Mg. UF ₄ may exacerbate reactivity despite not being GHS-classified. |
| | Magnesiothermic Reduction and Slag Removal | Magnesium (Mg) Hydrofluoric acid (HF) | HF may form from ${\rm MgF_2}$ or residual UF $_4$ contacting moisture. Slag may retain heat and promote reactions post-process. Unreacted magnesium within slag can remain pyrophoric at elevated temperatures. |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|---------------------------|--|--|---|
| | Casting and Final Conditioning | Hydrofluoric acid (HF) | HF reacts exothermically with oxides and many metals. Post-casting treatments involving HF on hot surfaces or reactive residues may release HF vapor or initiate surface corrosion reactions. |
| Physical Corrosivity | Precursor Preparation and Charging | None identified | N/A |
| | Magnesiothermic Reduction and Slag Removal | Hydrofluoric acid (HF) | HF may be generated in-situ during cleaning operations if MgF ₂ or residual UF ₄ contacts moisture. HF is a highly corrosive agent that can damage a wide range of materials, including stainless steel and glass. Post-reduction cleaning involving nitric acid or molten salt baths may exacerbate equipment degradation if HF is present and not effectively neutralized. |
| | Casting and Final Conditioning | Nitric acid (HNO₃) Hydrofluoric acid (HF) | Both HNO ₃ and HF are employed during post-casting surface cleaning. HNO ₃ , as a strong oxidizer, can corrode metallic surfaces, especially under heated or concentrated conditions. HF poses additional risk by penetrating oxide layers and reacting aggressively with both metal and ceramic components. Without adequate rinsing or pH neutralization, residues may degrade equipment surfaces or compromise mold coatings. Acid-resistant materials and ventilation are required to mitigate these hazards. |
| Pressurization Hazards | Precursor Preparation and Charging | None identified | If argon purging is initiated before verifying venting pathways, transient overpressurization may occur, particularly in improperly sealed or partially loaded reduction vessels. |
| | Magnesiothermic Reduction and Slag Removal | Nitrogen oxides (NO and NO ₂) | Gas evolution during slag dissolution or UF ₄ hydrolysis may lead to overpressurization if venting is restricted. |
| | Casting and Final Conditioning | None identified | Volatile degradation products from coatings (e.g., binders, oxides) may evolve gases during heating. If trapped within crucibles or mold cavities, localized pressure buildup may lead to sudden release or structural stress. |
| Oxidizing Hazards | Precursor Preparation and Charging | None identified | N/A |
| | Magnesiothermic Reduction and Slag Removal | None identified | N/A |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|----------------------|--------------------------------|---------------------------------|--|
| | Casting and Final Conditioning | Nitric acid (HNO ₃) | HNO ₃ may intensify combustion if in contact with flammables or process residues. |
| N/A = not applicable | e. | | |

Table 10. Health Safety Considerations – Summary for Uranium Metal Fuel Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|-----------------------------------|--|--|--|
| Acute Toxicity | Precursor Preparation and Charging | Uranium tetrafluoride (UF ₄) | UF ₄ is acutely toxic by inhalation and ingestion. Dust exposure during weighing or transfer, if not properly enclosed or ventilated, may result in systemic toxicity and chemical pneumonitis. |
| | Magnesiothermic Reduction and Slag Removal | Hydrofluoric acid (HF) Nitrogen oxides (NO and NO ₂) Lithium carbonate (Li ₂ CO ₃) Lithium fluoride (LiF) | Fume evolution during slag cleaning may include additional respiratory irritants or particulates depending on conditions. |
| | Casting and Final Conditioning | Hydrofluoric acid (HF) | HF used in surface cleaning is highly toxic via dermal and inhalation routes. Even dilute solutions can be fatal if absorbed through skin, particularly on hands or face. |
| Skin and Eye Damage/Irritation | Precursor Preparation and Charging | Uranium tetrafluoride (UF ₄) | Residual powder handling during charging may result in skin or eye exposure if not properly contained. |
| | Magnesiothermic Reduction and Slag Removal | Hydrofluoric acid (HF) Magnesium fluoride (MgF ₂) Potassium carbonate (K ₂ CO ₃) | Trace residues from slag may pose skin or mucous membrane irritation risks during maintenance or cleaning. |
| | Casting and Final Conditioning | Hydrofluoric acid (HF) Nitric acid (HNO ₃) Yttrium oxide (Y ₂ O ₃) Zirconium dioxide (ZrO ₂) | Oxide removal steps and thermal residue handling can create local eye/skin contact hazards in unshielded operations. |
| Sensitization | Precursor Preparation and Charging | None identified | N/A |
| | Magnesiothermic Reduction and Slag Removal | None identified | N/A |
| | Casting and Final Conditioning | Beryllium oxide (BeO) | Respiratory sensitization may occur from residual BeO particulates during brazing, grinding, or inspection. |
| Chronic/Systemic Toxicity | Precursor Preparation and Charging | Uranium tetrafluoride (UF ₄) | Potential for cumulative internal exposure exists if UF ₄ is handled outside of containment or fume hood controls. |
| | Magnesiothermic Reduction and Slag Removal | Nitrogen oxides (NO and NO ₂) | Chronic exposure risks may arise during prolonged or repeated slag processing with insufficient ventilation. |
| | Casting and Final Conditioning | Beryllium oxide (BeO) | Improper containment of BeO-bearing dusts during post-processing may increase the risk of berylliosis. |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations | |
|-----------------------|--|-----------------|-----------------------------------|--|
| Aspiration Hazard | Precursor Preparation and Charging | None identified | N/A | |
| | Magnesiothermic Reduction and Slag Removal | None identified | N/A | |
| | Casting and Final Conditioning | None identified | N/A | |
| N/A = not applicable. | | | | |

3.2.1.3 Chemical Process Step Assessments for Sodium-Bonded Metal Fuels

This subsection presents a summary of chemical safety considerations for sodium-bonded metallic fuel fabrication. The assumed process steps include vacuum-pressure casting of metallic uranium fuel slugs, incorporation of sodium bonding material into cladding, and associated cleaning and inspection operations. <u>Table 11 Table 11</u> provides a summary description of these process steps. <u>Table 12 Table 12</u> and <u>Table 13 Table 13</u> present a synthesis of relevant physical and health safety considerations for the chemicals involved in each process step, based on GHS hazard classifications.

Table 11. Sodium-Bonded Metallic Fuel Fabrication Process Summary.

| Fabrication Process Step | Description | | |
|----------------------------------|---|--|--|
| Alloy Casting and Fuel Formation | Metallic uranium and zirconium are melted and cast into slugs or pins in an inert atmosphere. Sodium may be introduced as a constituent in the fuel or used for mold interface. Tetrachloroethylene (C ₂ Cl ₄) is applied to degrease casting equipment. Argon ensures oxygen-free processing conditions. | | |
| Sodium Bonding and Encapsulation | Elemental sodium is introduced into the fuel-to-cladding gap using pressure-driven or capillary methods. Cladding is sealed via welding, often performed under Argon to avoid oxidation and sodium ignition during high temperature steps. | | |
| Cleaning and Inspection | Encapsulated fuel elements are cleaned using HNO₃ to remove oxides and reaction residues. Tetrachloroethylene is used as a solvent degreaser to eliminate oils or handling residues prior to inspection. | | |

Table 12. Physical Safety Considerations – Summary for Sodium-Bonded Metallic Fuel Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|---------------------------------------|----------------------------------|--------------------|--|
| Flammability | Alloy Casting and Fuel Formation | Sodium (Na) | Sodium reacts violently with moisture and may ignite on contact with air or water. Fine droplets or surface oxidation may exacerbate flammability. |
| | Sodium Bonding and Encapsulation | Sodium (Na) | Ignition risk from residual sodium during bonding or handling operations is elevated under humid conditions or during vacuum breach. |
| | Cleaning and Inspection | None identified | While not GHS-classified as flammable, tetrachloroethylene may support combustion under high temperature or oxidizing conditions. Solvent vapor ignition is possible in confined spaces. |
| Explosivity | Alloy Casting and Fuel Formation | None identified | N/A |
| | Sodium Bonding and Encapsulation | None identified | N/A |
| | Cleaning and Inspection | None identified | N/A |
| Thermal or Reactive Instability | Alloy Casting and Fuel Formation | Sodium (Na) | Sodium is highly reactive with water and air, generating heat and hydrogen. Thermal runaway may occur if inerting fails or oxidized sodium is reheated. |
| | Sodium Bonding and Encapsulation | Sodium (Na) | Entrained sodium within cladding or surface oxide layers may react exothermically under vacuum breach or during hot handling. |
| | Cleaning and Inspection | None identified | N/A |
| Physical Corrosivity | Alloy Casting and Fuel Formation | None identified | N/A |
| | Sodium Bonding and Encapsulation | None identified | N/A |
| | Cleaning and Inspection | Nitric acid (HNO₃) | Nitric acid used during cleaning can corrode exposed metal surfaces. Residual sodium may also react with acid to evolve heat and nitrogen oxides. |
| Pressurization Hazards | Alloy Casting and Fuel Formation | Argon (Ar) | Argon supplied from pressurized cylinders for inerting. Overpressure risk exists during casting or glovebox transfer without proper flow control. |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations | |
|----------------------|----------------------------------|---------------------------------|---|--|
| | Sodium Bonding and Encapsulation | Argon (Ar) | N/A | |
| | Cleaning and Inspection | None identified | N/A | |
| Oxidizing Hazards | Alloy Casting and Fuel Formation | None identified | N/A | |
| | Sodium Bonding and Encapsulation | None identified | N/A | |
| | Cleaning and Inspection | Nitric acid (HNO ₃) | Nitric acid is a strong oxidizer and may intensify combustion if spilled onto organic residues or sodium-contaminated surfaces. | |
| N/A = not applicable | N/A = not applicable. | | | |

Table 13. Health Safety Considerations – Summary for Sodium-Bonded Metallic Fuel Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|-----------------------------------|-------------------------------------|--|---|
| Acute Toxicity | Alloy Casting and Fuel Formation | None identified | Sodium vapor may be irritating under accidental heating or moisture exposure, but sodium is not Globally Harmonized System-classified for acute toxicity. |
| | Sodium Bonding and Encapsulation | None identified | N/A |
| | Cleaning and Inspection | Nitric acid (HNO ₃), Tetrachloroethylene (C ₂ Cl ₂₄) | Vapor accumulation could occur in enclosed glovebox or inspection areas if solvent handling or acid cleaning steps lack ventilation. |
| Skin and Eye Damage/Irritation | Alloy Casting and Fuel Formation | Sodium (Na) | Reactive residues on casting equipment or gloves may contact moisture and result in delayed-onset burns. |
| | Sodium Bonding and Encapsulation | None identified | N/A |
| | Cleaning and Inspection | Nitric acid (HNO ₃), Tetrachloroethylene (C ₂ Cl ₄) | Inadvertent contact with residual acid or solvent on tools or surfaces may cause dermal or eye irritation during inspection tasks. |
| Sensitization | Alloy Casting and Fuel Formation | None identified | N/A |
| | Sodium Bonding and Encapsulation | None identified | N/A |
| | Cleaning and Inspection | None identified | N/A |
| Chronic/Systemic Toxicity | Alloy Casting and Fuel Formation | None identified | N/A |
| | Sodium Bonding and Encapsulation | None identified | N/A |
| | Cleaning and Inspection | Tetrachloroethylene (C ₂ Cl ₄) | Extended solvent exposure in confined spaces or leak-prone systems could increase risk of chronic effects despite short-duration tasks. |
| Aspiration Hazard | Alloy Casting and Fuel Formation | None identified | N/A |
| | Sodium Bonding and Encapsulation | None identified | N/A |
| | Cleaning and Inspection | Tetrachloroethylene (C ₂ Cl ₄) | Aspiration risks are limited but may be relevant during large-scale degreasing or improper transfer to open containers. |

3.2.1.4 Chemical Process Step Assessments for Dry Metallic Fuels

This subsection presents a summary of chemical safety considerations associated with dry metallic fuel fabrication, i.e., fuel pin designs excluding sodium bonding. The assumed process includes uranium or alloy casting, machining, degreasing, and assembly. Table 14 Table 14 Table 15 and Table 16 present a synthesis of relevant physical and health safety considerations for the chemicals involved in each process step, based on GHS hazard classifications.

Table 14. Dry Metallic Fuel Fabrication Process Summary.

| Fabrication Process Step | Description | | |
|---------------------------------|--|--|--|
| Forming and Joining | Metallic fuel components are extruded or pressed into form. Cladding or structural parts are attached by welding or brazing using materials such as Zircaloy-2 alloy with 5% Be. BeO may be used to improve brazing joint integrity and thermal properties. | | |
| Heat Treatment and Conditioning | Fuel rods undergo annealing or molten salt treatment. Molten salt baths composed of Li ₂ CO ₃ , K ₂ CO ₃ , and additives like LiF are used to dissolve slag or refine surfaces. Oxide ceramics such as KMgF ₃ , MgZrO ₃ , Y ₂ O ₃ , and ZrO ₂ serve as protective coatings or structural stabilizers. | | |
| Final Cleaning | Chemical etching with HNO_3 and HF removes oxide layers and slag residues from fuel surfaces. Tetrachloroethylene (C_2Cl_4) is used to degrease the elements before inspection or packaging. | | |

Table 15. Physical Safety Considerations – Summary for Dry Metallic Fuel Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|---------------------|---------------------------------|--|--|
| Flammability | Forming and Joining | None identified | N/A |
| | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | None identified | Although tetrachloroethylene is used, it is not Globally Harmonized System (GHS)-classified as flammable. Vapors may pose ignition risk only in confined, oxygen-rich atmospheres. |
| Explosivity | Forming and Joining | None identified | Dry machining or polishing of metallic fuel components may generate fine uranium or alloy particulates. These may present a combustible dust hazard under abnormal dispersion and ignition conditions, even if not GHS-classified. |
| | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | None identified | N/A |
| Thermal or Reactive | Forming and Joining | None identified | Beryllium oxide (BeO) is not GHS-classified for reactive instability but may release fumes under extreme thermal conditions. |
| Instability | Heat Treatment and Conditioning | None identified | Carbonates and fluorides used in molten salt baths are thermally stable under normal use and are not GHS-classified for this hazard. |
| | Final Cleaning | Nitric acid (HNO₃) Hydrofluoric acid (HF) | HNO ₃ and HF are highly reactive and require careful segregation from incompatible materials and moisture during use. |
| Physical | Forming and Joining | None identified | N/A |
| Corrosivity | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | Nitric acid (HNO₃) Hydrofluoric acid (HF) | Both acids are corrosive to metals. HF also etches glass and requires specialized handling systems. |
| Pressurization | Forming and Joining | None identified | N/A |
| Hazards | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | None identified | N/A |
| | Forming and Joining | None identified | N/A |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|----------------------|---------------------------------|--------------------|---|
| Oxidizing Hazards | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | Nitric acid (HNO₃) | HNO₃ is a strong oxidizer. Oxidizer–organic contact should be avoided, especially if residual degreaser is present from earlier stages. |
| N/A = not applicable |) . | | |

Table 16. Health Safety Considerations – Summary for Dry Metallic Fuel Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|---------------------------|---------------------------------|--|--|
| Acute Toxicity | Forming and Joining | Beryllium oxide (BeO) | Inhalation of BeO particulates during brazing or machining can cause acute respiratory effects. |
| | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | Nitric acid (HNO₃) Hydrofluoric acid (HF) | Both acids are highly toxic via inhalation and skin contact; HF can penetrate tissue and cause systemic toxicity. |
| Skin and Eye | Forming and Joining | Beryllium oxide (BeO) | BeO particulates may cause skin irritation upon contact. |
| Damage/Irritation | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | Nitric acid (HNO ₃) Hydrofluoric acid (HF) Tetrachloroethylene (C ₂ Cl ₄) | HNO_3 and HF cause severe burns; C_2CI_4 can cause skin and eye irritation. |
| Sensitization | Forming and Joining | Beryllium oxide (BeO) | BeO is a known respiratory sensitizer; repeated exposure may lead to chronic beryllium disease. |
| | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | None identified | N/A |
| Chronic/Systemic Toxicity | Forming and Joining | Beryllium oxide (BeO) | Chronic inhalation exposure to BeO can lead to lung cancer and other systemic effects. |
| | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | Tetrachloroethylene (C ₂ Cl ₄) | Prolonged exposure to C ₂ Cl ₄ vapors may cause liver and kidney damage and is a suspected human carcinogen. |
| Aspiration | Forming and Joining | None identified | N/A |
| Hazard | Heat Treatment and Conditioning | None identified | N/A |
| | Final Cleaning | Tetrachloroethylene (C ₂ Cl ₄) | Aspiration of C ₂ Cl ₄ during ingestion can lead to chemical pneumonitis. |
| N/A = not applicable. | | | |

3.2.1.5 Chemical Process Step Assessments for Salt Fuels

This subsection presents a summary of chemical safety considerations associated with salt-based fuel fabrication. Two general process pathways were considered for fluoride-based fuels: (1) reaction of uranium dioxide (UO₂) with anhydrous hydrogen fluoride (HF) at elevated temperatures, and (2) direct reduction of uranium hexafluoride (UF₆) with hydrogen gas (H₂). For chloride-based fuels, the assumed steps include carbochlorination of UO₂ to produce uranium tetrachloride (UCl₄), followed by reduction with hydrogen to form UCl₃. Carrier salt preparation (e.g., purification of NaCl, KCl, LiCl, or Flibe) is also incorporated. Table 17 provides a summary description of these process steps. Table 18 and Table 19 present a synthesis of relevant physical and health safety considerations for the chemicals involved in each process step, based on GHS hazard classifications.

Table 17. Salt Fuel and Carrier Salt Fabrication Process Summary.

| Fabrication Process Step | Description |
|-------------------------------|--|
| Fluoride Salt Fuel Production | Uranium tetrafluoride (UF ₄) is produced by reacting uranium dioxide (UO ₂) with anhydrous hydrogen fluoride (HF) at 400–600°C or by reducing uranium hexafluoride (UF ₆) with hydrogen (H ₂). These routes generate HF as a reagent or byproduct and are used in fluoride-based molten salt fuels. The reactions may involve off-gassing of H ₂ O and fluorinated impurities. |
| Chloride Salt Fuel Production | Chloride-based salt fuels are synthesized by carbochlorination of uranium dioxide (UO ₂) with carbon tetrachloride (CCl ₄) at ~450°C to form uranium tetrachloride (UCl ₄), which is reduced with hydrogen (H ₂) to yield uranium trichloride (UCl ₃). The process can produce toxic and reactive byproducts such as carbon monoxide (CO), carbonyl dichloride (COCl ₂), chlorine gas (Cl ₂), and uranium pentachloride (UCl ₅). |
| Carrier Salt Preparation | Carrier salts such as Flibe (LiF-BeF ₂) are prepared by blending high purity powders. HF/H ₂ gas treatment at 525–700°C removes oxides and sulfates. Sulfur is converted to hydrogen sulfide (H ₂ S) and removed. Metallic Be may be added to improve reduction of sulfates. Nickel, chromium, and iron fluoride corrosion products (e.g., NiF ₂ , FeF ₂ , FeF ₃) may form in metal processing vessels. |
| Fuel Salt Purification | Both fluoride and chloride fuel salts are purified to remove oxide, hydroxide, and sulfate impurities using hydrofluorination (HF/H ₂) or reactive metals. HCl and Be may be used for refining. This step eliminates corrosive impurities before final blending. Off-gas products (e.g., H ₂ O, H ₂ S) are captured and removed. |
| Fuel Salt Blending | Purified fissile materials (UF ₄ or UCl ₃) are blended with carrier salts such as Flibe (for fluoride systems) or NaCl-MgCl ₂ -KCl (for chloride systems) under vacuum or inert atmosphere at elevated temperature. Oxide ceramic additives like ZrF ₄ may be used in fluoride systems for oxygen gettering and corrosion mitigation. |

Table 18. Physical Safety Considerations – Summary for Salt Fuel and Carrier Salt Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|---------------------------------------|----------------------------------|--|--|
| Flammability | Fluoride Salt Fuel Production | Hydrogen (H ₂) | Hydrogen use during UF ₆ reduction requires controlled inerting and pressure relief to prevent flammable atmosphere formation. |
| | Chloride Salt Fuel Production | Carbon monoxide (CO) Hydrogen (H ₂) | CO may accumulate if ventilation fails; flammability risk increases in confined processing zones. |
| | Carrier Salt Preparation | Hydrogen (H ₂) | Hydrogen employed during HF treatments may leak at fittings or joints under heat, necessitating flame arrestors or purge design. |
| | Fuel Salt Purification | Hydrogen (H ₂) | Purge failure or off-gas recirculation malfunction could allow hydrogen to accumulate. |
| | Fuel Salt Blending | None identified | N/A |
| Explosivity | Fluoride Salt Fuel Production | None identified | N/A |
| | Chloride Salt Fuel Production | None identified | N/A |
| | Carrier Salt Preparation | None identified | Fine powders of fluoride or chloride salts may be handled during purification. While these salts are non-combustible, airborne particulates could support dust layering or act as carriers in reactive dust clouds |
| | Fuel Salt Purification | None identified | N/A |
| | Fuel Salt Blending | None identified | N/A |
| Thermal or Reactive Instability | Fluoride Salt Fuel Production | None identified | Thermal risks from COCl ₂ or CCl ₄ are process-specific and not supported by Globally Harmonized System (GHS) classification; managed through thermal control. |
| | Chloride Salt Fuel Production | None identified | N/A |
| | Carrier Salt Preparation | None identified | Metallic Be may remain reactive under abnormal cooling conditions but is not GHS-classified for reactivity. |
| | Fuel Salt Purification | None identified | N/A |
| | Fuel Salt Blending | None identified | N/A |
| Physical Corrosivity | Fluoride Salt Fuel Production | Hydrogen fluoride (HF) | N/A |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|---------------------------|----------------------------------|--|--|
| | Chloride Salt Fuel Production | Chlorine (Cl ₂) Hydrogen chloride (HCl) | Residual chlorinated gases may condense in downstream systems, causing corrosive degradation in valves and internal linings. |
| | Carrier Salt Preparation | Hydrogen fluoride (HF) | HF from oxide removal steps may slowly degrade Inconel if purge gas stream is interrupted. Corrosion products such as NiF ₂ , FeF ₃ , and FeF ₂ may accumulate in salt mixtures due to degradation of structural alloys. These compounds are not added reagents but can contribute to downstream corrosion if not filtered. |
| | Fuel Salt Purification | Hydrogen fluoride (HF) | Improper sealing of off-gas paths may allow HF leakage that damages ductwork over time. |
| | Fuel Salt Blending | None identified | N/A |
| Pressurization Hazards | Fluoride Salt Fuel Production | Hydrogen (H ₂) | Hydrogen feed lines must be pressure-regulated during UF_6 reduction to avoid unintended buildup. |
| | Chloride Salt Fuel Production | Hydrogen (H ₂) | UCl ₄ reduction with hydrogen may cause transient pressure surges if flow control is not actively monitored. |
| | Carrier Salt Preparation | Hydrogen (H ₂) | Gas buildup can occur during desulfurization without sufficient venting. |
| | Fuel Salt Purification | Hydrogen (H ₂) | Recirculation or exhaust blockage could lead to localized pressurization in salt reactors. |
| | Fuel Salt Blending | None identified | N/A |
| Oxidizing Hazards | Fluoride Salt Fuel Production | None identified | N/A |
| | Chloride Salt Fuel Production | Chlorine (Cl ₂) | Chlorine present as byproduct from UCl ₄ synthesis may intensify combustibility of organics or reactor wall deposits if leaks occur. |
| | Carrier Salt Preparation | None identified | N/A |
| | Fuel Salt Purification | None identified | N/A |
| | Fuel Salt Blending | None identified | N/A |

Table 19. Health Safety Considerations – Summary for Salt Fuel and Carrier Salt Fabrication.

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|-----------------------------------|----------------------------------|---|--|
| Acute Toxicity | Fluoride Salt Fuel Production | Hydrogen fluoride (HF) | HF exposure during UF ₄ synthesis may become acute if off-gas capture fails or venting is obstructed. |
| | Chloride Salt Fuel Production | Hydrogen chloride (HCI) Carbonyl dichloride (COCl ₂) | COCl ₂ may evolve from side reactions involving CCl ₄ ; rapid containment is essential to prevent toxic exposure. |
| | Carrier Salt Preparation | Hydrogen fluoride (HF) Hydrogen sulfide (H ₂ S) | If reactor temperature overshoots or purge flow is interrupted, HF and H ₂ S concentrations may spike unexpectedly. |
| | Fuel Salt Purification | Hydrogen fluoride (HF) | Acute exposure may occur during unplanned maintenance or ruptures in high temperature scrubber zones. |
| | Fuel Salt Blending | None identified | N/A |
| Skin and Eye Damage/Irritation | Fluoride Salt Fuel Production | Hydrogen fluoride (HF) | Splashes or HF vapor from etching reactions can cause rapid tissue damage under poor shielding or personal protection equipment failure. |
| | Chloride Salt Fuel Production | Hydrogen chloride (HCI) | Residual HCl in containment vessels may irritate operators during inspection or valve replacement tasks. |
| | Carrier Salt Preparation | Hydrogen fluoride (HF) Hydrogen sulfide (H ₂ S) | H₂S and HF vapors may irritate mucosal membranes during desulfurization if fume hoods are undersized. |
| | Fuel Salt Purification | Hydrogen fluoride (HF) | Trace HF leaks near process flanges or cracked sight glasses may pose localized skin contact risks. |
| | Fuel Salt Blending | None identified | N/A |
| Sensitization | Fluoride Salt Fuel Production | None identified | N/A |
| | Chloride Salt Fuel Production | None identified | N/A |
| | Carrier Salt Preparation | Beryllium fluoride (BeF ₂) | Inhalation of airborne BeF ₂ particulates during powder handling may result in sensitization, especially during cleaning or refill. |
| | Fuel Salt Purification | None identified | N/A |
| | Fuel Salt Blending | None identified | N/A |
| Chronic/Systemic Toxicity | Fluoride Salt Fuel Production | Hydrogen fluoride (HF) | Long-term exposure from repetitive microleaks in HF systems could cause cumulative respiratory irritation. |
| | Chloride Salt Fuel Production | Carbonyl dichloride (COCl ₂) Chlorine (Cl ₂) | Persistent low-level COCl ₂ or Cl ₂ emissions may contribute to cumulative pulmonary or organ stress in adjacent operations. |

| Hazard Type | Fabrication Process Step | Chemicals | Hazard Context and Considerations |
|----------------------|----------------------------------|---|--|
| | Carrier Salt Preparation | Beryllium (Be) Beryllium fluoride (BeF ₂) Beryllium oxide (BeO) | Chronic inhalation risks from Be-containing particulates may persist even under controlled operations. Corrosion-derived fluorides (e.g., NiF ₂ , FeF ₃ , FeF ₂), though not deliberately introduced, may contribute to systemic toxicity during maintenance or salt transfer operations if disturbed. |
| | Fuel Salt Purification | Hydrogen fluoride (HF) Beryllium (Be) | Continuous exposure to HF and unreacted beryllium in filters or reactor scale may accumulate systemic health burdens. |
| | Fuel Salt Blending | None identified | N/A |
| Aspiration Hazard | Fluoride Salt Fuel Production | None identified | N/A |
| | Chloride Salt Fuel Production | Carbon tetrachloride (CCl ₄) | Though not GHS-flammable, accidental ingestion or spillage during chlorination may present aspiration hazard. |
| | Carrier Salt Preparation | None identified | N/A |
| | Fuel Salt Purification | None identified | N/A |
| | Fuel Salt Blending | None identified | N/A |
| N/A = not applicable |). | | |

3.2.2 Safety Review Considerations

Section 0 provided a structured summary of the chemical process safety assessments for TRISO-based, metallic, and salt fuel fabrication processes. The safety considerations, which are organized according to physical and health-related considerations, reflect the full range of hazards identified across relevant process environments. While most of the hazards are well-established and align with existing regulatory expectations, the specific ways in which they arise during advanced fuel fabrication can vary significantly depending on material form, processing conditions, and chemical transformations. For example, hazards may emerge through thermal decomposition of organic compounds, gas evolution during high temperature reactions, or the presence of fine powders or reactive metals not typically encountered in legacy fuel cycles.

Although these phenomena do not represent new hazard categories, they may influence how known hazards present in advanced fuel systems, potentially under conditions that are not fully represented in existing NRC regulated facilities. As described in Section 0, regulatory guidance documents provide a strong foundation for evaluating chemical safety in fuel cycle facilities. However, due to their technology-inclusive nature, these documents may not always explicitly account for the diversity of material combinations, processing temperatures, or environmental conditions encountered in modern fuel fabrication. In particular, current guidance documents may offer limited examples for evaluating hazard behavior in multi-step thermal processes, closed-system gas evolution scenarios, or in-situ generation of reactive byproducts.

To support the application of current guidance to advanced fuel types, <u>Table 20 Table 20 and Table 21 Table 21</u> present a summary of safety review considerations organized by chemical hazard type, physical and health, respectively. These considerations are based on the process-specific insights presented in Section 0, along with the chemical classifications documented in Appendix B. Each entry identifies conditions, behaviors, or material characteristics that may warrant additional attention during regulatory review, particularly in cases where existing guidance does not provide directly applicable process examples.

Table 20. Physical Safety Considerations.

| Hazard Type | Safety Review Considerations |
|---------------------------------|---|
| Flammability | Consider flammability from thermal decomposition products, combustible powders, and pyrophoric or reactive metals, especially where ignition may arise during heating, off-gassing, or air/moisture exposure. These conditions may not be well characterized by flash point or vapor pressure alone. |
| Explosivity | Evaluate risks from dust deflagration and gas evolution (e.g., H ₂ , CO) in enclosed or thermally active systems, even where materials are not Globally Harmonized System-classified as explosives. Explosion potential may depend on material form, confinement, and upset response capability. |
| Thermal or Reactive Instability | Account for multi-step exothermic reactions, unstable intermediates, or delayed gas evolution during thermal treatment, especially under upset or reduced ventilation conditions. Some instabilities may not be evident from bulk chemical properties. |
| Physical Corrosivity | Include corrosive effects from both introduced chemicals and process-derived residues, particularly where cleaning or deposition |

| Hazard Type | Safety Review Considerations |
|------------------------|--|
| | occurs. Corrosivity may result from transient reactions or cumulative surface degradation. |
| Pressurization Hazards | Consider transient pressure buildup from gas-evolving reactions or inert gas failures, especially in sealed or poorly vented systems during thermal or chemical processing. These events may occur rapidly and without typical pressure system indicators. |
| Oxidizing Hazards | Address oxidizer presence from introduced chemicals or in-situ formation, particularly in reactive atmospheres involving metal residues or organics. Oxidizing conditions may intensify other hazards if not identified early in system planning. |

Table 21. Health Safety Considerations.

| Hazard Type | Safety Review Considerations |
|----------------------------------|--|
| Acute Toxicity | Toxic gases and vapors may be produced during decomposition, reduction, or chlorination steps. Some of these substances may lack clear short-term exposure limits or may only be relevant under specific thermal or chemical process conditions. |
| Skin and Eye Damage / Irritation | Address splash, vapor, or contact hazards from corrosive liquids and residues that may not appear in input chemical lists but can form during processing or cleaning. Secondary exposure via contaminated surfaces may also warrant attention. |
| Sensitization | Recognize sensitization risks from recurring exposure to binders, particulates, or coating residues. These risks may not always be covered by general occupational exposure thresholds. |
| Chronic/Systemic Toxicity | Evaluate cumulative exposure potential to organics, actinides, or metal particulates, particularly in contexts with limited ventilation or repeated processing. Some materials may present chronic risks even at low acute exposure levels. |
| Aspiration Hazard | Certain solvents may present aspiration risks when handled in ways that produce aerosols or inhalable droplets. These hazards may not be apparent based solely on conventional usage or labeling. |

3.2.3 Considerations on Exposure Threshold Coverage and Limitations

As described in Section 3.1.2, this assessment relied on PAC values, NIOSH IDLH concentrations, and NIOSH skin notations to identify exposure thresholds for process-relevant chemicals. These benchmarks are widely used in consequence screening and emergency planning and provide a consistent foundation for identifying threshold values across diverse fuel fabrication scenarios. While most of the substances evaluated were associated with PAC values, typically TEELs, Appendix B shows that complete threshold coverage was not available for certain chemicals, particularly with regard to IDLH values and formal skin notations. In some cases, surrogate IDLH values were presented for a constituent element (e.g., "as U" or "as F"), reflecting the toxicity of the elemental component rather than the compound in its applied form.

Additional chemical information sources, such as the PubChem® database, the GESTIS database, the Haz-Map® database, manufacturer SDSs, and the CAMEO Chemicals software, were reviewed where PAC or IDLH data were unavailable, primarily to determine whether other threshold-related information existed. These sources may include occupational exposure guidelines, hazard descriptors, or chemical compatibility insights (see Appendix B). However,

they are derived under different regulatory frameworks, which may reflect differing assumptions about exposure duration or severity, and often vary in population sensitivity and derivation transparency. Applying such values in consequence evaluations requires chemical-specific interpretation and was outside the scope of this assessment. In general, substances lacking PAC or IDLH values also tended to lack clearly applicable thresholds in these alternative sources.

Even where PAC values were available, supporting documentation was not always comprehensive. In some cases, references, derivation methods, or assumptions underlying listed values were not specified. The PAC database is currently undergoing a thorough review and revision, as appropriate, to reaffirm values and improve transparency through the inclusion of updated references and methodology documentation. Until that process is complete, users are to rely on the underlying DOE review process when applying PAC values that lack detailed supporting information.

Appendix B presents a consolidated summary of the available threshold data, with missing values clearly indicated. It reflects the current state of knowledge appropriate for bounding analyses and hazard screening across the fuel types addressed in this report. While additional information may exist in other sources, interpreting such data for use in consequence evaluation would require additional effort and substance-specific analysis.

3.2.4 Additional Discussion on Particular Considerations

3.2.4.1 Beryllium Use and Regulatory Considerations

Beryllium and its compounds appear across multiple stages of fluoride-based carrier salt and metallic fuel fabrication. BeF₂ is a key constituent of Flibe carrier salts, while metallic beryllium may be introduced during carrier salt purification to reduce sulfate impurities, forming BeO as a byproduct. BeO is also used as a crucible liner or mold coating in metallic fuel melting operations due to its favorable thermal properties. In some metallic fuel designs, alloying or brazing materials may also contain beryllium. Notably, beryllium compounds are not used in TRISO fuel fabrication, underscoring the fuel type specificity of this hazard.

Beryllium-based materials have known inhalation risks. As facilities currently licensed by NRC do not have chemical exposure hazards that are comparable to the use of beryllium, beryllium exposure hazards are not currently found in NRC guidance documents.

Under DOE operations, beryllium health safety is specifically regulated under 10 CFR 850 (Chronic Beryllium Disease Prevention Program), which focuses on minimizing worker exposure and ensuring rigorous exposure monitoring and medical surveillance. Separately, OSHA's beryllium standard (29 CFR 1910.1024) provides extensive requirements for exposure assessment, personal protective equipment, medical removal, and training. In 29 CFR 1910.1024, OSHA defines *chronic beryllium disease (CBD)* as a chronic granulomatous lung disease caused by inhalation of airborne beryllium by an individual who is beryllium sensitized. The corresponding OSHA standards are focused on OSHA-defined chronic occupational health risks and differ in structure and intent from NRC's existing chemical safety requirements under 10 CFR Part 70, Subpart H, which emphasizes accident scenarios and ISAs.

As discussed in Section 1.1, the NRC and OSHA signed an MOU (NRC-OSHA 2013), which can be referred to in order to ascertain whether NRC has a regulatory role or not for

occupational hazards associated with the use of beryllium and its compounds. As noted in the MOU: "The NRC has broad statutory authority to protect against radiation hazards produced by radioactive materials, chemical hazards produced by radioactive materials, and facility conditions that affect the safety of radioactive materials and thus present an increased radiation risk to workers and the general public." Whereas "OSHA standards contain requirements designed to protect employees against workplace hazards. In general, safety standards are intended to protect against traumatic injuries. Health standards are designed to address potential overexposure to toxic substances and harmful physical agents, and to protect employees against illnesses and disorders, including those that may not manifest until years after exposure." and "NRC does not conduct industrial safety and health inspections at NRC-licensed facilities. However, in the course of inspections of radiological and nuclear safety at such facilities, NRC inspectors may observe industrial safety and health hazards or receive complaints from employees that are within OSHA's authority and responsibility."

Applicants pursuing Part 50 or Part 52 reactor licenses with beryllium present in licensed material operations may look to ISA-style approaches for chemical hazards by referencing NRC Interim Staff Guidance (ISG) documents associated with NUREG-1537, including:

- Final Interim Staff Guidance Augmenting NUREG-1537, Part 1, "Guidelines for Preparing and Reviewing Applications for the Licensing of Non-Power Reactors: Format and Content," for Licensing Radioisotope Production Facilities and Aqueous Homogeneous Reactors, dated October 17, 2012 (NRC 2012b).
- Final Interim Staff Guidance Augmenting NUREG-1537, Part 2, "Guidelines for Preparing and Reviewing Applications for the Licensing of Non-Power Reactors: Standard Review Plan and Acceptance Criteria," for Licensing Radioisotope Production Facilities and Aqueous Homogeneous Reactors, dated October 17, 2012 (NRC 2012c).

These ISGs have previously been used to support chemical safety evaluations for non-power reactors and may serve as a precedent for evaluating non-radiological hazards.

3.2.4.2 Process Safety and Licensing Considerations for Carrier Salt Preparation and Blending

This assessment characterizes the chemical hazards and process conditions associated with both the preparation of carrier salts (e.g., Flibe) and the subsequent blending of carrier salts with fuel salts, as described in Section B.3.4. These operations involve high temperature handling, use of reactive gases (e.g., HF/H₂), and material compatibility concerns that are important from a chemical safety standpoint. However, the regulatory framework under which these steps are licensed may vary depending on site-specific implementation, particularly whether radiological materials are present and whether blending occurs at a fuel cycle facility or a reactor site. While the chemical and process safety aspects are addressed in this report, the regulatory implications of where and how these operations are licensed are not evaluated here. For additional discussion of licensing boundaries and oversight responsibilities, see Section 4.4.

3.2.4.3 Combustible Gas Risk and Fire Safety

Appendix B includes TEEL values for several combustible gases (such as hydrogen, acetylene, and propylene) that exceed their respective lower explosive limits (LELs). This reflects the fact that PAC-derived threshold values (e.g., TEEL-2, TEEL-3) are based on acute toxicity or asphyxiation potential rather than flammability or explosion risk. Consequently, the onset of

flammable or explosive conditions may occur well before the listed exposure thresholds are reached. This distinction is particularly relevant for advanced fuel fabrication processes where combustible gases may be present in closed systems, off-gas streams, or process atmospheres.

While not a new regulatory issue, this observation highlights the need to clearly distinguish between chemical exposure hazards and fire/explosion safety concerns during licensing reviews. The absence of a technical basis in the DOE PAC system for evaluating flammability consequences, especially when threshold values are equal to or exceed the LEL, suggests that separate fire safety analyses remain critical. This issue is noted as a cross-cutting consideration for both TRISO-based and salt-based fuel fabrication processes.

3.2.5 Summary of Assessment Findings

The assessment confirmed that chemical hazards associated with TRISO-based, metallic, and salt-based fuel fabrication processes are well characterized by established GHS physical and health hazard classifications. However, the specific conditions under which these hazards emerge (such as gas evolution in closed systems, formation of reactive byproducts, and exposure to high temperature or moisture-sensitive materials) highlight the importance of process-informed interpretation. In many cases, hazard significance is shaped not by the base chemical properties alone but rather by how materials are transformed, combined, or handled in the fabrication environment. This reinforces the need for tailored hazard evaluation in advanced fuel applications, particularly where operating conditions diverge from conventional fuel cycle examples used in regulatory guidance.

For most chemicals, at least one applicable benchmark was available. However, some non-availability of data was noted, especially for dermal exposure indicators and compounds lacking AEGL or ERPG data. In such cases, TEELs were identified when available, and supplementary information from databases or Safety Data Sheets was reviewed qualitatively to provide context. Appendix B presents the most complete available threshold information for each substance, enabling transparent reference during safety evaluations.

Several cross-cutting issues emerged that extend beyond traditional chemical classification and merit consideration in licensing or regulatory application.

<u>Beryllium Use:</u> Beryllium and beryllium compounds (e.g., BeF₂, BeO) appear across multiple stages of metallic and salt fuel fabrication. These materials are subject to stringent occupational health controls under DOE and OSHA frameworks. Beryllium based materials have known inhalation risks. As facilities currently licensed by NRC do not have chemical exposure hazards that are comparable to the use of beryllium, beryllium exposure hazards are not currently found in NRC guidance documents.

<u>Salt Preparation and Blending:</u> High temperature salt handling operations present process-specific chemical safety challenges that may not fall neatly under existing licensing frameworks. The regulatory treatment of these activities may vary depending on whether they are conducted at a fuel cycle facility or reactor site, suggesting a need for clear guidance on jurisdictional boundaries and applicable safety expectations.

<u>Combustible Gas and Fire Risk:</u> The presence of flammable gases such as hydrogen, acetylene, and propylene in fuel fabrication processes raises safety concerns that may not be adequately captured through toxicity-based screening thresholds. In several cases,

threshold exposure values for these gases exceed their LELs, meaning fire or explosion hazards could become significant at concentrations below those used for consequence classification. The NRC licensing review process includes separate chemical safety and fire safety reviews.

4.0 Assessment of Safety Review Guidance and Technical Basis Documents on Chemical Process Safety for TRISO-Based Fuels, Metallic-Based Fuels, and Salt-Based Fuels

Fuel cycle facilities for the fabrication of advanced reactor fuel types would be licensed, in part, per 10 CFR Part 70, *Domestic Licensing of Special Nuclear Material* (NRC 2024c), which establish procedures and criteria for the issuance of licenses to receive title to, own, acquire, deliver, receive, possess, use, and transfer special nuclear material and establish and provide for the terms and conditions upon which the NRC will issue such licenses. The NRC has developed various guidance and technical basis documents to assist the NRC staff and applicants in understanding the underlying objectives of these regulatory requirements, the relationships among different requirements, and approaches to the safety review of applications for fuel cycle facilities. These guidance documents address a breadth of topics, including hazard identification, risk evaluation, model selection, and emergency planning, emphasizing flexible, and risk-informed strategies to manage unique chemical and radiological hazards effectively while safeguarding workers, the public, and the environment. Pertinent to this report, the guidance documents provide a structured framework for evaluating chemical process safety within fuel cycle facilities.

Reviews of NUREG-1520, Revision 2 (NRC 2015), NUREG-1513 (NRC 2001), NUREG-1601 (NRC 1997a), and NUREG/CR-6481 (NRC 1997b) were conducted to identify process-specific considerations to augment the technology-inclusive nature of the reports. NUREG/CR-6410 (NRC 1998) was reviewed to identify any chemical processes at fabrication facilities for advanced fuel types that are not provided in the NUREG. Descriptions of such processes are included in this report, to the extent available, with the aim to support efficient licensing reviews.

The following discussions provide an overview of each guidance or technical basis document and identify cases of new chemicals and new fabrication processes at advanced fuel fabrication facilities. Within this section, process-specific considerations and descriptions are provided. Additionally, it is noted that the DOE protective action criteria database includes TEELs for process-specific chemicals.

4.1 Standard Review Plan for Fuel Cycle Facilities License Applications (NUREG-1520, Revision 2)

NUREG-1520, Revision 2, *Standard Review Plan for Fuel Cycle Facilities License Applications – Final Report* (NRC 2015), is the primary guidance document for the safety review of fuel cycle facilities. The SRP outlines a structured, adaptable approach for reviewing applications to construct and operate fuel cycle facilities. It provides a comprehensive yet flexible framework, offering detailed guidance for the NRC staff to evaluate safety, environmental protection, and regulatory compliance aspects of proposed facilities. The SRP is designed to adapt to various facility types and configurations, ensuring that diverse fuel cycle facilities, such as uranium enrichment or mixed-oxide fuel fabrication, meet safety standards without a one-size-fits-all approach.

The SRP emphasizes a risk-informed and performance-based review method, allowing reviewers to consider the unique characteristics and potential risks of each facility. The SRP is centered around verifying that licensees conduct a thorough ISA, which adequately identifies

hazards, accident sequences, and necessary controls tailored to the facility's specific processes. This flexibility allows facilities to implement customized safety measures appropriate to their operations while still meeting the NRC's stringent safety standards.

The SRP covers essential review areas, including radiation protection, criticality safety, chemical safety, and fire protection, providing checklists and criteria to address all aspects of safety. Additionally, it encourages coordination across multiple safety disciplines, fostering a comprehensive safety culture.

The SRP provides specific guidance for chemical safety in fuel cycle facilities, ensuring that chemical hazards are systematically identified, evaluated, and controlled within the facility's ISA. It requires licensees to assess potential chemical hazards, including toxic, reactive, and flammable chemicals that could endanger personnel, the public, or the environment. The SRP encourages the use of well-established hazard analysis techniques, such as Hazard and Operability (HAZOP) and Failure Mode and Effects Analysis (FMEA), to identify accident sequences related to chemical processes.

Facilities must also establish controls, such as containment, ventilation, and emergency shutdown systems, to prevent and mitigate chemical accidents. The SRP emphasizes robust training, emergency preparedness, and regular safety reviews to maintain effective chemical safety management across operations.

The generic and flexible nature of the SRP enables licensing reviews for different technologies while being adequate for addressing the specifics of the fabrication processes at individual fuel cycle facilities. This approach supports regulatory oversight that balances safety with operational flexibility, fostering robust protection for workers, the public, and the environment.

4.1.1 Assessment of NUREG-1520, Revision 2, for Advanced Fuel Cycle Facilities

The guidance in NUREG-1520, Revision 2 (NRC 2015) was evaluated with respect to chemical process safety at potential fabrication facilities for new fuel types.

Sources of information for exposure limits are identified in both NUREG-1520, Revision 2 Section 3.4.3.2, Item 7 (Quantitative Standards for Chemical Consequences), p. 3-26, as well as in NUREG-1520, Revision 2, Appendix A, Section A.2 (Consequence Category Assignment), p. 3-A-5. Specifically, ERPGs and AEGLs are discussed. It is noted that the DOE protective action criteria database includes TEELs for process-specific chemicals that could serve as a source of information to support licensing reviews.

4.2 Integrated Safety Analysis Guidance Document (NUREG-1513)

NUREG-1513, *Integrated Safety Analysis Guidance Document* (NRC 2001), provides a systematic approach for conducting an ISA at nuclear fuel cycle facilities. It establishes a comprehensive framework for identifying and analyzing hazards to evaluate facility safety. The document emphasizes a structured process to recognize potential accident scenarios, assess associated risks, and develop necessary safety controls to prevent accidents or mitigate their consequences. Key elements in an ISA include hazard identification, analysis of accident sequences, evaluation of potential consequences, and defining reliable safety controls.

The ISA process in NUREG-1513 relies on using various hazard analysis techniques, such as HAZOP, FMEA, and fault tree analysis. These tools help facilities assess how potential failures in systems or processes could lead to safety risks. By identifying accident sequences that could lead to unplanned releases of radioactive or hazardous materials, the ISA framework supports the implementation of robust preventive and mitigative controls.

Moreover, NUREG-1513 encourages facilities to integrate process safety measures across different domains, including radiological safety, fire protection, criticality safety, chemical safety, and physical security, ensuring a holistic view of facility safety (NRC 2001). The report supports ongoing compliance with regulatory requirements, aiming to create a dynamic and flexible safety management system. This generic approach provides licensees with adaptable guidance suited to various fuel cycle operations, reinforcing a proactive, risk-informed culture of safety in nuclear materials handling.

NUREG-1513 addresses chemical safety within the ISA framework by guiding fuel cycle facilities to systematically identify, evaluate, and manage chemical hazards (NRC 2001). It encourages facilities to use established hazard analysis methods to pinpoint and analyze potential accident sequences involving chemicals, including toxic or reactive substances that could pose risks to workers and the public. The ISA process supports identification and implementation of effective preventive and mitigative controls, such as containment systems, ventilation, and emergency response measures. Training and clear procedures are also emphasized, promoting and ongoing commitment to chemical safety management across operations.

No further considerations for new processes were identified for NUREG-1513 to address chemical process safety at fabrication facilities for the advanced reactor fuel types discussed in this report (NRC 2001). NUREG-1513 is technology-neutral with respect to chemical hazards (that is, NUREG-1513 is not specific to fuel fabrication plants for light-water reactor fuel), although the examples in Appendix B of ISA hazard evaluation methods applications are for uranium enrichment and UO_2 fuel fabrication plants. However, two of these examples (i.e., HAZOP analysis of the vaporization step of the UF_6 dry conversion process and fault tree analysis of a UF_6 release) would also be applicable to advanced reactor fuel fabrication plants that utilize UF_6 feedstock from an enrichment plant. A third example (interaction matrix for ammonium diuranate (ADU) process) would be applicable to TRISO fuel fabrication processes for the manufacture of UO_2 kernels (rather than UCO kernels). Regarding this example, it is noted that, while most TRISO-based fuel designs in the United States are expected to utilize UCO fuel kernels, UO_2 kernels have also been historically used (IAEA 2010).

4.3 Chemical Process Safety at Fuel Cycle Facilities (NUREG-1601)

NUREG-1601, Chemical Process Safety at Fuel Cycle Facilities (NRC 1997a), focuses on chemical safety processes within fuel cycle facilities, outlining a structured approach to identifying, evaluating, and mitigating chemical hazards. It emphasizes integrating chemical safety into overall facility operations by documenting process steps, material properties, and specific hazards relating to licensed nuclear materials. It provides recommended hazard analysis methods to assess risks of chemical reactions, toxic releases, and potential explosive conditions.

The document highlights the importance of preventive controls, such as containment, ventilation, and emergency shutdown systems, as well as training and regular audits to support

operational safety. This comprehensive guidance supports a proactive, risk-based approach to chemical safety.

No further considerations for new processes were identified for NUREG-1601 (NRC 1997a) to address chemical process safety at fabrication facilities for the advanced reactor fuel types discussed in this report. NUREG-1601 is technology-neutral with respect to chemical hazards. The broad guidance it provides on chemical process safety at fuel cycle facilities, including the identified general/standard methods of preventing or mitigating the consequences of chemical incidents, is also applicable to fuel fabrication facilities for the advanced fuels discussed in this report. No unique hazard mitigation methods for fabrication of advanced fuels were identified.

4.4 Nuclear Fuel Cycle Facility Accident Analysis Handbook (NUREG/CR-6410)

NUREG/CR-6410, *Nuclear Fuel Cycle Facility Accident Analysis Handbook* (NRC 1998), provides comprehensive guidance on evaluating and mitigating chemical hazards in nuclear fuel cycle facilities. It emphasizes the integration of chemical process safety into overall facility safety management, highlighting the importance of identifying potential chemical hazards, assessing associated risks, and implementing effective controls.

The handbook outlines methodologies for hazard evaluation and scenario development, focusing on identifying accident sequences involving hazardous chemicals. It discusses source term determination, detailing how to estimate the quantity and characteristics of chemical releases during potential accidents. Additionally, it covers transport within containment and confinement, providing insights into how chemicals may spread within facility boundaries. Atmospheric dispersion and consequence modeling are also addressed, offering tools to predict the impact of chemical releases on the environment and public health.

To support these analyses, NUREG/CR-6410 includes appendices with descriptions of various fuel cycle facilities, methods for calculating source terms for hazardous chemical releases, and comparisons of NRC, EPA, and OSHA chemical safety programs. It also summarizes the performance of HEPA and other filters and discusses uncertainties in safety analyses.

The document presents sample problems, such as free-fall spills of powder, explosions with radioactive releases, fires, filter failures, and releases of chemicals like HF and UF₆. These examples illustrate practical applications of the methodologies discussed, aiding in the development of robust chemical safety strategies.

By providing this detailed guidance, NUREG/CR-6410 (NRC 1998) assists in systematically addressing chemical process safety, ensuring the protection of workers, the public, and the environment from chemical hazards associated with nuclear fuel cycle operations.

4.4.1 Assessment of NUREG/CR-6410 for Fuel Cycle Facilities for TRISO-Based Fuel

This section identifies and provides process descriptions for the unique chemicals and processes associated with fabricating TRISO fuels that are not found in NUREG/CR-6410 (NRC 1998). These descriptions are analogous to those in Appendix A of NUREG/CR-6410 (NRC 1998), for the new fabrication processes for TRISO fuels. The following identifies some of the unique elements of the TRISO fuel fabrication process by major process step:

Receipt of enriched, either low-enriched uranium (LEU) or high-assay low-enriched uranium (HALEU) UF₆ feedstock:

This process is no different than that for LWR UO₂ fuel fabrication plants; therefore, the process description can be found in NUREG/CR-6410 for this process step.

Deconversion of UF₆ for TRISO kernel fabrication:

These processes are similar to those for LWR UO_2 fuel fabrication plants; therefore, the process description can be found in NUREG/CR-6410 for this process step. The preparation of other uranium oxides (UO_3 , U_3O_8) for kernel fabrication may be conducted by oxidation and calcination treatments.

Fabrication of UO₂ or UCO kernels:

This process starts with the preparation of an ADUN solution by dissolution of uranium oxides (UO₂, UO₃, U₃O₃) in HNO₃ to achieve a NO₃/U molar ratio in the range 1.5 to 1.7 (Beatty et al. 1979; Haas et al. 1980). A broth is then prepared by mixing the ADUN solution, urea, HMTA, carbon black (for UCO kernels) (Beatty et al. 1979) (Sowder and Marciulescu 2020), and a carbon black dispersant (such as Tamol™) at a temperature near or below 0°C (Stinton et al. 1982; Hunt et al. 2018; Raftery 2019). The broth is then gelled by controlled drop injection into organic forming fluid (a hot immiscible fluid, such as a mixture of TCE and Span® 80) at temperatures ranging from 50 to 100°C (Beatty et al. 1979; Collins et al. 2004; Sood 2010). The gel particles are further washed in both organic (e.g., TCE) and aqueous solutions (e.g., NH₄OH) to remove excess urea, HMTA, and byproduct salt (Sood 2010; Marshall 2019).

The resulting green spheres are dried in air at approximately 60 to 70°C, followed by calcination in H_2 , H_2/Ar , Ar or air between 300°C and 550°C to remove residual volatiles and to reduce the uranium oxide in the kernel to UO_2 (Collins et al. 2004; Marshall 2019; Battistini et al. 2023). The calcined particles are then reduced under a H_2 , H_2/Ar , or Ar atmosphere at temperatures ranging from ~900°C to 1700°C. A final sintering step is conducted under a H_2 , H_2/Ar or CO/Ar atmosphere at ~1550°C to 1900°C, which assures densification of the kernels (Petti et al. 2002; Marshall 2019; Battistini et al. 2023). The use of CO/Ar causes the carbon black to react with the UO_2 to produce UC, UC_2 , and CO (for UCO kernels). While very high temperature processes, such as sintering, are addressed in NUREG/CR-6410 (NRC 1998) (e.g., in the LWR UO_2 fuel fabrication process), the majority of the chemicals/materials used in the kernel fabrication process (HMTA, Tamol TM , TCE, Span® 80, carbon black, and UCO) are not considered in NUREG/CR-6410.

Chemical vapor deposition of the carbon layers on the fuel kernels:

The four coatings are sequentially applied to the kernels without interruption at temperatures ranging from ~1250°C to 1500°C (Sowder and Marciulescu 2020; Nickel et al. 2002). The porous pyrolytic carbon (PyC) buffer layer is deposited by chemical vapor deposition from a mixture of C_2H_2 and argon (Ar) diluent. The inner and outer pyrolytic carbon layers (IPyC and OPyC, respectively) are deposited from a mixture of C_2H_2 , CH_2CHCH_3 , and Ar diluent. The SiC layer is deposited from CH_3SiCl_3 diluted with H_2 and Ar. Most of these chemicals are not addressed in NUREG/CR-6410 (NRC 1998). Also, while not a new process, the chemical vapor deposition process is not explicitly addressed in NUREG/CR-6410 (NRC 1998). However, processes using fluidized bed furnaces are explicitly considered in NUREG/CR-6410, although at much lower temperatures than 1250°C to 1500°C.

Overcoating process:

Before the fuel compact is made, TRISO particles are put through a process of "overcoating," where graphitic matrix material is applied to the exterior of the TRISO particles (Demkowicz et al. 2019; Heit et al. 2017; IAEA 2015). Prior to overcoating, the TRISO particles may be washed in methanol (CH $_3$ OH) to reduce the amount of contamination on the particles. The overcoating process starts by placing the particles in a drum. The drum is slowly rotated and the graphitic matrix material and solvent (resin binder, such as C $_6$ H $_5$ OH, and a curing agent, such as HMTA) are added. The particles are then dried at 80 to 100°C. While NUREG/CR-6410 does address various types of solvents, phenol and HMTA are not identified.

Fuel compact fabrication:

Whether spherical (pebble) or right cylindrical-shaped, fuel compacts are a mixture of thousands of TRISO particles (that typically have been overcoated) and matrix material composed of graphite flour or powder (both natural and synthetic electrographite), graphite shim (if needed), a binder material (a resin such as C₆H₅OH in a solvent), and possibly other additives (e.g., a curing agent such as HMTA). The mixture is pressed in a silicone mold for pebble shapes at pressures up to 30 MPa, while for right cylindrical shapes, is pressed in a die at varying pressures (~ 10 MPa) and at a temperature that can range between room temperature and 165°C (Nabielek et al. 1984; Heit et al. 2017; Wolf et al. 1975; Nickel et al. 2002; IAEA 2015); (Sawa et al. 1999) (Marshall 2019). After being pressed, as described previously, the product is both carbonized at a temperature up to 900°C in an inert atmosphere (e.g., helium, Ar) and then heat treated (at a temperature up to 1800°C) (Nickel et al. 2002; Heit et al. 2017; Mehner et al. 1990; Wolf et al. 1975). While similar compaction processes are discussed in NUREG/CR-6410 (such as in the fabrication of UO₂ pellets), and very high temperature furnace processes (up to 1800°C) are also considered in NUREG/CR-6410 (such as for sintering of UO₂ pellets), the majority of the chemicals used in compaction process (CH₃OH, C₆H₅OH, HMTA, graphite powder, SiC for FCM pellets) are not considered in the chemicals evaluated in NUREG/CR-6410 (NRC 1998).

4.4.2 Assessment of NUREG/CR-6410 for Fuel Cycle Facilities for Metallic Fuel

The NRC has experience in the licensing of a facility for the fabrication of metallic fuel, namely the BWX Technologies, Inc. fuel fabrication facility located in Lynchburg, Virginia, that manufactures solid metal fuel for the U.S. Navy (NNSA 2017). A hazard associated with manufacturing metallic fuel, that is not associated with manufacturing UO₂ fuel, is the generation of metal fines or chips that are pyrophoric or can spontaneously ignite when exposed to air or moisture (although very fine UO₂ powder, and finely divided zirconium, can also be pyrophoric). This type of hazard is explicitly considered in Appendix B of NUREG/CR-6410 (NRC 1998).

NUREG/CR-6410 does not include descriptions of the process for production of uranium metal. The most common process historically used in the United States for production of uranium metal is reduction of UF₄ with Mg. Descriptions of the substeps of this process, including the slag recovery process are provided below. For sodium-bonded fuel and extruded metallic fuel, alloying is involved. Accordingly, descriptions of the alloying and fabrication of sodium-bonded fuel and extruded metallic fuel are provided below.

Magnesiothermic Reduction of UF₄ with Mg metal:

The use of Mg metal as a reductant of feedstock UF₄ is the most common industrial approach for the preparation of U metal (Durazzo et al. 2017; LaHaye and Burkes 2019; Jang et al. 2022). The process is conducted at high temperatures and pressures produced

by the exothermic reaction. In this process the UF $_4$ and Mg metal (referred to as the "charge") are loaded into a sealed chemical reactor, to contain the superatmospheric vapor pressure of Mg developed when the reactants are heated to the melting point of MgF $_2$, which is about 1263°C. Because the heat of reaction is too low to melt the reaction products at room temperature, the reactants must be preheated. The reactor may be lined with MgF $_2$ to prevent contamination of the uranium metal from reactor vessel corrosion products. The reactor is preheated in a furnace (that has been purged of oxygen using a gas such as Ar) to a temperature of 570–620°C, at which point spontaneous ignition occurs (Durazzo et al. 2017). After melting and fusing of the reactants, the molten uranium metal collects in the bottom of the reactor and the molten MgF $_2$ slag collects on top of the molten uranium. The reactor is cooled after which the solidified metal ingot and slag are removed as one large mass. Complete cooling is important to avoid the potential for a pyrophoric reaction of the metal with atmospheric oxygen.

The slag is then removed from the ingot by mechanical means such as chipping, thermal shocking, grit blasting, etc. However, this mechanical removal process does not remove all the slag and so an additional slag removal process is used. Depending on how effective the mechanical process is at removing the slag, the additional process may be a simple as immersing the ingot in a warm solution of HNO₃ solution (e.g., 35–50 wt% HNO₃) to remove any remaining salt and reaction products from the surface of the ingot (Durazzo et al. 2017). A more rigorous process would be to first soak the ingot in an alkali metal salt bath, such as in a eutectic composition of 35 wt% lithium carbonate (Li₂CO₃) and 65 wt% potassium carbonate (K_2CO_3) having a melting point of less than 600°C (Banker et al. 1979). The byproducts of the reactions of MgF₂ and this bath salt are MgO, CO₂, LiF, and KMgF₃. After the MgF₂ slag has been dissolved, the ingot is immediately quenched in water to remove the salt and decomposition products from the surface of the ingot. After the quenching process, the ingot is immersed in a warm solution of HNO₃ solution, as described previously, to remove any remaining salt and reaction products from the surface of the ingot. The ingot is then rinsed in water to remove the acid.

Subsequently, the ingots may be remelted into specific sized ingots or shapes by vacuum -induction melting and casting (the method predominantly used in the United States) that depends on the ingot specification for the metallic fuel being fabricated (Jackson 1989). The temperature in this melting and casting process needed to maintain fluidity is $1300-1450^{\circ}\text{C}$. Uranium at these temperatures is a highly reactive metal with most container materials and most atmospheres. A vacuum or inert atmosphere is therefore required. Chemicals used in this process for coating the crucible and molds may include Y_2O_3 , ZrO_2 , $MgZrO_3$, BeO, and sodium carboxymethyl cellulose.

Slag recovery:

The MgF $_2$ slag contains a significant amount of uranium metal that is typically recovered because of the cost of producing the metal (Ladola et al. 2012) (Durazzo et al. 2017). A potential recovery process (Durazzo et al. 2017) includes calcination of the slag in air to convert the uranium metal to an oxide, crushing and grinding of the calcined slag, and leaching in a HNO $_3$ solution to produce an impure uranyl nitrate solution (UO $_2$ (NO $_3$) $_2$) that is then vacuum filtered and treated for purification with an organic solvent such as tributylphosphate (TBP). The purified uranyl nitrate solution is then reacted with gaseous ammonia to precipitate ADU. The ADU is calcined at 600°C to obtain U $_3$ O $_8$, which is then converted to UF $_4$ by reacting it with stannous chloride (SnCl $_2$) and HF. Lastly, the UF $_4$ is heated in a furnace at 400°C under an argon atmosphere to remove water of crystallization.

Alloying:

There are several methods to alloy uranium by induction melting. One method is direct addition of the alloying ingredient (e.g., zirconium, molybdenum, niobium) into the molten uranium during vacuum-induction melting. Alloying can also be done during the metal reduction stage (Burkes et al. 2009a; Burkes et al. 2009b).

Fabrication of sodium-bonded metallic fuel:

The uranium (and/or plutonium with other alloying elements) metal feedstock for sodium-bonded fuel can be prepared using the induction melting and casting process (Burkes et al. 2009a; Burkes et al. 2009b). The fuel slug produced from the casting process is inserted in a fuel jacket that has been loaded with sodium to facilitate bonding of the uranium metal to the jacket (or cladding). It is unlikely that fabrication of the fuel jackets will be at the fuel fabrication facility, and in that case the fuel jackets fabrication will not be NRC regulated. After fuel and sodium loading the fuel jacket is welded closed. The resulting fuel rods are heated in a settling furnace at a temperature of 150°C to settle the fuel slugs into the molten sodium within the jackets. Following a short period of cooling, the fuel rods are inserted into a bonder magazine and impacted/agitated at 500°C to allow the sodium to encapsulate the fuel slug and remove bond defects/voids. After leak testing and other quality assurance testing, the fuel rods are incorporated into fuel assemblies much like that for LWR fuel assemblies.

Fabrication of dry metallic fuel:

Dry metallic fuel rods are fabricated from uranium metal ingots using an extrusion process, which historically was used extensively by DOE (Ballinger and Hall 1991). The primary chemicals used in this process are tetrachloroethylene (C₂Cl₄) as a degreaser, hot HNO₃ to remove surface impurities, nitric and sulfuric acid to chemically mill or remove excess uranium on the fuel element ends, hydrofluoric acid and HNO₃ for etching, and brazing with a material consisting of Zircaloy-2 alloyed with about 5 percent beryllium (Gerber 1996). Additionally, the brazed elements are heat treated in a molten salt bath. Recovery of uranium metal scrap from the cutting/shearing process would be similar to that described above for recovery of uranium metal from the MgF₂ slag.

4.4.3 Assessment of NUREG/CR-6410 for Fuel Cycle Facilities for Molten Salt Reactor Fuel and Blanket Salts

NUREG/CR-6410 does not include descriptions of the unique chemicals and processes associated with fabricating certain fuel salts. Descriptions, as available, are provided below.

4.4.3.1 Production of Fluoride-Based Salt Fuel

The production of fluoride-based salt fuel, specifically uranium tetrafluoride (UF₄), may involve either fluorination of UO_2 produced from deconversion, followed by reduction to UF_4 , or direct deconversion of received UF_6 feedstock.

Receipt of enriched (either LEU or HALEU) UF₆ feedstock:

This process is no different than that for LWR UO₂ fuel fabrication plants; therefore this process is described in NUREG/CR-6410.

Deconversion of UF₆:

The process to convert UF₆ to UO₂ is the same as that used in LWR UO₂ fuel fabrication plants; this process is described in NUREG/CR-6410.

Fluorination of UO₂ and reduction to UF₄:

Different potential processes exist for producing UF₄, but the most common process currently used involves reacting UO₂ with anhydrous HF in a kiln or furnace at a temperature of 400– 600° C; the temperature is dependent on the uranium concentration in the salt (Grenthe et al. 2006a; Souček et al. 2017). This is the first step for producing UF₆ from natural uranium oxides at a conversion plant prior to enrichment, so the chemical hazards would be the same. The primary chemical used in the process to convert UF₆ to UF₄ is HF gas, which is toxic and corrosive. Fluorine gas (F₂), which is used to produce UF₆ from UF₄ at a conversion plant, is more toxic than HF gas, so the current UF₆ production facility in the U.S. is, in some ways, more chemically hazardous than a facility that would only produce UF₄ using this process. Also, UF₄ is much more chemically stable than UF₆, so the product from a UF₄ production plant is less dangerous than a UF₆ product.

Appendix A of NUREG/CR-6410 already contains toxicological data on UF₆, HF, and F₂, Section A.5 of NUREG/CR-6410 discusses the process for reducing UO₂ to UF₄, and an accident scenario involving the spillage of HF from a tank car is already included as a sample problem in NUREG/CR-6410. It is identified that no unique chemical or process hazards, from those already discussed in NUREG/CR-6410, are involved in the production of fluoride-based salt fuel using the above specific process.

Direct reduction of UF₆ to UF₄ with H₂:

An alternative approach for producing fluoride-based salt fuel is direct reduction of UF $_6$ to UF $_4$ with H $_2$ (Smiley and Brater 1959). The production of fluoride-based salt fuel using this specific process is a process that was used historically to produce industrial quantities of UF $_4$ salt. Both the "hot wall" and "cold wall" processes may be implemented (International Nuclear Fuel Cycle Evaluation Working Group 7 1979) (Smiley et al. 1956; Bester et al. 1993). Appendix A of NUREG/CR-6410 already contains toxicological data on the chemicals involved in the "hot wall" process (UF $_6$, NH $_3$, H $_2$, and F $_2$) and an accident scenario involving the release of ammonia is already included as a sample problem in NUREG/CR-6410. Thus, these activities do not introduce any chemical or process hazards that are unique relative to those identified in NUREG/CR-6410 Appendix A of NUREG/CR-6410.

The "cold wall" process involves a very simple reaction with only one byproduct (HF). This process does not introduce any chemical or process hazards that are unique to NUREG/CR-6410. However, there are no current indications that this process will be used by licensees to produce UF₄ salts.

Other processes for producing UF₄ salt from UO₂:

As noted in Section A.5.1, McFarlane et al. (2019) and Torres et al. (2022) identified several other methods/processes that have been investigated for producing UF_4 salt from UO_2 or UF_6 feedstock. However, there is currently no indication that any of these processes will be used by licensees to produce UF_4 salts for use in MSRs.

4.4.3.2 Production of Chloride-Based Salt Fuel

The production of industrial quantities of chloride-based salt fuels, uranium trichloride (UCl₃) or uranium tetrachloride (UCl₄), is expected to start with uranium oxides or fluorides (e.g., UO₂, UO₃, UF₄, or UF₆). UCl₄ is expected to be a precursor to the fabrication of UCl₃.

Receipt of enriched (either LEU or HALEU) UF₆ feedstock:

This process is no different than that for LWR UO₂ fuel fabrication plants; therefore, the process description can be found in NUREG/CR-6410.

Deconversion of UF₆:

The process to convert UF₆ to UO₂ is the same as that used in LWR UO₂ fuel fabrication plants; therefore, this process description can be found in NUREG/CR-6410.

UCl₃ production:

The most likely process for producing UCl₃ involves reduction of UCl₄ with H₂ (Suttle and Hoekstra 1957; Patterson et al. 1967). The products of this reaction are UCl₃ and HCl. NUREG/CR-6410 (NRC 1998) does not address the potential hazards associated with this process nor does it address the hazards associated with the potential release of UCl₃, However, it is unclear that this process will be used to produce industrial quantities of UCl₃ salts.

Various other approaches may be used for UCl₃ production, including reduction of UCl₄ using metals, reaction of metallic uranium with HCl, reaction of uranium metal with transition metal chlorides, electrochemical processing, and chlorination of uranium metal with NH₄Cl. Processes starting from uranium metal have been explored but are unlikely due to their pyrophoric nature. This same conclusion was expressed in McFarlane et al. (2019). It is unclear that any of these processes would be used to produce industrial quantities of UCl₃ fuel salts, particularly as some have limited development.

UCl₄ production:

The reaction of uranium oxides with CCl_4 in the gas phase, referred to as carbochlorination, is the most likely approach for UCl_4 production (Wagner 1946) McFarlane et al. (2019). In this process a CO_2 gas stream saturated with CCl_4 vapors at atmospheric pressure is passed over UO_2 at a temperature of $400-500^{\circ}C$ (Wagner 1946). NUREG/CR-6410 (NRC 1998) does not address the potential hazards associated with the carbochlorination process nor does it address the hazards associated with the potential release of UCl_4 , UCl_5 , $COCl_2$, or CO. It is unclear that this process will be used to produce UCl_4 salts.

Other chlorinating agents including C_3Cl_6 , Cl_2 , $COCl_2$, or mixtures of CO with Cl_2 have been studied for UCl_4 production (McFarlane et al. 2019). In most cases the vapors of chlorinating agents are highly toxic. It is unclear that any of these processes would be used to produce industrial quantities of UCl_3 fuel salts, particularly as some have limited development.

³⁷Cl Enrichment:

Removal of ³⁵Cl from the fuel salt is necessary to avoid complications introduced by that isotope including formation of radiologically problematic ³⁶Cl, unfavorable nucleonics due to

the high neutron cross-section of ³⁵Cl, and formation of corrosive sulfur-containing species. The most likely technologies to be used for ³⁷Cl enrichment are centrifugation and thermal diffusion isotopic separation (TDIS) (Huber et al. 2024). This process does not involve radiological materials.

4.4.3.3 Carrier Salts

Flibe is the primary carrier salt for use in liquid-fueled MSRs with UF $_4$ or, potentially thorium fluoride (ThF $_4$) fuel, as well as solid-fueled MSRs with TRISO-based fuel. Other potential carrier salts—such as Flinak (a mixture of fluoride, lithium, sodium, and potassium) and sodium chloride—have also been noted in the literature (e.g., Torres et al. 2022; Mausolff et al. 2021). The preparation of carrier salts generally does not involve radiological materials and is expected to occur at industrial chemical facilities not within NRC purview per 10 CFR Part 70 (NRC 2024c). This report has evaluated the chemical process safety associated with carrier salt production, including beryllium use and regulatory considerations. These operations would likely be performed at facilities that do not require NRC regulation.

4.4.3.4 Mixing/Blending of Fuel Salt and Carrier Salt

This report has considered the blending of fuel salts with carrier salts from a process safety and chemical hazard standpoint. This operation involves elevated-temperature handling under inert atmosphere and is an important step in preparing the final fuel composition for molten salt reactors. This mixing is expected to be performed at the reactor facility rather than at a fuel production or processing plant, in which case the site of the mixing may be licensed under reactor frameworks such as 10 CFR Part 50 (NRC 2024a), or Part 52 (NRC 2024b), rather than under 10 CFR Part 70 (NRC 2024c). This report has evaluated the chemical process safety associated with carrier salt production, including beryllium use and regulatory considerations.

4.5 Review of Models used for Determining Consequences of UF₆ Release (NUREG/CR-6481)

NUREG/CR-6481, Review of Models used for Determining Consequences of UF $_6$ Release (NRC 1997b), complements other NRC documents like NUREG-1513 (NRC 2001), NUREG-1520 (NRC 2015), and NUREG-1601 (NRC 1997a) by focusing specifically on modeling the chemical safety aspects of UF $_6$ releases at nuclear fuel cycle facilities. While NUREG-1513 (NRC 2001) and NUREG-1520 (NRC 2015) outline general safety analysis and licensing criteria, NUREG-1601 (NRC 1997a) addresses chemical process safety comprehensively, and NUREG/CR-6481 (NRC 1997b) provides detailed evaluation criteria for models that simulate the behavior of UF $_6$ following an accidental release, a critical chemical hazard in fuel cycle operations.

For chemical safety, NUREG/CR-6481 (NRC 1997b) emphasizes the importance of understanding the interaction of UF₆ with atmospheric moisture, where it forms HF, a highly toxic corrosive gas. Accurate modeling of such reactions is vital to anticipate the dispersion and concentration of hazardous byproducts. The document reviews various models for predicting the thermodynamic behavior, reaction pathways, and atmospheric spread of UF₆, evaluating them based on criteria such as accuracy, reliability, and relevance to site-specific scenarios.

NUREG/CR-6481 (NRC 1997b) also underscores the importance of using models to support ISA and emergency preparedness. Models evaluated within the report are assessed for their effectiveness in predicting chemical exposure risks, enabling facilities to create robust

emergency response plans. By providing insights into both the immediate and long-range consequences of chemical releases, the report helps facilities implement controls and mitigation strategies for chemical safety.

In essence, NUREG/CR-6481 (NRC 1997b) strengthens chemical safety by offering tailored guidance on evaluating and selecting models that accurately reflect UF₆ hazards, reinforcing NRC's overall safety framework for nuclear facilities handling hazardous chemicals.

The consequences of a UF $_6$ release are independent of the type of fuel fabrication facility utilizing this material as the feed to the fuel production process. Therefore, NUREG/CR-6481 (NRC 1997b) addresses the consequences of UF $_6$ releases for fuel cycle facilities for TRISO-based, metallic-based, and salt-based fuels.

5.0 Conclusions and Findings

This report provides a structured technical and regulatory guidance assessment of chemical processes related to the fabrication of advanced fuel forms, including TRISO-, metallic-, and salt-based fuels. A review of open public literature sources was conducted to identify chemicals, materials and process reactions and conditions for fabrication approaches that may be implemented at advanced fuel cycle facilities. The information was used to develop structured assessments on chemical process safety.

A general framework was developed to assess the chemical process safety associated with the materials and operations involved in fuel fabrication. The framework facilitated consistent evaluation across all fuel types discussed in the report, ensuring that safety considerations were appropriately identified, reviewed, and communicated. The hazard assessment reflects a consideration of normal and abnormal process conditions, as well as accidental scenarios that may exacerbate chemical risks. The Globally Harmonized System (GHS) for classification of physical and health hazards was used to group chemicals and discuss safety considerations per the fabrication process conditions. In addition, detailed information on physical, health, and process considerations for the specific chemicals in the fabrication process were provided.

<u>Finding 1:</u> The assessment confirmed that chemical hazards associated with TRISO-based, metallic, and salt-based fuel fabrication processes are well characterized by established GHS physical and health hazard classifications. However, the specific conditions under which these hazards emerge (such as gas evolution in closed systems, formation of reactive byproducts, and exposure to high temperature or moisture-sensitive materials) highlight the importance of process-informed interpretation. In many cases, hazard significance is shaped not by the base chemical properties alone but rather by how materials are transformed, combined, or handled in the fabrication environment.

A comprehensive assessment of threshold limit values for process chemicals relevant to advanced fuel fabrication was also provided. Exposure guidelines and limits for consequence severity were provided for chemicals involved in the processes. The assessment incorporated a broad set of exposure threshold values, including Acute Exposure Guideline Levels (AEGLs), Emergency Response Planning Guidelines (ERPGs), Temporary Emergency Exposure Limits (TEELs), Immediately Dangerous to Life or Health (IDLH) concentrations, and National Institute for Occupational Safety and Health (NIOSH) skin notations, to support consequence severity screening and assessment.

<u>Finding 2:</u> For most chemicals, at least one applicable benchmark was available. However, some non-availability of data was noted, especially for dermal exposure indicators and compounds lacking AEGL or ERPG data. In such cases, TEELs were identified when available, and supplementary information from databases or Safety Data Sheets were reviewed qualitatively to provide context. Appendix B presents the most complete available threshold information for each substance, enabling transparent reference during safety evaluations.

<u>Finding 3:</u> Several cross-cutting issues emerged that extend beyond traditional chemical classification and merit consideration in licensing or regulatory application.

<u>Beryllium Use:</u> Beryllium and beryllium compounds (e.g., BeF₂, BeO) appear across multiple stages of metallic and salt fuel fabrication. These materials are subject to stringent occupational health controls under DOE and OSHA frameworks. Beryllium-based materials have known inhalation risks. As facilities currently licensed by NRC do not have chemical exposure hazards that are comparable to the use of beryllium, beryllium exposure hazards are not currently found in NRC guidance documents.

<u>Salt Preparation and Blending:</u> High temperature salt handling operations present process-specific chemical safety challenges that differ from existing standard review plans. The regulatory treatment of these activities may vary depending on whether they are conducted at a fuel cycle facility or reactor site, suggesting a need to consider jurisdictional boundaries and applicable safety expectations.

Combustible Gas and Fire Risk: The presence of flammable gases such as hydrogen, acetylene, and propylene in fuel fabrication processes involve safety hazards that have different thresholds from the toxicity-based screening thresholds. In several cases, threshold exposure values for these gases exceed their lower explosive limits, meaning fire or explosion hazards could become significant at concentrations below those used for consequence classification.

A review was also conducted on various regulatory guidance and technical basis documents to identify new chemicals and new processes to be considered by the U.S. NRC staff to facilitate efficient reviews of potential chemical process safety at fabrication facilities for advanced fuel types.

<u>Finding 4:</u> NUREG-1520, Revision 2, Standard Review Plan for Fuel Cycle Facilities License Applications – Final Report, notes AEGL and ERPG values as sources of exposure limits. It is noted that the U.S. Department of Energy protective action criteria database includes Temporary Emergency Exposure limits (TEELs) for process-specific chemicals.

<u>Finding 5:</u> There are new fuel fabrications will involve processes with descriptions that are not found in NUREG/CR-6410, *Nuclear Fuel Cycle Facility Accident Analysis Handbook* (NRC 1998). To address the unique chemicals and processes associated with fabricating TRISO fuels and metallic fuels, descriptions of these new fuel fabrication processes have been provided in this report, when available. Unique elements of TRISO fuel fabrication include (1) deconversion of UF₆, (2) fuel kernel fabrication, (3) chemical vapor deposition, (4) overcoating and (4) fuel compact fabrication. Unique elements of metallic fuel fabrication include (1) magneisothermic reduction of UF₄, (2) slag recovery process, (3) alloying, and (4) fabrication of sodium-bonded and dry (non-sodium-bonded) metallic fuels. For synthesis of UF₄ or UCl₃ salt fuels, there is uncertainty in which processes will be used, and information that is available has been included in this report.

<u>Finding 6:</u> NUREG-1513, Integrated Safety Analysis Guidance Document (NRC 2001), and NUREG-1601, Chemical Process Safety at Fuel Cycle Facilities (NRC 1997a), are considered adequate for addressing chemical process safety at fabrication facilities for the advanced reactor fuel types. Both documents are technology-neutral with respect to chemical hazards (i.e., not specific to fuel fabrication plants for light-water reactor fuel). NUREG/CR-6481, Review of Models used for Determining Consequences of UF₆ Release (NRC 1997b), is also considered to be adequate. The consequences of a UF₆ release are independent of the type of fuel fabrication facility utilizing this material as the feed to the fuel production process.

The information and considerations presented in this report were developed to provide a technical basis to support NRC staff during safety evaluations of license applications per 10 CFR Part 70, *Domestic Licensing of Special Nuclear Material* (NRC 2024c). This report provides descriptions of chemicals and processes involved in the fabrication of TRISO-, metallic-, and salt-based fuels to support licensing reviews.

The regulatory framework per 10 CFR Part 70 is robust and flexible such that no regulatory changes are anticipated to be needed to address fabrication processes at advanced fuel cycle facilities.

6.0 References

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Appendix A – Fabrication Processes for TRISO, Metallic and Salt-Based Fuels

A.1 Fabrication of TRISO Fuel Particles

A.1.1 Fuel Kernel

UO₂ or UCO are the most common kernel materials incorporating the fissile material. UCO kernels have been preferred for modern advanced reactors as these limit oxygen activity, thereby reducing the generation of carbon monoxide (CO) and carbon dioxide (CO₂), which is beneficial for reducing both kernel migration and gas pressure in the particle (Sowder and Marciulescu 2020). This allows for higher burnup limits and thermal gradients. The fuel kernel is generally sintered to near theoretical density and typically uses uranium enriched to 7–9 weight percent (wt%) ²³⁵U. Modern TRISO particle designs may use high-assay low-enriched uranium (HALEU) up to 19.75 wt% enriched ²³⁵U.

Various approaches have been used for fuel kernel production for use in TRISO particles (Beatty et al. 1979; Haas et al. 1980; Sowder and Marciulescu 2020; Spence and Haas 1980). The production methods involve first creating a sol, which is a colloidal solution with dispersed solid particles. These approaches involve the following major steps (1) preparation of a sol or of a special solution ("broth"), (2) gelation of droplets from the sol or broth to produce semirigid spheres of a controlled size distribution, (3) washing (for internal and external gelation only), (4) drying, (5) calcination and (6) sintering to increase kernel density. The initial sol or broth solution will depend on the gelation process. Gelation may be accomplished by water extraction (suitable only for sols) or ammonia gelation (suitable for both sols and broths but used almost exclusively with broths). Ammonia gelation can be accomplished either externally or internally. In the external gelation process, mass transfer of ammonia (NH₃) gas or ammonium hydroxide (NH₄OH) into the liquid drop is required. In the internal gelation process, ¹ the ammonia is supplied internally by the breakdown of an ammonia-donor chemical, hexamethylenetetramine [(CH₂)₆N₄, HMTA], present in the liquid drop itself (Beatty et al. 1979; Spence and Haas 1980).

The AGR Fuel Program elected to qualify TRISO particles with HALEU UCO kernels. These kernels had been produced for earlier irradiation testing in the United States by General Atomics and BWX Technologies Inc. (INL 2022). The internal gelation kernel production process developed by BWX Technologies Inc. was selected for the AGR Fuel Program with the understanding that additional process development would be needed to improve the overall quality of the product and adjust for the kernel diameters specified. These included achieving the specified kernel density, improving carbon dispersion in the acid-deficient uranyl nitrate (ADUN) solution used in kernel formation, optimizing the sintering process and reducing process sintering variability. Since testing under the AGR Fuel Program is likely to provide the basis for TRISO particle performance for future advanced reactors, as demonstrated by the referencing by X-Energy and Kairos Power, this report will focus on fabrication of fuel kernels by internal gelation. Figure A-1 provides a process flowsheet of the internal gelation process for fabrication of TRISO fuel kernels, per AGR Fuel Program references (Phillips et al. 2012; Marshall 2019).

¹ The internal gelation process is also referred to as the KEMA process, as it was developed by Keuring van Electrotechnics Materialen at Arnhem in the Netherlands.

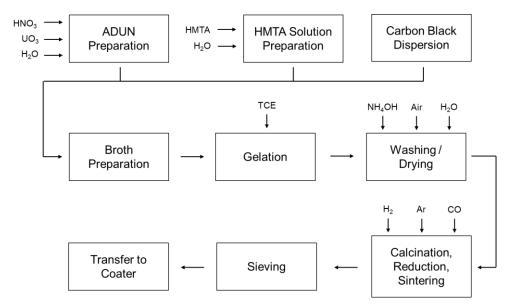


Figure A-1. Process Flowsheet for Fabrication of TRISO Fuel Kernels by Internal Gelation per the AGR Fuel Program.

A.1.1.1 Preparation of Starting Broth Solution Before Gelation

The internal gelation process requires an ADUN solution where the uranium form is represented by $UO_2(OH)_x(NO_3)_{2-x}$, where x = 0.3 - 0.5. The ADUN solution can be prepared by any of the following methods (Beatty et al. 1979; Haas et al. 1980):

Method 1: Adding UO_3 to a substoichiometric amount of nitric acid (HNO₃), or to a stoichiometric amount of uranyl nitrate hexahydrate ($UO_2(NO_3)\cdot 6H_2O$) (moderately heated to less than 60°C as higher temperatures may precipitate $UO_3\cdot H_2O$).

Method 2: Adding U₃O₈ or UO₂ to a substoichiometric amount of HNO₃.

Method 3: Amine extraction of acid from a UO₂(NO₃)·6H₂O solution followed by evaporation.

The first two methods lead to exothermic reactions, and the formation of the nitrogen oxide (NO_x) gases that would need to be managed (Collins et al. 2004). These first two methods, with dissolution of UO_2 , UO_3 or U_3O_8 in HNO_3 , have been the preferred approaches. The ADUN solution is generally prepared with a NO_3 -/U molar ratio in the range 1.5 to 1.7 (Haas et al. 1980). Initial experiments to support the AGR Fuel Program targeted an optimized composition of the broth, per Table A-1 (Collins et al. 2004). The specific broth composition for the AGR-5/6/7 test could not be identified. Density and pH measurements are used to quantify the uranium concentration and the NO_3 -/U molar ratio.

| Table A-1. | Target Co | mposition of C | optimized Broth (| (Collins et al. 200₄ | 1). |
|------------|-----------|----------------|-------------------|----------------------|-----|
| | | | | | |

| Constituent | Concentration (<i>M</i> = mol/L) | | |
|------------------------|-----------------------------------|--|--|
| Uranium | 1.29–1.30 | | |
| Hexamethylenetetramine | 1.68 | | |
| Urea | 1.68 | | |
| Nitrate | 2.00–2.08 | | |

The broth is obtained by mixing the ADUN solution with an NH_3 donor solution (HMTA: urea, $CO(NH_2)_2$) at a volume ratio of about 1:1. Before mixing, the ADUN and NH_3 donor solutions are highly stable (Beatty et al. 1979). Upon mixing in the broth, the uranium concentration is reduced by about half relative to the ADUN solution. The urea in the broth serves to complex the uranyl ion (UO_2^{2+}) and protect it from slowly decomposing the HMTA. To prevent premature gelation, the solution is maintained at a low temperature, ideally in the range of -5 to 0°C, to reduce the decomposition rate of HMTA. Once combined, the stability of the broth is highly dependent on temperature; the broth being stable for ~24 hours at -5°C (Beatty et al. 1979). Gelation is then initiated by physical processing and heating.

For the fabrication of UCO kernels, as conducted per the AGR Fuel Program, carbon black is added to the broth formulation prior to gelation (Sowder and Marciulescu 2020). A dispersing agent (e.g., Tamol™) may also be used during this process (Stinton et al. 1982; Hunt et al. 2018; Raftery 2019).

A.1.1.2 Fuel Sphere Forming and Gelation

Under the previous conditions, the uranium form in the broth solution is a uranyl urea complex, $UO_2[CO(NH_2)_2]_2^{2+}$. During the overall process to make the gel particles, chemical reactions occur to convert this complex to hydrated UO_3 . At the start of the process to obtain the gel particles, the cold broth is pumped by a rate-controlled droplet disperser or injector, which forms drops of the required size deposited in a hot (temperature ranging from 50 to 100°C) immiscible organic liquid loaded in a column (Beatty et al. 1979; Collins et al. 2004; Sood 2010). Figure A-2 illustrates the dispenser and gelation approach.

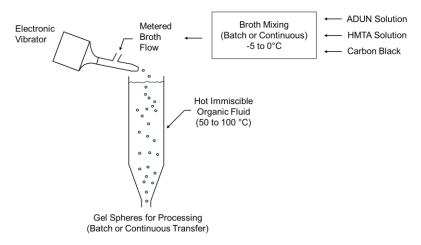


Figure A-2. Internal Gelation of Fuel Kernel Spheres.

As the aqueous droplets fall through the heated organic medium, the product, hydrated uranium trioxide (UO₃·2H₂O), is formed by a reaction sequence described by five primary chemical reactions (Collins et al. 1987). The first reaction involves decomplexation of the uranyl urea complex according to Equation (1).

$$UO_2[CO(NH_2)_2]_2^{2+} \rightleftharpoons 2 CO(NH_2)_2 + UO_2^{2+}$$
 (1)

The free uranyl ion (UO_2^{2+}) formed by Equation (1)(1) reacts with water in the aqueous droplets to yield uranyl hydroxide $(UO_2(OH)_2)$ per Equation (2):

$$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)_2 + 2H^+$$
 (2)

UO₂(OH)₂ then converts to hydrated UO₃ per Equation (3):

$$2UO2(OH)2 \rightleftharpoons 2UO3·2H2O$$
 (3)

A key feature of the process chemistry is the driving of the reaction per Equation (2) to the right by other compounds consuming hydrogen ions (H⁺) via the separate reactions in Equations (4) and (5):

$$(CH_2)_6N_4 + H^+ \rightleftharpoons [(CH_2)_6N_4H]^+$$
 (4)

$$[(CH2)6N4H]+ + 3H+ + 6H2O \Rightarrow 4NH4+ + 6CH2O$$
 (5)

Various organic media and gelation temperatures have been investigated or proposed, depending on the desired sphere size. Haas et al. proposed the use of trichloroethylene (TCE, C₂HCl₃) as the organic medium in the gelation column (Haas et al. 1980). The medium was chosen for the AGR Fuel Program (Marshall 2019). The use of Span® 80, a sorbitan monooleate ester and a surface-active compound, has also been investigated, which showed minimization of gel particle aggregation and clumping with its addition to TCE.

Based on environmental concerns over using TCE, other liquid media such as silicone oil may be used (Katalenich 2017). Hass and Spence also cite other potential organic media, including perchloroethylene (PERC, C_2Cl_4), 2-ethyl-1-hexanol ($C_8H_{18}O$), and mineral or silicone oils (Spence and Haas 1980; Sood 2010). Although, this typically will require a more extensive protocol for washing of the hydrated UO_3 spheres to remove the entrained organic liquid.

A.1.1.3 Washing

The gel fuel particles, also referred to as green spheres, are further washed with TCE and NH₄OH to remove excess urea, HMTA, and their byproduct, ammonium nitrate (NH₄NO₃) salt (Sood 2010; Marshall 2019). The AGR Fuel Program has also used the addition of Tween[®] 20, a non-hazardous, non-ionic surfactant that lowers surface tension with small additions to aqueous solutions (Marshall 2019). The duration of a typical wash cycle is described to be less than an hour (Marshall 2019).

A.1.1.4 Drying

The washed gel particles are then generally dried under air at approximately 60 to 80°C, although temperatures as high as 200°C have been used (Battistini et al. 2023). The AGR Fuel Program conducted this step for approximately 12 hours followed by 3 to 4 hours of unheated air flow (Marshall 2019). The drying process reduces the average diameter of the gel particles

by approximately 30 to 40 percent (Collins et al. 2004; Marshall 2019; Battistini et al. 2023). Figure A-3 illustrates UO₃·H₂O spheres of an average diameter of ~1000 μm following air drying (Collins et al. 2004). Infrared heating instead of thermal heating has also been reported (Battistini et al. 2023).



Figure A-3. Air Dried UO₃·H₂O Spheres of ~1000 μm Average Diameter (Collins et al. 2004).

A.1.1.5 Calcination, Reduction and Sintering

The hydrated UO₃ spheres are then loaded into a furnace for further thermal treatment for calcination, reduction and sintering. There is wide variability in the approaches used for these processes with differences between approaches by different countries and between different DOE programs over the years (Petti et al. 2002; Marshall 2019; Battistini et al. 2023). Calcination is conducted in H₂, H₂/Ar, Ar or air between 300°C and 550°C to remove residual volatiles and to reduce the uranium oxide in the kernel to UO₂. Reduction is conducted under a H₂, H₂/Ar, or Ar atmosphere at temperatures ranging from ~900°C to 1700°C. Sintering is conducted under a H₂, H₂/Ar or CO/Ar atmosphere at ~1550°C to 1900°C, which assures densification of the kernels. Some authors describe the calcination step to also encompass the reduction step (Collins et al. 2004; Sood 2010). The baseline process characteristics for fabrication of fuel kernels for the AGR-5/6-7 test are used to provide a general approach on chemicals and general temperatures involved (Phillips et al. 2012; Marshall 2019).

The spheres are initially purged with argon at $\sim 100^{\circ}\text{C}$ for a few minutes. Hydrogen gas is then added (4 to 6 percent, remaining argon) at $\sim 550^{\circ}\text{C}$ for over an hour. The hydrogen gas is then valved off and the temperature is increased to $\sim 1680-1920^{\circ}\text{C}$ for carbothermic reduction, which reduces the dehydrated UO₃ to UO₂. The temperature is then increased to $\sim 1890^{\circ}\text{C}$ for further sintering in an atmosphere of 60 percent CO and 40 percent Ar, which increases the density of the kernel. The furnace is then cooled to room temperature. The entire process results in the fuel kernels generally shrinking by approximately 50 percent involved (Phillips et al. 2012; Marshall 2019). Figure A-4 shows fuel kernels after the sintering process.

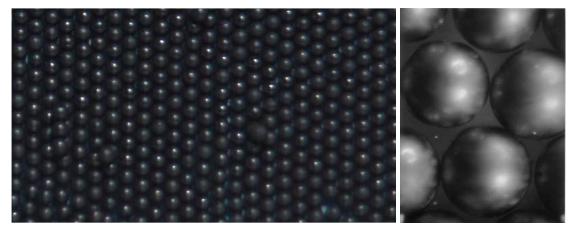


Figure A-4. Sintered UO₂ Kernels of 500–532 µm Diameter (Collins et al. 2004).

A.1.2 TRISO Particle Coatings

Coatings are sequentially applied to the fuel kernel via chemical vapor deposition (CVD) in a fluidized bed reactor (Sowder and Marciulescu 2020; Nickel et al. 2002). Figure A-5 illustrates a reactor used for the CVD process of TRISO coatings (Jolly et al. 2016). The reactor unit consists of a graphite chamber with a conical bottom that is surrounded by a resistively heated graphite element. These are both housed within a water-cooled shell. The fluidizing gas, typically Ar, is injected through the bottom of the coating chamber and the fuel kernels are fed in from the top. The fluidizing gas continues to flow throughout the process as the different reacting gases are introduced. Table A-2 provides typical CVD reagent gas mixtures, deposition temperatures and process reactions (IAEA 2015).

Table A-2. Parameters for Chemical Vapor Deposition of TRISO Particle Coatings (IAEA 2015).

| Coating Layer | Gas Mixture | Operating Temperature Range (°C) | Primary Chemical Reaction(s) |
|------------------------|----------------------------|-------------------------------------|--|
| Buffer | $Ar + C_2H_2$ | 1400–1500 | $C_2H_2(g) \rightarrow 2C(s) + H_2(g)$ |
| IPyC | $Ar + C_2H_2 + C_3H_6$ | 1250–1350 | $C_2H_2(g) \rightarrow 2C(s) + H_2(g)$ $C_3H_6(g) \rightarrow 3C(s) + 3H_2(g)$ |
| SiC | $Ar + H_2 + Si(CH_3)_4$ | 1400–1500 | $CH_3SiCl_3(g) \rightarrow SiC(s) + 3HCl$ |
| OPyC | $Ar + C_2H_2 + C_3H_6$ | 1250–1350 | $\begin{array}{l} C_2H_2(g) \rightarrow 2C(s) + H_2(g) \\ C_3H_6(g) \rightarrow 3C(s) + 3H_2(g) \end{array}$ |
| IPyC = inner pyrolytic | c carbon; SiC = silicon ca | rbide; OPyC = outer pyrolytic carbo | n; TRISO = tri-structural isotropic. |

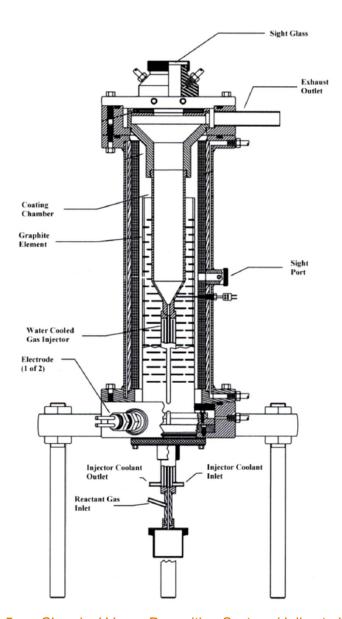


Figure A-5. Chemical Vapor Deposition System (Jolly et al. 2016).

After addition of the fuel kernels, the reactor is brought to the desired temperature for deposition of the porous carbon buffer layer ($1400-1500^{\circ}$ C). The buffer layer is produced by introducing acetylene (C_2H_2) into the reactor. Upon completion of the deposition of the porous carbon layer, the reacting gas is changed to a mixture of propylene (C_2H_2) and acetylene (C_2H_2) and the temperature is adjusted for the deposition of the IPyC layer ($1250-1350^{\circ}$ C). The SiC layer is produced by changing the reaction gas to a mixture of hydrogen and methyltrichlorosilane (C_3SiCl_3); again, the temperature must be adjusted to obtain optimal formation of SiC ($1400-1500^{\circ}$ C). Finally, the reacting gas is changed back to a mixture of propylene and C_2H_2 , accompanied by a lowering of the temperature ($1250-1350^{\circ}$ C). Upon completion of the coating process, the apparatus is allowed to cool, and the coated particles are drained through the bottom of the device.

C₂H₂ and CH₂CHCH₃ are highly flammable gases. Poisonous gases (e.g., CO) may be produced in fires involving these compounds and their containers may explode when exposed

to fire. Hydrogen is also a highly flammable gas—hydrogen is present both during the SiC deposition and as a byproduct of the deposition of the carbon layers. CH₂CHCH₃ is also a highly flammable liquid, which is acutely toxic. Harmful gases such as HCl are formed during fires involving CH₃SiCl₃. Gaseous HCl is also the primary byproduct formed during the CVD of the SiC layer.

A.2 Fabrication of TRISO-Based Fuel Compacts

A.2.1 Pebble (Spherical) Graphite Compacts

Figure A-6 provides a process flow diagram for the fabrication of pebble fuel elements, as informed by (IAEA 2015). The process appears to be consistent with that proposed by companies such as X-Energy (Pappano 2018).

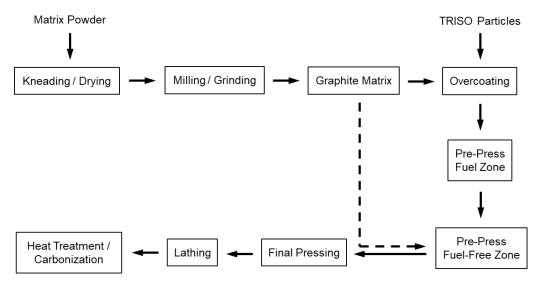


Figure A-6. Process Flow Diagram for Fabrication of Pebble Graphite Fuel Elements.

Compacts may be fabricated from thermoplastic or thermosetting resin matrices. Pitch resin, a thermoplastic material, softens (when heated) during the carbonization step and thus requires the particles to be supported in a pack of alumina powder. Pitch resin, being derived from oil or coal, may contain transition metal impurities that could potentially attack the SiC coating of the TRISO particles and lead to failure of the fuel compact. Therefore, consideration should be provided to the purity of the starting material. Synthetic thermosetting resins harden during warming and heating steps and can also be tailored to contain low levels of chemical impurities. These resins do not require restraining of the compact in alumina during carbonization thereby reducing the volume of low-level process waste (by eliminating contaminated alumina) (Schulze et al. 1982).

Two graphitic resin matrix materials are primarily used in fabrication of pebble compacts, namely A3-3 and A3-27. The matrix names were established per previous developmental activities supporting operations of Germany's Arbeitsgemeinschaft Versuchsreaktor (AVR) and THTR units, and there is no current consensus standard on the composition and preparation for these materials at this time. Table A-3 provides composition and fabrication characteristics for these materials, as used in AVR and THTR compacts (Schulze et al. 1982).

The A3-3 matrix is a standard material matrix, which is also used in X-Energy's design of the TRISO pebble fuel elements for the Xe-100 HTGR (Mulder 2021b; Helmreich et al. 2017). A nearly identical variant to the A3-3 matrix was also specified for the AGR-5/6/7 fuel compacts (INL 2017; Collin 2018). The A3-27 was developed after the A3-3 standard matrix and has also been implemented for AVR fuel compacts (Nabielek et al. 1984). The two matrix materials exhibit differences with respect to the type of resin binder and cross-linking fabrication

approach. The resin binder used for the standard A3-3 matrix graphite is a thermoplastic synthesized from phenol (C_6H_5OH) and formaldehyde (CH_2O) and crosslinked anisotropically (primarily two dimensionally). For the A3-27 matrix material, the binder is synthesized from C_6H_5OH and HMTA and crosslinked isotropically. Therefore, the resulting binder cokes formed from these resin binders during the carbonization and heat treatment processes are of different structures.

Table A-3. Composition and Fabrication of Matrix Materials Used for Pebble Fuel Compacts.

| Matrix material | A3-3 ^(a) | A3-27 ^(a) | |
|---|-------------------------------|----------------------------------|--|
| Component nominal weight fraction (%) | | | |
| Natural graphite | 64 | 62.4 | |
| Petroleum coke graphite (electrographite) | 16 | 15.6 | |
| Resin binder ^(b,c) | 20 | 22 | |
| Pebble molding method | Quasi-isostatic cold molding | | |
| Pebble heat treatment temperature (°C) | | | |
| Inner fueled region | 1800 or 1950 | 1950 | |
| Outer fuel-free region | 1800 | 1950 | |
| (a) Reported properties for Arbeitsgemeinschaft V | ersuchsreaktor (AVR) fuel cor | npacts (A3-3, A3-27) and Thorium | |

- (a) Reported properties for Arbeitsgemeinschaft Versuchsreaktor (AVR) fuel compacts (A3-3, A3-27) and Thorium High Temperature Reactor (THTR) fuel production (A3-3) per Schulze et al. (1982).
- (b) The A3-3 resin binder is a prefabricated thermoplastic resin from phenol (C₆H₅OH) and formaldehyde (CH₂O).
- (c) The A3-27 resin binder is a thermosetting resin synthesized from C₆H₅OH and hexamethylenetetramine during matrix heat treatment.

The TRISO particles are overcoated by a resinated graphite powder matrix via a warm-mixing process of graphite powder with the resin binders listed in <u>Table A-3</u>Table A-3, i.e., C_6H_5OH and CH_2O for the A3-3 matrix, or C_6H_5OH and hexamethylenetetramine for the A3-27 matrix (Demkowicz et al. 2019; Heit et al. 2017; IAEA 2015). The overcoating process is conducted inside a heated rotating drum system. The overcoating (in the range of 200 μ m) aids the binding of the TRISO particles with the pebble's graphite matrix and prevents any undesired mechanical damage of the particles during pressing/compaction. The overcoated particles are then heated to ~80–100°C to remove volatiles from the organic resin (IAEA 2015). The TRISO particles are later screened to remove any odd or uneven-shaped particles.

The graphite matrix overcoated particles are then mixed with additional graphite powder-resin material and are pre-molded in silicone rubber molds at pressures between 5–30 MPa and room temperature to form the inner fuel region of the pebbles (generally 5 cm in diameter) (Heit et al. 2017; Wolf et al. 1975; IAEA 2015). Additional resinated powder is loaded into the molds to form the fuel-free zone by isostatic pressing at 300 MPa and room temperature (Nabielek et al. 1984; Heit et al. 2017; Wolf et al. 1975; Nickel et al. 2002; IAEA 2015). The pebble spheres are then machined by a lathe to final shape and size (generally 6 cm in diameter) (Heit et al. 2017; Mehner et al. 1990; IAEA 2015). Carbonization of the resin binder is then induced at ~800–900°C in the presence of an inert gas, followed by heat treatment at ~1900–1950°C under vacuum to extract residual gases and other volatile impurities (Nickel et al. 2002; Heit et al. 2017; Mehner et al. 1990; Wolf et al. 1975). Generally, a pebble fuel element contains approximately 9,000 to 18,000 TRISO particles.

A.2.2 Cylindrical Graphite Compacts

The preparation of TRISO-based cylindrical fuel compacts for the High Temperature Engineering Test Reactor in Japan has been previously described (Sawa et al. 1999). Figure A-7 provides a process flow diagram for fabrication of cylindrical fuel compacts as described in the reference provided.

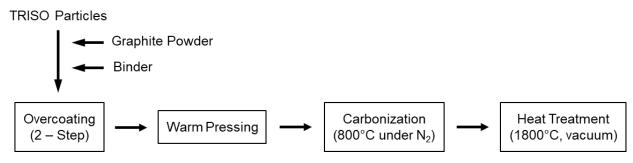


Figure A-7. Process Flow Diagram for Fabrication of Cylindrical Graphite Fuel Compacts.

In the process described by Sawa et al. (1999), the TRISO particles are overcoated by a resinated graphite powder matrix formed via grinding a mixture of natural graphite powder, electrographite powder, and C₆H₅OH resin (binder). The coating thickness is approximately 200 µm, similar to that for pebble fuel elements. It has been observed that the single-step coating approach used for TRISO particle coating for pebble fuel elements was not effective for the preparation of cylindrical compacts. The single-step process did not provide for good adhesion of the coating during warm pressing of the compacts and also resulted in mechanical contact between particles. Therefore, a two-step process was developed where a thin 80 µm overcoating is first performed by curing at 180°C, followed by a second overcoating of 120 µm (Minato et al. 1997). Curing of the inner, thinner layer ensures good adhesion of the second overcoating to the coated particle and ensures maintenance of an acceptable distance during warm pressing of the compacts. All overcoated particles are screened by means of a vibrating table to exclude odd or uneven-shaped particles (Sawa et al. 1999). To form cylindrical compacts, the overcoated TRISO particles are warm-pressed in metal dies. Carbonization of the binder is performed in flowing N₂ at 800°C (Sawa et al. 1999). Additional heat treatment is provided at temperatures up to 1800°C for ~1 hour in vacuum to degas compacts. The final fuel particle loading fraction in the compacts is 30 ± 3 vol.% (Sawa et al. 1999; Yoshimuta et al. 1991).

The DOE AGR Program has fabricated cylindrical compacts by a different process (Marshall 2019). The compacts for the AGR-5/6/7 test are based on an A3-27-based matrix using novolac resin flake based on partially crosslinked C_6H_5OH and CH_2O -based. The graphite blend was a 20:80 blend of synthetic and purified natural flake graphites. The resinated graphite powder was produced in a two-step milling process. The novolac resin was co-milled with HMTA, and the resultant powder was subsequently blended and co-milled with the graphite powders. The HMTA served as the hardener/curing agent for the novolac resin. Both milling operations were performed in a jet mill. The single-layer overcoated particles were warm-pressed in dies heated to ~165°C, at pressure of ~10 MPa. The compacts were then heat treated at 900°C under argon for 30 minutes and subsequently under vacuum at 1800°C for an hour. This final phase in the heat treatment ensured devolatilization and dimensional stabilization of the compacts. Typically, an AGR-5/6/7 fuel compact contained ~13,000 TRISO particles.

A.2.3 Ceramic Compacts

The fabrication process for encapsulation of TRISO particles in SiC to form FCM® fuel pellets was initially developed by DOE's Transformational Challenge Reactor Program. Public information and references by USNC and the Transformational Challenge Reactor Program were reviewed to discuss fabrication considerations, although USNC may implement specific processes not in the public domain. Figure A-8 illustrates the general approach for fabrication of FCM® fuel pellets, as informed by Van den Akker (2022).

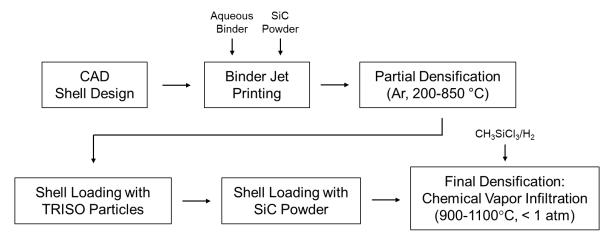


Figure A-8. Process Flow Diagram for Fabrication of Ceramic Fuel Compacts.

The initial step to the fabrication of ceramic pellets with TRISO particles involves the manufacturing of the shell in the form of a cylinder or annular cylinder. The shell, referred to as a "green body," is fabricated by advanced (additive) manufacturing using a binder jet system (printer) coupled to a computer-aided design (Terrani et al. 2019; UIUC 2023). The printer head deposits an aqueous binder onto a bed of SiC powder in a series of layers. After printing, the green shell is removed from the powder bed and excess powder is removed. The green shell is then heated to cure the binder and to improve its strength for handling (UIUC 2023). Figure A-9 shows the reported ideal particle size distribution for the SiC powder bed for fabrication of the green shell, which suggests particle diameter distribution ranging between 10–40 µm (Terrani et al. 2019).

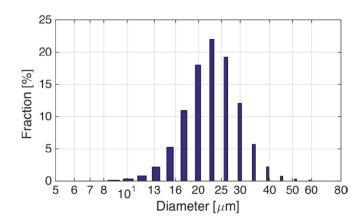


Figure A-9. Reported Ideal Silicon Carbide Particle Distribution for Fabrication of Ceramic Element Shells (Terrani et al. 2019).

The curing step is performed under argon to drive off the majority of the agueous or organic-based binder via decomposition and volatilization of the binder (Terrani et al. 2019). The specific curing temperature will vary depending on the binder choice and composition. Terrani et al. (2019) has reported use of a proprietary aqueous binder of unknown composition (ExOne™, Binder 05). The resulting green body was highly porous, with a reported binder content (Binder 05) of ~2 weight percent (wt%) following initial curing (190°C, 6 hour in air) and subsequent heating between 250°C and 500°C. Cramer et al. (2021) has reported on the use of other binders, a phenolic-based binder (ExOne™, FB101) and a phenol-formaldehyde binder $((C_6H_5OH)_x (CH_2O)_y)$ diluted in ethanol (C_2H_5OH) . After printing, specimens fabricated from these binders were cured (200°C, 2 hours in air) and subsequently heated (850°C, 30 min in N₂) to pyrolyze the phenolic binder to carbon. These studies suggest that curing, following printing of the shell, may involve two steps: one initial heating at temperatures near 200°C followed by one heating at higher temperatures (up to 850°C), depending on the binder. The composition of generated volatiles will likely include a variety of gaseous species with carbon, oxygen and hydrogen (e.g., CO, CO₂, CH₄). Characterization via thermogravimetric analyses with mass spectrometry/gas chromatography could be used to determine the decomposition characteristics for the specific binder.

After partial densification, the shells are filled with TRISO fuel particles and vibrated to homogenize their distribution and achieve compaction (UIUC 2023; Terrani et al. 2021). The mass of TRISO particles loaded into each shell is determined by the specified uranium content of the pellet (UIUC 2023). The next step is to fill the interstitial space between the TRISO fuel particles with additional SiC powder, reported as the same as used for binder jet printing at the start of the process (Terrani et al. 2021).

The loaded shells are then loaded onto graphite fixtures and placed in a furnace for chemical vapor infiltration to create further SiC filling (UIUC 2023; Terrani et al. 2019). The chemical vapor infiltration process further fills the loaded shell with highly pure, stoichiometric, and crystalline SiC. To do so, a precursor gas, CH₃SiCl₃, is heated to decompose on the surface of the newly loaded SiC powder in the green body to yield still more SiC, per Equation (6). This further fills any voids in the green body with SiC. This chemical vapor infiltration process is carried out between 900 to 1100°C with H₂ as a carrier gas (Terrani et al. 2019; Naslain 2004).

The process is conducted at reduced pressures (~0.25 to <1 atm) to increase the diffusion rate of the gas species thereby increasing the rate of mass transport (Terrani et al. 2019; Naslain 2004). The final density of the element (< 90 percent theoretical) is governed by mass transport, in which CH₃SiCl₃ transports from the bulk gas and within the pores to the deposition site, and vice versa for the product HCl gas (see Equation (6)) (Terrani et al. 2021). Residual binder not previously pyrolyzed may further volatilize yielding carbon and H₂ gas per general Equation (7).

$$CH_3SiCl_3(g) \rightarrow SiC(s) + 3HCl(g)$$
 (6)

$$2C_xH_y(g) \to 2xC(s) + yH_2(g) \tag{7}$$

A.3 Fabrication of Graphite Prismatic Blocks

Figure A-10 provides a general process flow for the manufacture of graphite blocks for application in HTGRs, as informed by Marsden (2001) (IDS [Industrial Quick Search]). The process refers to the fabrication of graphite blocks without any fissile or fertile material. Following fabrication, cylindrical fuel compacts with TRISO particles are loaded inside annular holes in the graphite block.

The feed to the process is coke, which is obtained as a byproduct from the petroleum or coal industry, or as naturally occurring pitch coke. The raw coke is first calcined at 900–1300°C to drive off volatile components; this step also reduces the amount of shrinkage that occurs in later processing steps.

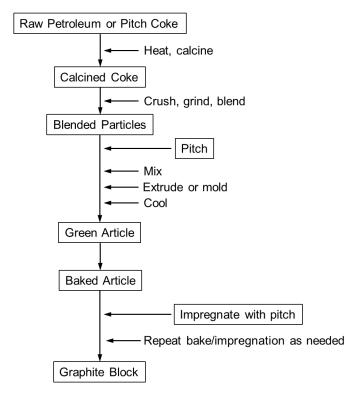


Figure A-10. General Process Flow for Manufacturing Prismatic Graphite Blocks.

The calcined coke is crushed, ground, and blended as needed to achieve the desired specifications for the graphite blocks to be manufactured. The blended material is mixed with a binder, usually coal tar pitch. This mixture is converted to the desired shape for the hexagonal prismatic graphite block. Extrusion is the most common method used, but various molding techniques can also be employed. In the extrusion method, the mixture is forced through a die of the desired shape under pressure. To maintain the shape of the object, it is rapidly cooled by immersion in water.

The resulting "green article" is baked at 800–1000°C to drive off additional volatile material and to decompose or "coke" the binder. The baked green article is typically porous due to the evolution of volatile gases. To close the pores and increase the density of the final product, the green article is impregnated with additional pitch. This baking and impregnation process may be repeated as needed to achieve the desired specifications for the final prismatic graphite block. The final step in the process is "graphitization" in which the impregnated green article is heated to nearly 3000°C.

A.4 Fabrication of Metallic-Based Fuels

A.4.1 Uranium Metal Production

The most common industrial approach for uranium metal preparation involves the high temperature chemical reduction of the feedstock UF₄ by Group II metals (Jang et al. 2022). Uranium tetrachloride (UCl₄) can similarly be reduced to uranium metal using the same Group II metals, although UCl₄ is less likely to be used as the U metal precursor. Metallothermic reduction may be conducted with magnesium (Mg) metal (magnesiothermic reduction) or calcium (Ca) metal (calciothermic reduction). Both processes are highly exothermic reductions that occur at very high temperatures. Calciothermic reduction of UF₄ is more thermochemically favorable as the exothermic heat is -109.7 kcal/mol when compared to the less exothermic heat of -49.85 kcal/mol (values at 640°C) of magnesiothermic reduction (Durazzo et al. 2017).

Prior to 1943, large quantities of uranium metal were produced at two different plants using the calciothermic reduction process for the reduction of UF $_4$ and at one other plant using a fused salt electrolysis process with KUF $_5$ in a CaCl $_2$ -NaCl fused salt bath. Beginning in 1943, each of these plants were replaced by four production plants using the magnesiothermic reduction process to produce industrial quantities of uranium metal from reduction of UF $_4$. These plants were subsequently replaced in the 1950s by two entirely new industrial production plants at Fernald, Ohio, and Weldon Spring, Missouri, that utilized essentially the same magnesiothermic reduction process but were much more mechanized. The use of Mg metal as the reductant was ultimately chosen over calcium metal because it was significantly lower cost, it was much more readily available, and it was easier to obtain Mg of the required purity. It is noted that sodium metal was also investigated for reduction of UCl $_4$ and UCl $_3$ to uranium metal but was not pursued on an industrial-scale (Wilhelm 1960).

Considering prior experience on uranium metal production, the magnesiothermic approach appears to be the likely approach for implementation at an advanced fuel cycle facility. The process also has the advantage of avoiding handling of toxic and pyrophoric Ca metal, despite the less favorable thermochemistry of reduction (Durazzo et al. 2017; Jang et al. 2022; LaHaye and Burkes 2019).

A.4.1.1 Magnesiothermic Reduction

Magnesiothermic reduction employs a mixture (charge) of UF₄ and a stoichiometric excess (typically 10–15 percent) of Mg metal (Jang et al. 2022). The charge is loaded into a crucible made of refractory material (generally magnesium peroxide [MgO₂] or graphite) and the reagents are distributed (loaded by alternating layers of materials) or homogenized by mixing (Durazzo et al. 2017; LaHaye and Burkes 2019). The crucible is then capped by a lid lined with magnesium fluoride (MgF₂) and bolted to the reactor vessel, which may be fabricated from stainless steel and would be designed to allow inert gas fluxing during processing.

The reactor vessel is preheated in an induction coil or pit furnace to 500–640°C, although temperatures above 600°C are preferred to aid fluidity of the charge materials (Durazzo et al. 2017; LaHaye and Burkes 2019). The reduction reaction, per Equation (8), then initiates by spontaneous ignition from the exothermic reduction reaction (Durazzo et al. 2017). Figure A-11 describes the proposed sequence of events and temperatures reached during the various stages of magnesiothermic reduction, as informed by Durazzo et al. 2017.

$$UF_4 + 2Mg \rightarrow U + 2MgF_2 \tag{8}$$

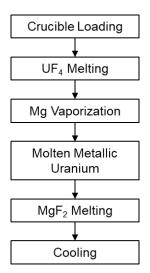


Figure A-11. Sequence of Events During Magnesiothermic Reduction of Uranium Tetrafluoride Toward Uranium Metal.

As the reaction temperature increases to $1500-1600^{\circ}$ C, the uranium metal and MgF₂ products are in the molten state. Due to the higher density of uranium metal relative to the reagents, the uranium metal product settles at the bottom of the crucible allowing its separation from the slag, primarily MgF₂. Upon cooling, the solidified slag can be separated from the uranium metal ingot.

Magnesiothermic reduction would necessitate adequate controls to mitigate safety risks due to the highly exothermic nature and elevated temperatures of the process. The crucible and reactor design would be adequately designed to withstand the blast impact from the spontaneous ignition reaction, as well as impacts of thermal cycling to the crucible design life. The charge and products would be kept fully contained during the loading, heating, reaction, cooling, and disassembly processes to avoid contamination. The reactor system would necessitate inerting with a noble gas to prevent the presence of moisture, oxygen and nitrogen, which would lead to various undesirable secondary reactions (Durazzo et al. 2017). For example, uranyl difluoride (UO_2F_2) and oxides are produced from the oxidation of UF_4 with air (Jang et al. 2022). Some of the reactions that can occur with the presence of moisture, oxygen, or nitrogen include:

$$UF_4 + H_2O \rightarrow UF_3(OH) + HF \tag{9}$$

$$UF_3(OH) \rightarrow UOF_2 + HF$$
 (10)

$$2\mathsf{UOF}_2 + \mathsf{O}_2 \to 2\mathsf{UO}_2\mathsf{F}_2 \tag{11}$$

$$UF_4 + 2H_2O \rightarrow UO_2 + 4HF \tag{12}$$

$$2UF_4 + O_2 \rightarrow UF_5 + UO_2F_2$$
 (13)

$$UF_5 + 2H_2O \rightarrow UO_2F_2 + 4HF$$
 (14)

$$UF_4 + 2H_2O + 2Mg \rightarrow UO_2 + 2MgF_2 + 2H_2$$
 (15)

$$2Mg + O_2 \rightarrow 2MgO \tag{16}$$

$$3Mg + N_2 \rightarrow Mg_3N_2 \tag{17}$$

Opening operations for the reactor vessel to extract the crucible and the uranium metal ingot inside would be carried out in an inerted atmosphere to prevent pyrophoricity of the uranium metal, which could create fire hazards as well as may generate toxic powder oxides in the presence of oxygen.

The uranium metal yield will vary depending on multiple parameters, including packing density of the charge, particle size, oxide content of the Mg metal, residual moisture and free acid content in the UF₄. (Jang et al. 2022; Agarwal et al. 2020). Uranium metal yields up to 96 percent have been reported (Durazzo et al. 2017; Ladola et al. 2012). The slag will retain small amounts of uranium metal, lowering the yield, with most of the uranium metal trapped at the interface of the slag and the uranium metal ingot. The interface may be mechanically cut in the form of a disc for further refinement and uranium recovery.

The recovery of uranium metal from the slag may be accomplished through different methods (Ladola et al. 2012). The dissolution of slag disc in HNO_3 would produce toxic NO_x gases and fluoride species that complex with uranyl (UO_2^{2+}) ions in the solution, which adversely affect impurity removal during the subsequent solvent extraction step for purification and refining. The fluoride ions also corrode the stainless steel reaction tank, which would be accounted for its design life, or by use of more corrosion-resistant alloys (Ladola et al. 2012).

A second method involves co-melting of slag discs with later UF₄/Mg charges for magnesiothermic reduction. The process has been demonstrated with average 92 percent recovery of uranium metal from the slag discs, with no effect on the purity of the uranium metal ingot (Ladola et al. 2012). This method would not necessitate an additional process setup and would be a reasonably simple alternative for slag refinement. The process would consider the maximum mass of slag discs that can be melted in a single batch while still achieving the process purity specifications.

A.4.1.2 Calciothermic Reduction

The calciothermic reduction method uses a charge of UF_4 or UCI_4 with calcium metal as the reducing agent. The charge is loaded in an alumina (AI_2O_3) crucible and inside a steel reactor, similar to magnesiothermic reduction, with an inert environment and heated to ignition temperature. Equation (18) provides the general equation for the reduction of UX_4 (X = F, CI) with calcium metal.

$$UX_4 + 2Ca \rightarrow U + 2CaX_2 \tag{18}$$

Unlike magnesiothermic reduction, the reactor vessel does not necessitate preheating. The reduction reaction has been measured to 2000° C, which well exceeds the melting point of CaF₂ (1418°C). The reactor vessel would be designed to sustain the high exothermic reaction to maintain a contained system. Similar to magnesiothermic reduction, the uranium metal has a higher density than CaF₂ slag and settles to the bottom of the crucible. The mass scales produced by this batch process would be lower than magnesiothermic reduction to properly manage the heat of reaction. Another disadvantage to this approach is that calcium metal is costlier than Mg metal, which is more easily purified (Jang et al. 2022).

A.4.1.3 Alternative Methods

The production of metallic uranium has been investigated or demonstrated by other methods (Jang et al. 2022; LaHaye and Burkes 2019). Table A-4Table A-4 provides experimental

parameters for these methods. It is unlikely that these approaches would be implemented for the industrial production of metal fuel as they yield uranium metal shards, shot or powder at lower volumes.

Table A-4. Summary of Experimental Parameters for Metal Fuel Production Methods (Jang et al. 2022).

| | Uranium | Reducing Agent or Redox | Mass | Uranium Metal | Temperature | Uranium Product |
|---|--|-------------------------------------|--|-----------------------------|---|----------------------------|
| Method | Precursors | Potential [†] | Scale | Yield (%) | (°C) | Morphology |
| Magnesiothermic reduction in MgF ₂ | UF ₄ | Mg | g to kg | ~80 / 92–96 from slag | 1600–1700 | Solid |
| Calciothermic reduction in CaF ₂ | UF4, UCI4 | Ca | g | N/R | 1100 | Solid |
| Carbothermic reduction | UO ₂ | С | g | N/R | 1670 | Shard-like (intermetallic) |
| Electrolytic reduction in molten salt | UCl ₃ | -1.52 V (Ag/AgCl) | g | N/R | 500–600 | Acicular/ dendritic |
| Electrolytic reduction in ionic liquid | UO ₂ , U organic complexes | -2.4–2.8 V (Fc/Fc ⁺) | mg | N/R | RT-100 | Amorphous |
| Electroreduction in acetic acid | Uranyl acetate (UO ₂ (CH ₃ CO ₂) ₂) | -1.8–2.3 V SCE | g | 88–99 | RT (Mercury distillation: 800) | Powder (from amalgam) |
| Electrochemistry in organic solvents | UCl ₃ , Cs ₂ UCl ₆ , Cs ₂ UO ₂ Cl ₄ | -2.8 V (Fc/Fc ⁺) | mg to g | N/R | RT | Amorphous |
| Chemical reduction in acetic acid (CH ₃ COOH) | UO ₂ , UO ₂ (NO ₃) ₂ | Na | g to kg | ~8 | RT (Amalgam decomposition: 1500) | Powder (from amalgam) |
| Chemical reduction in organic solvent | UF ₄ | Li salt | g to <kg< td=""><td>N/R</td><td>RT</td><td>Nanoparticles</td></kg<> | N/R | RT | Nanoparticles |
| Thermal decomposition by arc melting | UI ₃ | N/A | g | 20 | 2100+ | Solid |
| Laser-induced decomposition | UN | N/A | g | 96.2 | 2500–2850 | Monolith |
| Gamma irradiation in aqueous/ alcoholic/citrate media | UCI4 | N/A | <mg< td=""><td>N/R</td><td>RT</td><td>Nanoparticles</td></mg<> | N/R | RT | Nanoparticles |

N/A = not applicable; N/R, not reported; RT = room temperature; SCE = saturated calomel electrode.

†Redox potentials are all reported as relative to reference electrodes in parenthesis.

A.4.2 Sodium-Bonded Metallic Fuel

Figure A-12 provides a general process flow diagram for fabrication of sodium-bonded metallic fuel pins for SFRs, as informed by Burkes et al. (2009b). The following discussion addresses the processes involved for casting of alloyed fuel slugs and fuel rod fabrication, including loading of fuel slugs and sodium bonding. The discussion of these steps will be presented in separate subsections.

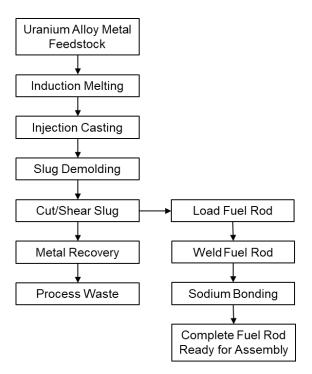


Figure A-12. Process Flow Diagram for Fabrication of Sodium-Bonded Metallic Fuel.

A.4.2.1 Alloying and Casting

Injection Casting

Injection casting, also referred to as vacuum injection melting or counter-gravity injection casting, was previously demonstrated as an effective method for production of metal alloy fuel for the Experimental Breeder Reactor (EBR)-II (Burkes et al. 2009a). The method allows for castings with high length-to-diameter (L/D) ratios, as needed for the fuel slug designs for SFRs. Figure A-13 shows a schematic of the injection casting system (Hayes 2017).

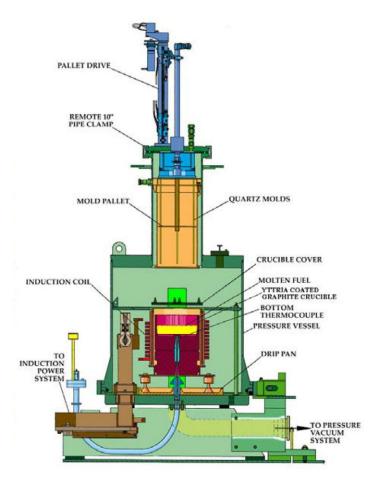


Figure A-13. Injection Casting System for Alloy Metal Fuel Slugs (Hayes 2017).

The alloy is produced by melting the charge (uranium and alloying metals, design additives) in yttria (Y_2O_3)-coated graphite crucibles inside a vacuum induction furnace at around 1500°C (Marschman et al. 2022; Burkes et al. 2009a; Porter and Crawford 2021). The individual metals are loaded in order of increasing melting temperatures (U > Zr > Pu) from bottom to the top of the crucible, which facilitates proper alloying and minimizes volatile losses of higher vapor pressure metals. The crucible is insulated with zirconia felt to prevent heat losses and heated by an induction coil made of high-conductivity copper to mitigate undesired resistive heating.

The charge is melted under a vacuum in an inert atmosphere (e.g., argon) and stirred by the induction fields generated by the induction heating coils and with a tantalum stirrer (Porter and Crawford 2021). An array of casting molds, fabricated of zirconium dioxide (ZrO₂)-coated silica or Vycor® silica and sealed at one end, has been previously attached to a pallet. Figure A-14 illustrates a pallet of casting molds used for the preparation of EBR-II fuel slugs. The pallet is attached to an elevator that can raise and lower the molds into the pool of molten fuel alloy contained inside the crucible. The pallet is then lowered into the crucible and the casting molds are inserted below the charge melt line and allowed to preheat for a few seconds.

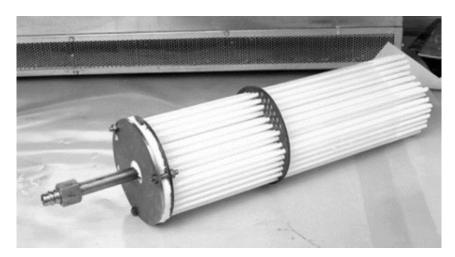


Figure A-14. Injection Casting Pallet with Zirconia-Coated Vycor® Molds For Preparation of EBR-II Fuel (Marschman et al. 2022).

The furnace is rapidly pressurized with inert gas, which develops a pressure differential between the mold's interior and the furnace's gas pressure to drive the molten metal up through the open ends of the casting molds. The casting molds are filled within a few seconds and solidification starts almost immediately. The molds are withdrawn from the charge melt when fuel has sufficiently solidified, and furnace heating is turned off. Once the molds have cooled to room temperature, the molds are removed from the furnace for further demolding and processing.

The next step in the process is to remove the fuel slugs from the molds for further machining. The fuel slugs are removed from the casting molds using a compressive force, which destroys the molds and creates quartz shards. The broken casting molds are discarded as waste. The demolding process is performed in an inert environment to avoid pyrophoricity hazards for metal particulate.

Once removed from the molds, the slugs are processed with a brusher for cleaning and removal of residual quartz shards. The brusher has electrically driven brushes that the casting is fed through. The brushes can have bristles made from polymeric materials, copper, or soft stainless steel. The fuel slugs are then inspected for quality and trimmed to design specifications. The end trimmings are collected per material accountability practices and either recycled or managed as radioactive waste. The fuel slugs are also heat treated, as needed, to produce a preferred crystallographic texture (grain orientation) or convert to a preferred uranium phase.

The fabrication of metallic fuel slugs by vacuum induction furnace is a batch-based process. Prior to use in the next batch, the crucible for the injection casting charge is removed, mechanically cleaned and recoated with Y_2O_3 .

Other Casting Approaches

Various other casting methods have been utilized and continue to be investigated. Centrifugal casting, which involves injecting the melt using centrifugal force, was used for fabrication of EBR-I fuel slugs (Burkes et al. 2009a; Burkes et al. 2009b). The EBR-I fuel slugs were significantly larger in diameter than for EBR-II fuel slugs (9.8 mm compared to 3.3–4.4 mm); the latter being more representative of fuel slug designs for modern SFRs. This method can achieve a uniform alloy for U-Zr alloys (Burkes et al. 2009a; Burkes et al. 2009b). The success rate and surface finish of the castings was improved by using mold materials made of brass, copper, or

silver. Centrifugal casting could potentially be used to fabricate fuel slugs, although it is generally undesirable compared to injection casting. The number and type of manipulations required to assemble and disassemble the furnace and molds are significant, lower L/D ratios of fuel slugs, and the relatively low production throughput per machine.

Continuous casting is another method that could potentially streamline the production process and increase efficiency by producing a continuous length of material that can be cut to desired sizes. The process would eliminate the need for molds and managing the associated waste streams. The method has been demonstrated for casting of bronze rods up to 91 cm long with a diameter within ± 0.06 mm with a smooth, uniform surface finish (Burkes et al. 2009a). The expectation was that U-10 Zr alloys would have more favorable thermal and mechanical characteristics for processing relative to bronze. However, although a continuous caster was built and staged to fabricate U–10 wt% Zr, tests were never conducted. The method also has additional challenges associated with proper alignment during pulling of the cast to avoid asymmetric variations in the rod diameter, increasing the complexity of the unit for remote operation (Burkes et al. 2009a). Figure 2 of Burkes et al. (2009a) provides schematics of the centrifugal and continuous casting methods.

Gravity casting is another method where the molten fuel is poured into molds via bottom-pour or tilt-pour approaches using Y_2O_3 -coated graphite molds (LaHaye and Burkes 2019). In the bottom-pour approach, a crucible with a knockout plug is directly placed above a mold. Once the metal charge is melted and held at temperature for the prescribed time, the knockout plug is mechanically removed to allow flow to the mold. The tilt-pour approach does not require a knockout plug, instead the crucible is tilted to pour into the mold. Tilt-pour tends to result in a more uniform alloy composition as lighter elements which settle to the top of the charge melt are mixed during the pouring process. Gravity casting does not require evacuation of the furnace, which is beneficial when processing recycled uranium because it suppresses the evaporation of americium, a major challenge to other casting methods (DOE 2018).

A.4.2.2 Fuel Pin Assembly, Including Sodium Bonding Step

Fuel pins are fabricated once the fuel slugs meet the design specifications and quality needs. Cladding tubes or jackets for SFRs are typically made from ferritic/martensitic stainless steels or advanced austenitic alloys, which offer good mechanical properties, corrosion resistance, and dimensional stability at high temperatures. Cladding jackets may be fabricated from a variety of austenitic 304L, 316, and D9 stainless steels, or the ferritic-martensitic HT9 stainless steel [tempered iron (Fe), 12 wt% chromium (Cr), 1 wt% molybdenum (Mo)], similar to American Iron and Steel Institute Grade 422) (Burkes et al. 2009a; Burkes et al. 2009b). Cladding jackets are produced by standard practices. Alloy ingots are forged into billets to break down the coarse grain structure and homogenize the material. The billets are then extruded into hollow tubes by pushing the billet through a die to form the tubular shape.

The extruded tubes then undergo cold pilgering, a process typically used to form tubing by reducing the outer diameter with tapered rolls and the wall thickness with a mandrel located inside the tubing. Cold drawing is used for further reduction in diameter and wall thickness per design specifications. The tubes are then subjected to a heat treatment to relieve stresses and achieve the desired microstructure per the design needs. This may include annealing of austenitic stainless steels or quenching/tempering for ferritic-martensitic stainless steels, which involves heating the material to high temperatures and then rapidly cooling it to enhance strength and toughness. The cladding jackets are inspected and cleaned.

Sodium handling and bonding operations are conducted in an inerted gas at reduced pressure (e.g., argon with limited helium, <50 ppm oxygen and water vapor) inside a glovebox or chamber to prevent sodium from significantly reacting with oxygen or moisture; while still allowing a minor amount of such impurities during the duration of the sodium loading process to reduce the adhesiveness of the sodium (Burkes et al. 2009b). A cladding jacket which has a welded bottom end plug is positioned vertically in the filling station. A machined sodium metal slug or extruded wire is inserted into the cladding jacket followed by the fuel slugs. Once the sodium and fuel slugs are positioned at the bottom of the cladding, the rod is backfilled with helium and the upper end plug is welded in place. Pins are leak tested using helium leak detection and decontaminated.

The next step is to create a layer of sodium between the cladding jacket and fuel slug to fill void space in the annulus. Sodium bonding is the process of wetting sodium to the fuel slug and cladding and removing any voids present in the annulus (the region between the fuel slug and cladding), each of which supports adequate heat transfer between the fuel and cladding. The fuel rods are placed in the bonding machine which heats the portion of the fuel rod loaded with the fuel slugs and sodium slug. Heating at 500°C is phased from top to bottom of the pin to avoid melting sodium in the lower section as otherwise, the still solid upper portion would not accommodate the thermal expansion. The lower ends of the fuel rods rest on an impact plunger. Once the sodium is melted the fuel rods are tapped by the plunger to impart a force to cause the fuel slug to sink into the sodium. Fuel rod displacement upon impact is set to a specific range to provide the necessary amount of energy for sodium bonding without damaging the rod. The impacting force needs to be sufficiently strong for movement of the fuel slug in order to remove voids present in the annulus. The rods are allowed to cool below 90°C from the bottom up, resulting in directional sodium solidification, before removing the bonded fuel pins from machine. Directional cooling is critical to reducing shrinkage voids in the excess sodium present above the fuel slugs (Burkes et al. 2009b).

Once the fuel rods are cooled and inspected for proper sodium bonding, the fuel rod is ready to be wire wrapped around its exterior. Wire wrapping of the fuel rod provides space between fuel rods and allows for heat to be extracted from the fuel rods more efficiently. Holes are drilled in the fuel rod end fittings. Using a wire wrap machine, the wire is secured to the lower end fitting using a bead weld, wrapped around the fuel rod, and secured to the upper end fitting using a bead weld. The tension is measured to ensure the fuel rod does not bend during irradiation. The fuel rods are inserted into grid assembly to form a hexagonal bundle, then the upper portion of the fuel assembly is lowered into place.

A.4.3 Dry Metallic Fuel (Non-Sodium-Bonded)

The following discussion addresses prior experience on the fabrication process for dry metallic fuel, i.e., fuel designs not incorporating sodium metal inside the fuel pins, as well as recent advancements per public information. The section begins with a discussion of the annular coextrusion process used for fabrication of N-Reactor fuel, which was conducted per an industrial-scale process at the DOE Hanford Site in Richland, Washington. The section continues with a discussion of a recent annular coextrusion development program at PNNL and concludes with a brief discussion of the TerraPower advanced annular coextruded fuel.

A.4.3.1 Prior Experience

The N-Reactor operated at the DOE Hanford Site from 1963 to 1987 utilizing fuel elements with a dual annular (tube-in-tube) design. Figure A-15 shows a schematic of the N-Reactor fuel

design with an inner fuel tube assembled within an outer fuel tube, each of which is fabricated by the coextrusion of metallic uranium and zircaloy cladding (Ballinger and Hall 1991). The design allowed for fuel coolant flow in between the inner and outer tubes. Figure 4.1 of National Research Council (2003) shows an assembled N-Reactor fuel element.

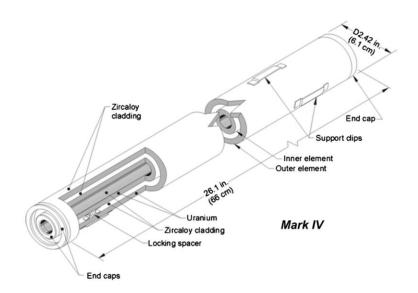


Figure A-15. Schematic of N-Reactor Fuel Design Showing Both the Inner and Outer Fuel Elements (Lavender et al. 2013).

The fuel tubes for the N-Reactor fuel elements were fabricated from coextrusion of zircaloy-2 cladding and metallic uranium enriched to 0.95 wt% U-235 (inner annular element) or 0.95–1.25 wt% ²³⁵U (Ballinger and Hall 1991). Although the coextrusion process for the N-Reactor fuel occurred some time ago, the basic or fundamental process steps have not changed. The sequence of operations involved in fabrication of N-reactor fuel included the following steps (Ballinger and Hall 1991):

- <u>Component Cleaning</u>: The metallic uranium billets, zircaloy-2 cladding shells and copper alloy cans were vapor degreased in tetrachloroethylene (C₂Cl₄), acid etched, rinsed in deionized water, and warm-air dried.
- <u>Assembly and Preheating</u>: The metallic uranium core, shells and can were assembled immediately after cleaning to mitigate oxidation. An inner zircaloy-2 shell was placed inside the metallic uranium core, an outer Zircaloy-2 shell outside the core, and the copper-silicon can outside the outer shell. End plates were fusion welded, helium leak tested, and sealed. Billet assemblies were preheated uniformly to 600°C.
- <u>Extrusion</u>: Preheated assemblies were extruded to the tubular fuel configuration in a high-pressure press. The copper alloy can prevent oxidation of metallic surfaces during heating and act as a lubricant during extrusion.
- <u>Element Shaping and Cleaning</u>: Extruded fuel tubes were cut into fuel element lengths by saw. The sawing was done under water to prevent ignition of small pyrophoric metal chips produced during cutting. Both ends of the fuel pieces were machined, then

processed through hot HNO₃ to remove the copper-silicon jacket. The cut elements were then chemically milled in an acid bath and etched in another acid solution.

• <u>End Cap Placement</u>: Zircaloy-2 end caps were heat treated in a high temperature salt bath. The ends were machined, degreased, and cleaned with an abrasive blast. The end caps were then welded to the extruded elements and further cleaned.

The N-Reactor program successfully demonstrated the industrial-scale annular coextrusion process for metallic U-Zr fuel elements at L/D ratios on the order of 10 to 20. Modern fuel pins for SFRs would likely have L/D ratios on the order of 140, assuming outer diameters in the range of 6 to 8 mm and an active fuel length in the range of 90 to 120 cm.

A.4.3.2 Recent Development of Annular Coextrusion

The ability to coextrude metallic annular fuel was further examined by a relatively recent PNNL development program using a benchtop extrusion press (Bennett et al. 2016; Lavender et al. 2013). The benchtop extrusion press, shown in Figure A-16, was capable of extruding billets at 800°C with a ram force of 70 tons (Lavender et al. 2013). Figure A-17 shows the cross section of the annular fuel design (U-10wt%Mo) investigated by PNNL (Youinou and Sen 2013). The program investigated principal variables in the coextrusion process which affect the quality of the extruded product. These include: the area reduction ratio, billet and tooling lubricant, extrusion temperature, extrusion rate, die design, coextruded product diameter, coextruded straightness, and surface condition. Figure 10.13 of (Wood et al. 2020)shows the initial billet with copper cladding before extrusion and the extruded product. The PNNL program showed that filled grease lubricants applied to the inside of the can and the face of the extrusion die, combined with coating of the billet with graphite, resulted in significant reduction in extrusion load and superior surface finish.

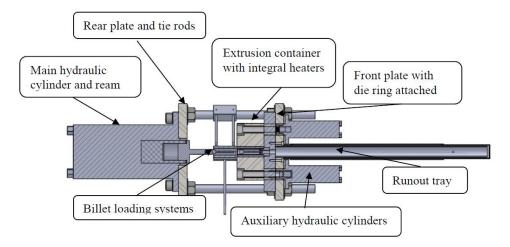


Figure A-16. Major Components of the Benchtop Extrusion Press (Lavender et al. 2013).

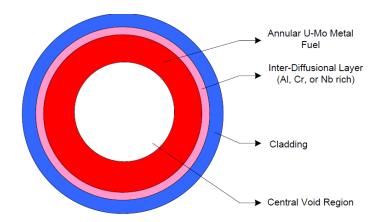


Figure A-17. Cross Section of Annular U-10wt%Mo Fuel Pin (Youinou and Sen 2013).

The PNNL program demonstrated the ability to perform triple-layer annular extrusion of an annular inner U-10 wt% Mo metallic core, a niobium diffusion layer and stainless steel cladding, as shown in Figure A-18. The L/D ratios achieved were on the order of 32, which although higher than those achieved for the N-reactor fuel, are still lower than those needed for advanced fuels for modern SFRs.

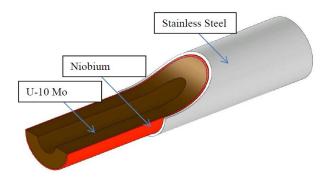


Figure A-18. Schematic of Multi-Layer Annular Fuel Coextruded with the Pacific Northwest National Laboratory (PNNL) Benchtop Extrusion Press (Bennett et al. 2016).

A.5 Fabrication of Salt-Based Fuels

A.5.1 Fabrication of Fluoride Salt Fuel

A.5.1.1 UF₄ Production

Although there are a number of chemical routes for production of the uranium tetrafluoride (UF₄) fuel salt, the most likely are either reaction of uranium dioxide (UO₂) with anhydrous hydrogen fluoride (HF) [per Equation (19)]) (Grenthe et al. 2006a; Souček et al. 2017) or direct reduction of UF₆ with hydrogen gas (H₂) [per Equation (20)] (McFarlane et al. 2019).

$$UO_2(s) + 4HF(g) \rightarrow UF_4(s) + 2H_2O(g)$$
 (19)

$$UF_6(g) + H_2(g) \rightarrow UF_4(s) + 2HF(g)$$
 (20)

Reaction (19) can be conducted in the range of 400–600°C (Souček et al. 2017). The process temperature is dependent on the uranium concentration in the salt. If non-stoichiometric oxides are present in the starting UO₂, it may be necessary to introduce H₂ into the reactor to avoid unwanted side reactions. Reaction (20) is highly exothermic but requires higher temperatures to initiate and requires a more complex reactor design (Smiley and Brater 1959). Therefore, Reaction (19) may be the most likely route to produce UF₄ for MSR fuel. Regardless, either route would involve similar chemical hazards, primarily the presence of HF and H₂.

Different processes may be implemented for direct reduction of UF₆ to UF₄ with H₂. The "hot wall" process was used at DOE facilities located in Fernald, Ohio, and in Paducah, Kentucky, to convert industrial quantities (10 metric tons U/day) of UF₆ tails to UO₂ with the reduction of UF₆ to UF₄ being the first step in this process (International Nuclear Fuel Cycle Evaluation Working Group 7 1979). The H₂ utilized in this process was obtained by cracking (dissociating) anhydrous NH₃ at a temperature of 900–950°C utilizing nickel-iron pellets as the reaction catalyst per Equation (21)(21).

$$2NH_3 \rightarrow N_2 + 3H_2$$
 (21)

The dissociated NH_3 was mixed with vaporized UF_6 and simultaneously fed to the top of a heated tower chemical reactor at high temperatures to form UF_4 and HF (temperatures up to about 730°C have been shown to result in highly efficient conversion rates). The UF_6 inlet to the tower was controlled at a pressure of 0.20 MPa (absolute) and the dissociated ammonia was controlled at about 0.17 MPa (absolute). A nozzle was used to mix and introduce the UF_6 and dissociated ammonia into the tower reactor. While the reaction is exothermic, the high activation energy prevents the reaction from proceeding at ambient temperature. To overcome this, electrical resistance heaters were used to preheat the tower walls before the gases were admitted to the tower and air blowers were provided to cool the tower during operation. The temperature gradient of the tower walls ranged from 650°C in the top zone to 450°C in the bottom zone.

Since some of the UF₄ produced from the reaction will accumulate on the wall of the tower, the tower was cooled to about 150°C and vibrated periodically to deslag the tower. The time required to perform this deslagging operation (which was daily) significantly impacted the efficiency of the production process. However, because the UF₄ agglomerates as a slag against the reactor walls, and because of the accumulation of UF₄ slag from the deslagging process,

this process may not meet nuclear safety requirements due to criticality concerns for HALEU UF₄ salts.

An alternative to the "hot wall" process is the "cold wall" process for the reduction of UF $_6$ to UF $_4$ (Smiley et al. 1956; Bester et al. 1993). The source of the UF $_4$ slag in the "hot wall" process is the high temperature of the reactor wall. The generation of UF $_4$ slag in the "cold wall" process is eliminated (or significantly reduced) by reducing the reactor wall temperature to 100 to 200°C. Because the "cold wall" process does not generate UF $_4$ slag, it does not have the criticality concerns for HALEU UF $_4$ salts that was discussed for the "hot wall" process above. In the "cold wall" process, the necessary energy for initiating and sustaining the reduction reaction is obtained by the addition of F $_2$ to the UF $_6$ feed and by utilizing the heat generated by the reaction between F $_2$ and H $_2$, per Equation (22)(22).

$$H_2 + F_2 \rightarrow 2HF \tag{22}$$

The "cold wall" process produces a large amount of excess HF and requires either the onsite storage of F_2 or an F_2 gas production unit that must be simultaneously operated with the reduction process. Additionally, the HF in the off-gas is toxic and corrosive, and the utilization of H_2 and F_2 makes this process more toxic and chemically hazardous than the previous processes.

McFarlane et al. (2019) and Torres et al. (2022) identified several other methods/processes that have been investigated for producing UF $_4$ salt from UO $_2$ or UF $_6$ feedstock. These include the application of ammonium bifluoride (NH $_4$ ·HF $_2$) to convert UO $_2$ to UF $_4$, reduction of UF $_6$ with carbon tetrachloride (CCl $_4$), reactions between UF $_6$ and nitrogen oxides (NO $_x$), and reaction of UF $_6$ with hydrogen halides. In addition, it is noted that the U.S. Atomic Energy Commission performed pilot scale tests on the reduction of UF $_6$ with TCE (C $_2$ HCl $_3$) and selected the H $_2$ reduction process discussed above for the industrial-scale plants that were constructed and operated (Smiley and Brater 1958). Out of these processes, only application of NH $_4$ ·HF $_2$ is further considered.

The use of NH₄·HF₂ to convert UO₂ to UF₄ has also been explored (Yeamans 2001) and similar chemistry has been proposed to remove oxide impurities (e.g., removal of UO₂ from commercially available UF₄) (Foster 2021; Polke 2023). The key chemical reactions involved in conversion of UO₂ to UF₄ with NH₄·HF₂ are represented by Equations (23)(23) through (28)(28).

Fluorination (80–125°C):

$$UO_2 + 4 NH_4 \cdot HF_2 \rightarrow (NH_4)_4 UF_8 \cdot 2H_2 O$$
 (23)

$$(NH_4)_4UF_8 \cdot 2H_2O \rightarrow (NH_4)_4UF_8 + 2H_2O$$
 (24)

Decomposition (125–425°C):

$$(NH_4)_4UF_8 \rightarrow (NH_4)_3UF_7 + NH_4F$$
 (25)

$$(NH_4)_3UF_7 \rightarrow (NH_4)_2UF_6 + NH_4F$$
 (26)

$$(NH4)2UF6 \rightarrow NH4UF5 + NH4F$$
 (27)

$$NH_4UF_5 \rightarrow UF_4 + NH_4F \tag{28}$$

A.5.1.2 UF₄ Purification

Methods for purifying the fluoride salts used in the MSRE at ORNL have also been described (Shaffer 1971). The fuel mixture for the MSRE contained nominally 65.0 mol% lithium fluoride (LiF), 29.1 mol% beryllium fluoride (BeF₂), 5.0 mol% zirconium tetrafluoride (ZrF₄), and 0.9 mol% UF₄. The Zr component was added as a safety measure to prevent precipitation of solid UO₂, should oxygen inadvertently enter the system; ZrO₂ would form preferably to UO₂. The salt fuel was prepared by combining two separate streams at the reactor site: (1) the barren fuel solvent mixture and (2) the fuel concentrate mixture. The barren fuel solvent mixture consisted of 64.7 mol% LiF, 30.1 mol% BeF₂, and 5.2 mol% ZrF₄. The fuel concentrate mixture contained 73 mol% LiF and 27 mol% UF₄. Purification steps for both these salt mixtures were similar.

The most important impurities of concern are oxides, sulfates, and structural material impurities (primarily Cr, Ni, and Fe). Oxides could be removed conveniently by reaction with hydrogen fluoride (HF) per Equation (29)(29).

$$O^{2-} + 2HF(g) \rightleftharpoons 2F^{-} + H_2O(g)$$
 (29)

Reaction (29) was conducted at 600°C during the MSRE campaign. Introduction of HF as a mixture with hydrogen (10 wt% HF in H₂) also aided in removal of sulfates (SO_4^{2-}). This occurred first through reduction of SO_4^{2-} to sulfide (S^{2-}), and then reaction of sulfide with HF to yield hydrogen sulfide (H_2S).

$$SO_4^{2-} + 4H_2(g) \rightleftharpoons S^{2-} + 4H_2O(g)$$
 (30)

$$S^{2-} + 2HF(g) \rightleftharpoons 2F^{-} + H_2S(g)$$
 (31)

The reduction of sulfates to sulfides was promoted by addition of elemental beryllium metal (Be) to yield beryllium oxide (BeO), according to the following equation.

$$SO_4^{2-} + 4Be(s) \rightleftharpoons S^{2-} + 4BeO(s)$$
 (32)

Early development work for the MSRE suggested that the structural metal impurities could be removed by reduction with elemental beryllium or zirconium. However, the report by Shaffer suggests that this was not performed in the salt production facility (Shaffer 1971). Rather, reduction of the structural metal impurities was achieved by sparging with H_2 at 700°C. It should be noted that the H_2 treatment would remove nickel (Ni) and iron (Fe) impurities, but would not be effective at removing Cr.

A.5.2 Fabrication of Chloride Salt Fuel

The primary chloride-based salt fuel considered for MSRs is uranium trichloride (UCl₃) (Mausolff et al. 2021), which may be possibly mixed with uranium tetrachloride (UCl₄). Other fissile actinide trichlorides (e.g., PuCl₃) could potentially be used.

A.5.2.1 UCI₃ Production

The likely route to production of UCl₃ will be from reduction of UCl₄ with hydrogen (H₂) at 500–580°C (Suttle and Hoekstra 1957) and at a pressure of 0.7 MPa (Patterson et al. 1967).

$$2UCI_4 + H_2 \rightarrow 2UCI_3 + 2HCI \tag{33}$$

Alternatively, UCl₄ may be reduced by metals to yield UCl₃. For example, reduction with aluminum (Al) at 400°C may be conducted per the following equation (Grenthe et al. 2006b):

$$3UCI_4 + AI \rightarrow 3UCI_3 + AICI_3$$
 (34)

The use of metallic zinc (Zn) has also been identified as an effective metal for reducing UCl₄ vapors to UCl₃ (at 450–480°C) because the zinc chloride (ZCl₃) byproduct is so volatile that it does not appreciably contaminate the UCl₃ product (Patterson et al. 1967). Other metals and reactants (e.g., hydrogen iodide [HI]) have also been experimentally evaluated (Young 1947; Friedman 1963).

Processes for the production of UCl₃ from uranium metal and metal hydrides have also been proposed. UCl₃ may be produced by reaction of metallic uranium powder or uranium hydride (UH₃) with HCl at 250°C (Friedman 1963). A recently issued patent describes the preparation of UCl₃ from U metal and transition metal chlorides (e.g., iron (II) chloride, FeCl₂) (Marsden et al. 2022). The reaction can be carried out in alkali or alkaline earth chlorides such that the resulting UCl₃ is already in a matrix suitable for use as fuel in an MSR; this can be customized to suit the specific needs of the MSR being fueled. An example reaction is provided as:

$$3FeCl2+2U \xrightarrow{600-850^{\circ}C} 2UCl3+3Fe$$
 (35)

In addition to its ability to directly lead to fuel salt mixtures applicable in MSRs, the latter method could be advantageous because it avoids use of hazardous chlorinating agents at the fuel salt fabrication facility. Although the patent describes purification of the UCl₃ material by repeated melt/filter/freeze cycles, it is likely that further purification would be required prior to introduction into an MSR. It is noted that McFarlane et al. (2019) concluded that routes involving uranium metal or uranium hydrides are not likely to be used industrially due to their pyrophoric characteristics.

A patent has also been issued describing an innovative electrochemical process whereby an electric current is applied to molten UCl₄ in an electrolysis chamber resulting in the reduction of UCl₄ to UCl₃ and the release of a Cl⁻ ion (Czerwinski et al. 2021). UCl₄ is reduced in a controlled manner to form a desired mixture of UCl₃ and UCl₄. The non-fissile component of the salt can be incorporated into the mixture during the electrolysis process. The net electrochemical reaction involved can be expressed as:

$$UCl_4 \rightleftharpoons UCl_3 + Cl_2 \tag{36}$$

The patent details how the electrochemical process can be controlled to produce a fuel salt with desired amounts of UCl₃, UCl₄, and MCl_n, where MCl_n is the supporting non-fissile chloride salt (such as NaCl). The patent also suggests that the process may be implemented at the reactor site.

Finally, chlorination of uranium metal with ammonium chloride (NH₄Cl) has also been proposed based on the following reaction (Eun et al. 2017).

$$U + 3NH_4CI \rightarrow UCI_3 + 3NH_3 + 1.5 H_2$$
 (37)

An initial investigation of this reaction led to a mixture of UCl₃ and UCl₄ being formed. However, extensive research would likely be needed to optimize this method.

A.5.2.2 UCl₄ Production

The precursor UCl_4 for reduction to UCl_3 is not known to be currently produced in industrial-scale quantities. A variety of approaches are available to produce UCl_4 , starting from uranium oxides and fluorides (e.g., UO_2 , UO_3 , UF_4 , or UF_6). In most cases, the vapors of the chlorinating reagents are highly toxic. These include chlorine gas (Cl_2) (sometimes mixed with CO), carbon tetrachloride (CCl_4), carbonyl dichloride ($COCl_2$), and hexachloropropene (C_3Cl_6 or $Cl_2C=CCICCl_3$) (Grenthe et al. 2006a); (McFarlane et al. 2019). It is unknown which process(es) will ultimately be selected to produce UCl_4 and generally there is very little process flow sheet information on these processes.

UCl₄ was previously produced in industrial quantities for use in the electromagnetic isotope separation process. In this process, UO₃ was converted to UCl₄, which was the feed for this uranium enrichment process (Scatchard et al. 1952). However, the use of UO₃ as starting material may be less likely relative to use of UO₂ for the production of UCl₄ for MSRs.

McFarlane et al. (2019) identifies production of UCl_4 by reaction of uranium oxides with CCl_4 in the gas phase, referred to as carbochlorination, as the best known process and it is extensively discussed in the literature. In this process a CO_2 gas stream saturated with CCl_4 vapors at atmospheric pressure is passed over UO_2 at a temperature of about $400-500^{\circ}C$, with about $450^{\circ}C$ being an optimum in limiting the production of UCl_5 (Wagner 1946). The process yields CO_2 in addition to UCl_4 per the following reaction:

$$UO_2 + CCI_4 \rightarrow UCI_4 + CO_2 \tag{38}$$

The process appears not to be completely selective to the desired product and other reactions occur resulting in the production of other byproducts. Specifically, the other byproducts are COCl₂, CO, Cl₂, and UCl₅ (Wagner 1946; Demkowicz et al. 2019). The chlorine byproduct is soluble in unreacted CCl₄, making this residual mixture both toxic and corrosive. Additional processing may also be required to further reduce the UCl₅ salt content in the desired UCl₄ salt product, such as by reacting the UCl₅ with H₂ gas at a temperature below about 300°C (Patterson et al. 1967).

 C_3Cl_6 may also be used to convert UO_3 , $UO_4 \cdot 2H_2O$, U_3O_8 , or UO_2Cl_2 to UCl_4 in a liquid phase reaction (Hermann et al. 1957). Both CCl_4 and C_3Cl_6 appear to have been primary chlorinating agents previously used in the electromagnetic isotope separation process for converting UO_3 to UCl_4 (Pitt et al. 1945; Haas 1992). However, C_3Cl_6 is not an effective chlorinating agent for UO_2 (Pitt et al. 1945; Tosolin et al. 2021): use of C_3Cl_6 would first require an additional process step to convert UO_2 or UF_6 to UO_3 or U_3O_8 . For this reason, C_3Cl_6 is not likely to be used in the production of UCl_4 for MSRs.

Based on historical information from over 50 years ago (Wagner 1946), other chlorinated organic compounds in the gas phase have not shown to offer any advantages over the use of CCl_4 nor have inorganic chlorinating agents in the gas phase (e.g., Cl_2 gas; $COCl_2$, sulfur chlorides such as S_2Cl_2 , $SOCl_2$ and SO_2Cl_2 ; inorganic reagents, such as HCl gas, PCl_5 , $SiCl_4$, etc.; anhydrous rare earth chlorides such as NH_4Cl). In addition, experiments showed that effective chlorination of UF_4 was typically much more difficult than chlorinating UO_2 because the reactions were at significantly higher temperatures (600–700°C), the reactions resulted in the generation of various contaminants, and the difficulty of recovering the UCl_4 from the chlorinating agent (Burkes et al. 2009a).

A.5.2.3 Fuel Salt Purification

Literature describing the purification of chloride-based fuel salts for MSR application appears to be scarce. However, it can be reasonably assumed that methods would parallel those used to purify fluoride salts. Thus, application of HCl and hydrogen gas to remove impurities can be anticipated. For example, oxide and hydroxide impurities may be removed through the following reactions.

$$O^{2-} + 2HCI(g) \rightleftharpoons 2CI^{-} + H_2O(g)$$
 (39)

$$OH^- + HCI(g) \rightleftharpoons CI^- + H_2O(g)$$
(40)

However, it has been reported that the purification of the chloride salts is more difficult than that of the fluoride salts and reactions (39) and (40) might not be sufficiently effective. CCl₄ has been shown to be more effective at oxide removal through the following reactions (Fredrickson et al. 2018):

$$2O^{2-} + CCI_4 \rightleftharpoons CO_2 + 4CI^-$$
 (41)

$$O^{2-} + CCl_4 \rightleftharpoons COCl_2 + 2Cl^{-} \tag{42}$$

The latter reaction would be problematic due to the formation of highly toxic carbonyl dichloride (COCl₂). Hydrogen and active metals might also be applied in the purification of chloride salts in the same way as described for the fluoride salts in Section A.5.1.

A.5.2.4 ³⁷Cl Enrichment

In addition to the chemical processes described above, enrichment of ³⁷Cl may be considered in the preparation of chloride fuel salts. Removal of ³⁵Cl from the fuel salt is necessary to avoid complications introduced by that isotope including formation of radiologically problematic ³⁶Cl, unfavorable nucleonics due to the high neutron cross-section of ³⁵Cl, and formation of corrosive sulfur-containing species. A recent study by PNNL concluded that the most likely technologies to be used for ³⁷Cl enrichment are centrifugation and thermal diffusion isotopic separation (TDIS) (Huber et al. 2024). Both methods require chlorine-containing gaseous species as feed stock (e.g., Cl₂, HCl). The PNNL team also concluded HCl is the preferable feed stock for ³⁷Cl enrichment primarily because (1) it is a potentially convenient reagent for preparation of fuel salt components and (2) other potential feeds such as Cl₂ or CCl₄ contain isotopic mixtures.

PNNL has been researching TDIS. The method involves moving the HCl gas through a series of reactors that consist of a tube within a tube (Figure A-19). The inner tube is heated while the outer tube is maintained at near ambient temperature. The HCl gas flows through the annulus between the two tubes. The lighter H³⁵Cl diffuses more rapidly than the heavier H³⁷Cl, thus resulting in isotope separation.

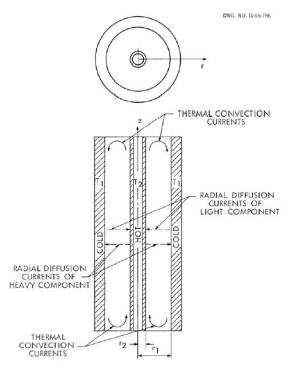


Figure A-19. Schematic Representation of Thermal Diffusion Isotopic Separation Reactor (Huber et al. (2024)).

Appendix B – Chemical Process Safety Assessment for Fabrication of TRISO-Based Fuels, Metallic-Based Fuels, and Salt-Based Fuels

A general framework was developed to assess the chemical process safety associated with the materials and operations involved in fuel fabrication. The purpose of this framework is to facilitate a consistent evaluation across all fuel types discussed in the report, ensuring that safety considerations are appropriately identified, reviewed, and communicated.

The hazards associated with key materials used in fuel fabrication, including primary chemical inputs, intermediates, and byproducts, were identified per the detailed chemical process descriptions in Appendix A. The approach used integrates chemical safety considerations, which address the intrinsic properties of materials, with process safety considerations, which reflect how these materials behave under operational conditions. By maintaining a consistent structure, the tables aim to summarize, at a high level, risks across the fuel types in a systematic and transparent manner.

The qualitative hazard descriptions for physical and health safety considerations presented in Appendix B were informed by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), which provides a structured framework for identifying and communicating chemical hazards. The GHS organizes hazards into hazard classes, which are grouped under broader categories such as physical hazards (e.g., flammable gases, corrosive to metals, oxidizing solids) and health hazards (e.g., acute toxicity, respiratory sensitization, carcinogenicity). Each hazard class is further divided into hazard categories that reflect the severity of the hazard. Associated with each class and category is a standardized hazard statement code (e.g., H314: 'Causes severe skin burns and eye damage'). The GHS framework is maintained by the United Nations and is typically updated on a biennial basis, ensuring periodic review and refinement of hazard classifications and statements. For this assessment, hazard statements assigned to individual chemicals, typically as reported in Safety Data Sheets (SDSs) or chemical hazard databases, were reviewed and qualitatively considered to develop the narrative descriptions used in the Physical Hazards and Health Hazards columns in the tables in Sections B.1.1 (TRISO-based fuels), B.2.1 (metallic-based fuels), B.3.1 (salt-based fuels). This same GHS-based classification structure was applied in Section 0 to assess and summarize the types of chemical hazards associated with each fuel fabrication process.

Sections B.1.2 (TRISO-based fuels), B.2.2 (metallic-based fuels), B.3.2 (salt-based fuels) provide information on chemical exposure guidelines and limits on essential Protective Action Criteria (PAC) for process chemicals relevant to fabrication of each fuel type, including Acute Exposure Guideline Levels (AEGLs), Emergency Response Planning Guidelines (ERPGs), and Temporary Emergency Exposure Limits (TEELs). Table B-1 provides descriptions of AEGL, ERPG, TEEL values. Further, IDLH (Immediately Dangerous to Life or Health) concentrations and NIOSH (National Institute for Occupational Safety and Health) skin notations (if available) are provided. Information sources of these guidelines and limits are discussed.

Table B-1. Description of AEGLs (Acute Exposure Guideline Levels), ERPGs (Emergency Response Planning Guidelines), and TEELs (Temporary Emergency Exposure Limits) Values.

AEGL ERPG TEEL

AEGL-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible on cessation of exposure.

ERPG-1 is the maximum airborne TEEL-1 is the airborne concentration below which it is believed that nearly all individuals or mg/m³) of a substance above could be exposed for up to 60 minutes without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor.

concentration (expressed as ppm which it is predicted that the general population, including susceptible individuals, who are exposed to the chemical could experience mild discomfort. irritation, or certain asymptomatic, non-sensory effects. However, these effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

concentration below which it is believed that nearly all individuals or mg/m³) of a substance above could be exposed for up to 60 minutes without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

ERPG-2 is the maximum airborne TEEL-2 is the airborne concentration (expressed as ppm which it is predicted that the general population, including susceptible individuals, when exposed for more than one hour, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

ERPG-3 is the maximum airborne TEEL-3 is the airborne concentration below which it is believed that nearly all individuals could be exposed for up to 60 minutes without experiencing or developing life-threatening health effects.

concentration (expressed as ppm or mg/m³) of a substance above which it is predicted that the general population, including susceptible individuals, when exposed for more than one hour, could experience life-threatening adverse health effects or death.

Source: Table 2.1 of DOE-HDBK-1046-2016 (DOE 2016).

Another important exposure guideline is the IDLH value, established by NIOSH. IDLH values represent the maximum concentration of a chemical in the air that a worker could be exposed to for 30 minutes without experiencing life-threatening effects or escape-impairing symptoms. These values are primarily used to inform respirator selection and workplace safety decisions but can also provide context in emergency scenarios. While IDLH values are not directly interchangeable with AEGLs, ERPGs, or TEELs, they complement these criteria by focusing on acute exposures in occupational settings. Unlike AEGLs and ERPGs, which provide detailed multi-tiered thresholds for broader populations, IDLH values are simpler, binary thresholds for immediate action. TEELs may sometimes align with IDLH values, particularly at higher levels of risk, but IDLH values are typically narrower in scope and application. These guidelines, like others, enhance the toolbox for managing chemical exposure risks effectively.

Dermal and ocular exposure limits are critical considerations for substances that pose risks through direct contact. While specific dermal exposure limits often do not exist, NIOSH uses skin notations to highlight chemicals that can be absorbed through the skin, contributing significantly to systemic exposure even when inhalation limits are not exceeded. Ocular exposure is generally considered a subset of dermal exposure, as both involve direct contact with surfaces vulnerable to chemical penetration and injury. NIOSH skin notations¹ provide detailed classifications, distinguishing between systemic effects (SK: SYS), fatal risks (SK: SYS [FATAL]), direct irritation or corrosion (SK: DIR [IRR] or SK: DIR [COR]), and sensitization potential (SK: SENS). These classifications help guide the implementation of protective measures, such as gloves, goggles, and other personal protective equipment, to prevent hazardous contact. Addressing both dermal and ocular risks within such frameworks supports comprehensive protection against chemical hazards, complementing inhalation-focused limits like AEGLs, ERPGs, TEELs, and IDLHs.

PAC, NIOSH IDLH values, and NIOSH skin notations were selected to inform quantitative exposure thresholds because they provide standardized, expert-reviewed thresholds commonly used in emergency planning and conservative hazard screening. PAC values, particularly the TEELs, are derived through DOE's standardized expert review of established benchmarks (such as TLVs, RELs, and PELs), reflecting values suitable for bounding analyses. While these served as the primary sources in this assessment, several other chemical information resources were qualitatively reviewed to help identify potential non-availability of data and to support contextual interpretation. These include publicly available databases such as the PubChem® database, the GESTIS database, the Haz-Map® database, and manufacturer-provided Safety Data Sheets (SDSs). These sources, summarized in Table B-2, offer information on chemical identity, general hazard classifications (e.g., GHS codes), and occupational health effects. However, due to variability in update cycles, derivation methods, and regulatory contexts, they were not used to derive or report any of the exposure values presented in this report. Their role was limited to qualitative reference in select cases, primarily to aid in hazard interpretation.

It should be noted that other tools, such as the CAMEO Chemicals software (accessible at https://cameochemicals.noaa.gov), developed by the U.S. EPA and NOAA, also offer consolidated chemical property data and enable users to explore potential reactivity between chemical pairs. While not used in this assessment, CAMEO is widely recognized and may be useful in future evaluations involving reactive chemical compatibility.

With regard to dermal and ocular hazards, data were limited in the available authoritative sources. While NIOSH skin notations were included where available, few such notations exist for the chemicals evaluated. To supplement this non-availability of data, GHS hazard statements, as previously described in Section 3.1.1, were reviewed qualitatively to identify dermal and ocular hazard indicators. These statements provided useful narrative insight to inform the health hazard descriptions in Appendix B. Furthermore, as outlined in Section 0, the GHS hazard classification structure was applied more systematically to categorize hazard types associated with each fuel fabrication process. That summary explicitly includes dermal and ocular hazards, offering an additional layer of interpretation where formal skin notation data were not available.

¹ The NIOSH skin notations are defined in Table G.2 of Current Intelligence Bulletin 61, A Strategy for Assigning New NIOSH Skin Notations, published by the Centers for Disease Control and Prevention (Centers for Disease Control and Prevention [CDC] 2017).

Table B-2. Supplemental Chemical Hazard Information Sources.

| Source | Description | Benefits | Limitations |
|--|--|---|---|
| PubChem® (Accessible at: https://pubchem.ncbi.nlm.nih.gov) | Public database maintained by the National Institute of Health that aggregates chemical information, including identity, toxicology data, physical properties, and GHS hazard classifications. | Useful for confirming chemical identity and retrieving general hazard classifications [e.g., signal words, pictograms, lethal dose 50% (LD ₅₀) values] when authoritative exposure limits are unavailable. | Aggregates data from multiple sources with varying derivation methods and update cycles. Values are not harmonized and may reflect environmental, academic, or pharmaceutical contexts rather than occupational or emergency screening needs. |
| GESTIS (Accessible at: https://gestis-database.dguv.de/) | European occupational safety database providing substance- specific workplace exposure limits, physical properties, and GHS classifications. | Offers curated exposure values and dermal hazard indicators when United States (U.S.)-specific data (e.g., NIOSH skin notations) are lacking. Provides technically detailed and transparent entries. | Values are derived under European regulatory frameworks, which may not align with U.S. standards. Differences in limit- setting philosophy and biological assumptions limit applicability. |
| Haz-Map® (Accessible at: https://haz-map.com/) | U.S. occupational health database linking chemicals to regulatory exposure values and health outcomes. | Supplements hazard understanding by identifying chronic health risks, target organs, and relevant exposure limits [e.g., Threshold Limit Value (TLVs), Recommended Exposure Limits (RELs), Permissible Exposure Limits (PELs)] from U.S. regulatory agencies. | Emphasizes chronic disease and occupational illness over acute hazard screening. Not routinely updated. Exposure values are not standardized across listings and are not directly applicable to emergency consequence assessment. |
| Safety Data Sheets (SDSs) (Accessible at manufacturer or vendor websites) | Occupational Safety and Health Administration (OSHA)-mandated documents summarize chemical hazards, handling practices, and exposure guidelines for specific products. | Provide formulation-specific GHS classifications and practical information on dermal, physical, or reactivity hazards. Useful when authoritative sources do not list the material. | Quality and completeness vary by supplier. Exposure limits may be outdated, inconsistently applied, or based on unverified or manufacturer-derived data. Not suitable for use in comparative or bounding hazard assessments. |

The exposure limits discussed, specifically AEGLs and ERPGs, are contemplated for assessing compliance with the performance requirements outlined in 10 CFR 70.61 and detailed in NUREG-1520, Revision 2, Standard Review Plan for Fuel Cycle Facilities License Applications - Final Report (NRC 2015). The regulations in 10 CFR 70.61 establish criteria to address adequate protection of workers and the public during potential accident scenarios involving licensed materials. Section A.2 of the Standard Review Plan (SRP) provides a structured framework for evaluating accident consequences and categorizing them into high, intermediate, or low severity levels, as defined in Table B-3Table B-3. The thresholds for chemical exposures. such as AEGL-3 and ERPG-3 for high consequence events, are explicitly referenced as part of the performance objectives. Appendix A of the SRP further provides critical context for the use of these limits within the ISA framework, which evaluates potential accident sequences and identifies preventive and mitigative measures to support compliance with performance requirements. The inclusion of AEGL and ERPG thresholds in the ISA process supports a systematic and consistent approach to analyzing accident scenarios and determining their potential impacts on workers and the public, while supporting adherence to regulatory expectations.

Table B-3. Consequence Severity Categories per 10 CFR 70.61.

| Consequence Category | Workers | Offsite Public | Environment |
|---|--|--|---|
| Category 3 – High Consequence | *RD > 1 Sv (100 rem) **CD > AEGL-3, ERPG- 3 | RD > 0.25 Sv (25 rem) 30 mg soluble U intake CD > AEGL-2, ERPG-2 | |
| Category 2 – Intermediate Consequence | 0.25 Sv (25 rem) < RD ≤ 1 Sv (100 rem) AEGL-2, ERPG-2 < CD ≤ AEGL-3, ERPG-3 | 0.05 Sv (5 rem) < RD ≤ 0.25 Sv (25 rem) AEGL-1, ERPG-1 < CD ≤ AEGL-2, ERPG-2 | Radioactive release > 5,000 × Table 2 in Appendix B to 10 CFR Part 20 |
| Category 1 – Low Consequence | Accidents with lower radiological and chemical exposures than those above in this column | Accidents with lower radiological and chemical exposures than those above in this column | Radioactive releases with lower effects than those referenced above in this column |

AEGL = Acute Exposure Guideline Level; CD = chemical dose; ERPG = Emergency Response Planning Guideline; RD = radiological dose; TEEL = Temporary Emergency Exposure Limit. Source: Table A-5 of NUREG-1520, Revision 2 (NRC 2015).

As noted in Section 3.1.2, DOE implements a different approach for assessing and mitigating chemical hazards, which differs in how exposure guidelines are applied relative to the NRC regulatory framework per 10 CFR Part 70. The DOE employs a hierarchy of PAC to manage chemical exposure risks during emergencies. For DOE, AEGLs are prioritized as the most scientifically rigorous and broadly applicable guidelines. For DOE, when AEGLs are unavailable, ERPGs provide established exposure limits for emergency response, and in their absence, TEELs serve as interim criteria to address this non-availability of data. This structured approach supports the DOE for effectively evaluating and mitigating chemical hazards, even for less-studied substances.

The DOE/National Nuclear Security Administration (NNSA) PAC database (accessible at: https://edms3.energy.gov/pac) provides a centralized resource for accessing chemical exposure limit values, offering a ready reference to AEGLs, ERPGs, and TEELs for over 3,000 chemicals.

This comprehensive tool supports users in easily identifying the appropriate limits based on the chemical and its associated hazards. Regular updates ensure the database reflects current scientific and regulatory standards, supporting informed decision-making and effective emergency response planning. Its accessible format makes it an essential resource for safety professionals and emergency planners within and beyond the DOE.

As of January 6, 2025, the PAC database contains values for 3,146 chemicals. A full revision is underway, with reaffirmed PAC and TEEL values being added on a bi-monthly basis. This revision is scheduled for completion in June 2027. Following that, the database will transition to a maintenance schedule, with a finite number of TEELs re-evaluated annually. Reaffirmed entries include updated references and methodology documentation to support transparency and consistency across chemical listings.

For DOE, these exposure limits are critical for assessing compliance with DOE safety standards for nonreactor nuclear facilities, as outlined in Table B-4. They establish DOE consequence thresholds for the public, co-located workers, and facility workers to categorize the severity of potential chemical releases based on PAC levels. These thresholds are integrated into their hazard analysis and accident evaluation framework to systematically assess accident scenarios and support consistent evaluation of chemical risks. By aligning consequence categories with PAC levels, the standard facilitates a structured approach to identifying and implementing preventive and mitigative controls. This supports facilities in meeting DOE's performance objectives for protecting workers and the public during potential chemical release events.

| Table B-4. | DOF (| Consequence | Thresholds | for (| Chemical R | eleases |
|------------|-------|---------------|------------|-------|---------------|----------|
| Table D-T. | | JULISCUUCITUC | THICOHOUS | ioi v | onchiloar i v | Cicases. |

| Consequence Level | Public¹,⁴ | Co-located Worker ^{2,4} | Facility Worker ³ |
|-------------------|--|---|--|
| High | ≥25 rem TED or ≥PAC⁵-2 | ≥100 rem TED or ≥PAC-3 | Prompt death, serious injury, or significant radiological and chemical exposure. |
| Moderate | ≥5 rem TED or ≥PAC-1 | ≥25 rem TED or ≥PAC-2 | No distinguishable threshold |
| Low | <5 rem TED or <pac-1< td=""><td><25 rem TED or <pac-2< td=""><td>No distinguishable threshold</td></pac-2<></td></pac-1<> | <25 rem TED or <pac-2< td=""><td>No distinguishable threshold</td></pac-2<> | No distinguishable threshold |

TED = total effective dose.

- 1 Maximally Exposed Offsite Individual (MOI): A hypothetical individual defined to allow dose or dosage comparison with numerical criteria for the public. This individual is an adult typically located at the point of maximum exposure on the DOE site boundary nearest to the facility in question (ground-level release) or at a farther distance where an elevated or buoyant radioactive plume is expected to cause the highest exposure (airborne release). The MOI used here is not the same as the Maximally Exposed Individual or the Representative Person used in Department of Energy (DOE) Order 458.1 for demonstrating compliance with DOE public dose limits and constraints.
- 2 A co-located worker at a distance of 100 m from a facility (building perimeter) or estimated release point.
- 3 A worker within the facility boundary and located less than 100 m from the release point.
- 4 Although quantitative thresholds are provided for the MOI and co-located worker consequences, the consequences may be estimated using qualitative and/or semi-quantitative techniques.
- 5 DOE's protective action criteria (PAC) are accessible at the current database website: https://edms3.energy.gov/pac.

Source: Table 1 of DOE-STD-3009-2014 (DOE 2014).

B.1 Chemical Process Safety for Fabrication of TRISO-Based Fuels

The following provides an assessment of chemical safety and process hazard considerations associated with TRISO-based fuel fabrication as well as summarizes key threshold limit values for chemicals involved in these processes. A discussion is provided on mitigative measures to address specific hazards and operational conditions for TRISO-based fuel fabrication. The assessment is organized by distinct tables and was performed using the methodology and approaches described in Section 3.0 and below.

B.1.1 Chemical Safety and Process Hazard Considerations

This section provides a summary of the chemical safety considerations associated with TRISO-based fuel fabrication. <u>Table B-5</u> outlines the physical and health hazards associated with chemicals identified in related processes. <u>Table B-6</u> identifies key process environments and the hazards associated with the chemicals used.

Table B-5. Chemical Safety Considerations for TRISO-Based Fuel Fabrication.

| Chemical Composition | Physical Hazard | Health Hazard |
|---|---|---|
| Uranyl nitrate UO ₂ (NO ₃) ₂ | This water-soluble uranium salt is a strong oxidizer. | This chemical is fatal if swallowed or inhaled and may cause damage to organs through prolonged or repeated exposure. |
| Nitric acid HNO ₃ | This acid is a strong oxidizer and may be corrosive to metals. | This chemical causes severe burns to skin and eyes upon contact and is toxic if inhaled. |
| Urea CH ₄ N₂O | No specific physical hazards are documented. | As a low-toxicity substance, hazards are limited to eye, skin, and respiratory irritation. |
| Hexamethylenetetramine (HMTA) C ₆ H ₁₂ N ₄ | HMTA is a flammable solid. | HMTA is harmful if swallowed and suspected of causing genetic defects. It may also cause allergic skin reactions as well as difficulties if inhaled. |
| Nitrogen oxides NO and NO ₂ | Nitrogen oxides are oxidizing gases. | Nitrogen oxides are toxic by inhalation and may cause severe respiratory irritation and pulmonary damage. High exposures can result in delayed-onset lung injury. |
| Trichloroethylene (TCE) C ₂ HCl ₃ | No specific physical hazards are documented. | TCE causes skin irritation, serious eye irritation, and drowsiness/dizziness. It may also cause genetic defects and cancer. |
| Perchloroethylene (PERC) C ₂ Cl ₄ | No specific physical hazards are documented. | PERC is harmful if inhaled. It causes skin irritation, serious eye irritation, and drowsiness/dizziness. It may also cause genetic defects, cancer, and damage to organs. |
| Mineral oils | This chemical is combustible. | These oils may be fatal if swallowed and enters airways (though, this varies based on type of oil). |
| Silicone oils | Some silicone oils are combustible, while others are non-flammable. | These oils may cause skin irritation, serious eye irritation, and drowsiness/dizziness (though, this varies based on type of oil). |
| 2-ethyl-1-hexanol C ₈ H ₁₈ O | This chemical is combustible. | This chemical may cause skin and serious eye irritation. It is also harmful if inhaled, causing respiratory irritation. |
| Ammonium hydroxide NH ₄ OH | When heated, ammonium hydroxide decomposes into ammonia gas and water vapor, which can be flammable in high concentrations. | This chemical may cause skin burns and eye damage. It is also harmful if inhaled or swallowed. |
| Acetylene C ₂ H ₂ | This chemical is extremely flammable, may react explosively even in the absence of air, and when under pressure, may explode if heated. | No specific health hazards are documented. |

| Chemical Composition | Physical Hazard | Health Hazard |
|--|--|---|
| Propylene C ₃ H ₆ | This chemical is extremely flammable, and when under pressure, may explode if heated. | No specific health hazards are documented. |
| Methyltrichlorosilane CH ₃ SiCl ₃ | This chemical is highly flammable and a severe hazard when exposed to heat, flame, or oxidizers. Violent reactions are possible with water, alcohols, acids, etc. | This chemical may cause skin burns and eye damage. It is toxic if inhaled. |
| Natural and synthetic graphite | This reducing agent is non-flammable in bulk form but combustible. Mixtures of graphite dust and air are explosive when ignited. It reacts violently with very strong oxidizing agents but is almost inert chemically when in bulk form. | Graphite dust and fumes can seriously irritate the respiratory system and throat, and cause coughing. Frequent inhalation over a long period of time can increase the risk of lung disease. |
| Phenol polymer with formaldehyde (C ₆ H ₅ OH) _x ·(CH ₂ O) _y | No specific physical hazards are documented. | This chemical may cause allergic skin reactions and serious eye irritation. |
| Phenol-HMTA resin | No specific physical hazards are documented. | This chemical may cause allergic skin reactions and serious eye irritation. |
| Nitrogen N ₂ | When under pressure, this chemical may explode if heated. | This chemical is a simple asphyxiant. |
| Hydrogen H ₂ | This chemical is extremely flammable, and when under pressure, may explode if heated. | No specific health hazards are documented. |
| Argon Ar | When under pressure, this chemical may explode if heated. | This chemical is a simple asphyxiant. |
| Ammonium nitrate NH ₄ NO ₃ | This chemical is an oxidizing solid. | This chemical can result in serious eye damage and irritation. |
| Hydrochloric acid HCl | This chemical may be corrosive to metals. | This chemical causes severe burns to skin and eye damage upon contact and is toxic if inhaled. It also can result in specific target organ toxicity. |
| Silicon carbide SiC | SiC is a hard, non-combustible crystalline solid that is chemically stable under normal conditions. Finely divided SiC particles may pose a dust explosion hazard in specific environments. | SiC dust can irritate the respiratory tract, eyes, and skin. Prolonged inhalation of fine particles may lead to lung damage, including pneumoconiosis or other chronic respiratory conditions. |
| Raw coke | Raw coke is a black, carbonaceous, and non-combustible solid under normal conditions, but fine coke dust may pose a dust explosion hazard in air. It can also smolder if exposed to heat or an ignition source. | Raw coke dust can irritate the respiratory tract, eyes, and skin upon exposure. Prolonged inhalation of dust may lead to chronic respiratory conditions, such as pneumoconiosis, and other lung damage. |
| Calcined coke | Calcined coke is a non-combustible, high-carbon | Calcined coke dust can irritate the respiratory tract, eyes, and skin upon |

| Chemical Composition | Physical Hazard | Health Hazard |
|-----------------------------------|--|--|
| | solid that is chemically stable under normal conditions. Fine particles of calcined coke can create a dust explosion hazard in air and may ignite under specific conditions. | exposure. Prolonged inhalation may result in chronic respiratory conditions, such as pneumoconiosis, and potential lung damage due to fine particulate accumulation. |
| TRISO = tri-structural isotropic. | | |

Table B-6. Chemical Process Hazards for TRISO-Based Fuel Fabrication.

| Chemical Composition | Process Environment | Process Hazard |
|---|---|--|
| Uranyl nitrate UO ₂ (NO ₃) ₂ | This chemical is involved in low -temperature batch processing (0–25°C) to produce the acid-deficient uranyl nitrate (ADUN) solution. | Spills or leaks can create aerosols that may pose significant inhalation or dermal contact hazards to workers. Improper handling or containment could exacerbate exposure risks. |
| Nitric acid HNO ₃ | This chemical is involved in lowtemperature batch processing (0–25°C) to produce the ADUN solution. | Overpressurization, spills, or leaks can release vapors, causing inhalation hazards. Direct contact with liquid nitric acid can result in severe burns and acute exposure risks for personnel. |
| Urea CH ₄ N ₂ O | This chemical is involved in low -temperature batch processing (0–25°C) with excess removal as byproduct from washing of gel spheres. | Residual urea may decompose, releasing ammonia gas, which can irritate the respiratory system. Handling errors may lead to inhalation or dermal exposure hazards for workers. |
| Hexamethylenetetramine (HMTA) C ₆ H ₁₂ N ₄ | This chemical is involved in low -temperature batch processing (0–25°C) with excess removal as byproduct from washing of gel spheres. | HMTA presents flammability risks, and its decomposition under heat can release toxic fumes. Workers may face inhalation hazards from residual material or mishandling during operations. |
| Nitrogen oxides NO and NO ₂ | Nitrogen oxides are evolved during the dissolution of uranium oxides in nitric acid as part of kernel precursor preparation. | Nitrogen oxides are toxic oxidizing gases that may accumulate in enclosed areas during exothermic reactions involving nitric acid. Without proper ventilation, they can pose serious inhalation risks and contribute to oxygen displacement. |
| Trichloroethylene (TCE) C ₂ HCl ₃ | This chemical is employed as a hot immiscible fluid (50–100°C) with excess removal as byproduct from washing of gel spheres. | Vapors released during operations may cause acute inhalation risks if ventilation is inadequate. Uncontrolled handling or spills could create localized exposure concerns for personnel. |
| Perchloroethylene (PERC) C ₂ Cl ₄ | This chemical is employed as a hot immiscible fluid (50–100°C) with excess removal as byproduct from washing of gel spheres. | Vapor emissions pose inhalation hazards to workers. Exposure to concentrated vapors may impair cognitive function and increase short-term health risks. |
| Mineral oils | This chemical is employed as a hot immiscible fluid (50–100°C) with excess removal as byproduct from washing of gel spheres. | Vapors generated from heated mineral oils may cause respiratory irritation. Contact with heated material poses dermal exposure risks for personnel. |
| Silicone oils | This chemical is employed as a hot immiscible fluid (50–100°C) with excess removal as byproduct from washing of gel spheres. | Heated silicone oils may emit irritant fumes that create respiratory discomfort for workers. Accidental contact with heated oils |

| Chemical Composition | Process Environment | Process Hazard |
|--|---|--|
| | | can also result in minor skin irritation. |
| 2-ethyl-1-hexanol C ₈ H ₁₈ O | This chemical is employed as a hot immiscible fluid (50–100°C) with excess removal as byproduct from washing of gel spheres. | Vapors released during use can cause respiratory and eye irritation, particularly in enclosed spaces. Mishandling or spills can increase worker exposure risks. |
| Ammonium hydroxide NH₄OH | This chemical is used to wash gel spheres, and excess is a byproduct from washing of gel spheres. | Decomposition produces ammonia gas, which poses acute inhalation risks in confined spaces. Splashes or leaks can also cause skin or eye irritation. |
| Acetylene C ₂ H ₂ | This chemical is used during porous carbon buffer overlayer deposition (1400–1500°C) as well as the creation of the inner and outer pyrolytic carbon layers (1250–1350°C). | Loss of an inert atmosphere can result in flammable mixtures forming, significantly increasing fire and explosion risks. Workers are at heightened risk if gas leaks or containment failures occur. |
| Propylene C₃H ₆ | This chemical is used during the creation of the inner and outer pyrolytic carbon layers (1250–1350°C). | Similar to acetylene, loss of inert atmosphere can lead to flammable gas accumulation. Leaks or uncontrolled release can pose immediate ignition and explosion hazards. |
| Methyltrichlorosilane CH₃SiCl₃ | The chemical is used with hydrogen gas during the creation of silicon carbide layers (1400–1500°C) and the densification of ceramic compacts to enhance their structural properties. These processes are carried out under controlled atmospheric conditions. | Reacting with moisture produces hydrochloric acid (HCI) and heat, creating risks of toxic vapor release and chemical burns. Uncontrolled leaks during ceramic compact processing may escalate worker exposure risks. |
| Natural and synthetic graphite | This chemical is used during particle overcoating (at room temperature) and for pebble fuel elements (at room temperature), which undergo carbonization (800°C) and heat treatment (1800–1950°C). | Fine graphite dust can become airborne, posing inhalation risks. Poor dust management may result in respiratory irritation or long-term health concerns. |
| Phenol polymer with formaldehyde (C ₆ H ₅ OH) _x ·(CH ₂ O) _y | This chemical is used as a binder during particle overcoating (at room temperature) and for pebble/cylinder compacts (at room temperature), which undergo carbonization (800°C) and heat treatment (1800–1950°C). | Heating resins can release fumes that pose acute respiratory hazards to workers. Direct contact with uncured resins may lead to skin irritation or allergic reactions. |
| Phenol-HMTA resin | This chemical is used as a binder during particle overcoating (at room temperature) and for pebble/cylinder compacts (at room temperature), which undergo carbonization (800°C) and heat treatment (1800–1950°C). | Heating resins can release fumes that pose acute respiratory hazards to workers. Direct contact with uncured resins may lead to skin irritation or allergic reactions. |

| Chemical Composition | Process Environment | Process Hazard |
|---|--|--|
| Nitrogen N ₂ | This chemical may be used during carbonization of pebble/cylinder compacts (800°C). | Nitrogen can displace oxygen in confined spaces, creating asphyxiation hazards. Accidental overuse or leaks may heighten these risks in poorly ventilated areas. |
| Hydrogen H ₂ | This chemical is used during porous carbon buffer overlayer deposition (1400–1500°C) as well as the creation of the inner and outer pyrolytic carbon layers (1250–1350°C). | Loss of inert atmosphere increases the risk of fire or explosion from hydrogen accumulation. Uncontrolled leaks or improper containment create significant hazards for personnel. |
| Argon Ar | This chemical is used during porous carbon buffer overlayer deposition (1400–1500°C); the creation of the silicon carbide layer (1400–1500°C); the creation of the inner and outer pyrolytic carbon layers (1250–1350°C); and the densification of ceramic compacts to maintain inert atmospheres. | Argon displaces oxygen, posing asphyxiation hazards in confined spaces. Leaks or overuse in enclosed areas may endanger workers without proper monitoring. |
| Ammonium nitrate NH ₄ NO ₃ | This chemical is a byproduct from washing of gel spheres. | Exposure to heat or mechanical shock can lead to decomposition, generation of toxic nitrous oxide (N ₂ O) or explosion risks. Improper handling of bulk material may escalate hazards for personnel. |
| Hydrochloric acid HCI | Hydrochloric acid is a byproduct of silicon carbide layer formation and ceramic compact densification processes involving methyltrichlorosilane and hydrogen gas. These processes occur at high temperatures of 1400–1500°C. | Vapor release or accidental splashes can cause respiratory irritation and chemical burns to workers. Mishandling during operations increases acute exposure risks, particularly in ceramic compact processes. |
| Silicon carbide SiC | Silicon carbide is present as a structural material in green bodies and interstitial spaces between fuel particles. It is also formed as a byproduct during the densification of ceramic compacts, which occurs at temperatures of approximately 1400–1500°C. | Silicon carbide dust can become airborne during handling or machining, posing significant inhalation hazards. Prolonged exposure to respirable silicon carbide dust may result in lung irritation or long-term respiratory health issues. |
| Raw coke | Raw coke is calcined at temperatures ranging from 900°C to 1300°C to drive off volatile components during the production of graphite prismatic blocks. This process occurs under atmospheric pressure. | The calcination process releases volatile organic compounds and gases, which can be flammable or toxic. These emissions require robust ventilation and monitoring systems. Elevated temperatures during calcination pose additional thermal hazards. |
| Calcined coke | Calcined coke, produced through high-temperature calcination, serves | Handling calcined coke can generate fine dust particles that |

| Chemical Composition | Process Environment | Process Hazard |
|----------------------------------|---|--|
| | as a precursor for graphite components. It is often subjected to further heat treatment processes at temperatures above 1800°C under controlled conditions. | pose inhalation hazards. Prolonged exposure to these particles may lead to respiratory irritation. High temperatures during subsequent processing present significant thermal hazards. |
| TRISO = tri-structural isotropic | | |

B.1.2 Exposure Guidelines and Limits for Consequence Severity Categorization

This section summarizes the threshold limit values for process chemicals related to the fabrication of TRISO-based fuels. <u>Table B-7 Table B-7</u> presents key exposure limits and associated notations for chemicals used in these processes.

Table B-7. Threshold Limit Values for Process Chemicals Related to Fabrication of TRISO-Based Fuels.

| Element or Compound | Limit Threshold Values | IDLH Concentration | Skin Notation |
|---|--|---|---|
| Uranyl nitrate UO ₂ (NO ₃) ₂ | TEEL-1 0.99 mg/m ³ TEEL-2 5.5 mg/m ³ TEEL-3 33 mg/m ³ | 10 mg/m³ (as U) | N/A |
| Nitric acid HNO ₃ | TEEL-1 0.16 ppm TEEL-2 24 ppm TEEL-3 92 ppm | 25 ppm | N/A |
| Urea CH ₄ N ₂ O | TEEL-1 12 ppm TEEL-2 110 ppm TEEL-3 690 ppm | N/A | N/A |
| Hexamethylenetetramine (HMTA) C ₆ H ₁₂ N ₄ | TEEL-1 9.6 ppm TEEL-2 110 ppm TEEL-3 630 ppm | N/A | N/A |
| Nitrogen oxides NO and NO ₂ | AEGL-1 0.5 ppm AEGL-2 12 ppm AEGL-3 20 ppm | 100 ppm (NO) 13 ppm (NO ₂) | N/A |
| Trichloroethylene (TCE) C ₂ HCl ₃ | AEGL-1 130 ppm AEGL-2 450 ppm AEGL-3 3,800 ppm | 1,000 ppm | Yes SYS-DIR (IRR)-SEN ^(b) |
| Perchloroethylene (PERC) C ₂ Cl ₄ | AEGL-1 35 ppm AEGL-2 230 ppm AEGL-3 1,200 ppm | 150 ppm | N/A |
| Mineral oils | TEEL-1 140 mg/m ³ TEEL-2 1,500 mg/m ³ TEEL-3 8,900 mg/m ³ | N/A | N/A |
| Silicone oils | Various ^(a) | N/A | N/A |
| 2-ethyl-1-hexanol C ₈ H ₁₈ O | ERPG-1 0.1 ppm ERPG-2 100 ppm ERPG-3 200 ppm | N/A | N/A |
| Ammonium hydroxide NH₄OH | TEEL-1 30 ppm TEEL-2 160 ppm TEEL-3 1,100 ppm | 300 ppm | N/A |
| Acetylene C ₂ H ₂ | TEEL-1 65,000 ppm*** TEEL-2 230,000 ppm*** TEEL-3 400,000 ppm*** | *N/A | N/A |
| Propylene C ₃ H ₆ | TEEL-1 1,500 ppm TEEL-2 2,800 ppm* TEEL-3 17,000 ppm** | *N/A | N/A |
| Methyltrichlorosilane CH ₃ SiCl ₃ | AEGL-1 0.6 ppm AEGL-2 7.3 ppm | N/A | N/A |

| | IDLH | | | |
|---|---|-------------------------|----------------------|--|
| Element or Compound | Limit Threshold Values | Concentration | Skin Notation | |
| | AEGL-3 33 ppm | | | |
| Natural and synthetic graphite | TEEL-1 12 ppm TEEL-2 670 ppm TEEL-3 4,100 ppm | 1,250 mg/m ³ | N/A | |
| Phenol, polymer with formaldehyde (C ₆ H ₅ OH) _x ·(CH ₂ O) _y | TEEL-1 30 mg/m ³ TEEL-2 330 mg/m ³ TEEL-3 2,000 mg/m ³ | N/A | N/A | |
| Phenol-HMTA resin | N/A | N/A | N/A | |
| Nitrogen N ₂ | TEEL-1 796,000 ppm TEEL-2 832,000 ppm TEEL-3 869,000 ppm | N/A | N/A | |
| Hydrogen H ₂ | TEEL-1 65,000 ppm*** TEEL-2 230,000 ppm*** TEEL-3 400,000 ppm*** | N/A | N/A | |
| Argon Ar | TEEL-1 65,000 ppm TEEL-2 230,000 ppm TEEL-3 400,000 ppm | N/A | N/A | |
| Silicon carbide SiC | TEEL-1 45 mg/m ³ TEEL-2 500 mg/m ³ TEEL-3 3,000 mg/m ³ | N/A | N/A | |
| Raw coke | N/A | N/A | N/A | |
| Calcined coke | TEEL-1 30 mg/m ³ TEEL-2 330 mg/m ³ TEEL-3 2,000 mg/m ³ | N/A | N/A | |
| Ammonium nitrate NH ₄ NO ₃ | TEEL-1 6.7 mg/m³ TEEL-2 73 mg/m³ TEEL-3 440 mg/m³ | N/A | N/A | |
| Hydrochloric acid HCl | AEGL-1 1.8 ppm AEGL-2 22 ppm AEGL-3 100 ppm | 50 ppm | N/A | |

AEGL = Acute Exposure Guideline Level; ERPG = Emergency Response Planning Guideline; IDLH = Immediately Dangerous to Life or Health; N/A = not available; TEEL = Temporary Emergency Exposure Limit; TRISO = tristructural isotropic.

⁽a) There are various types of silicone oils within the protective action criteria (PAC) database; limit threshold values would depend on the particular oil used.

⁽b) Refer to Table G.2 of Current Intelligence Bulletin 61, A Strategy for Assigning New NIOSH Skin Notations, for definitions associated with the NIOSH skin notation assignment (Centers for Disease Control and Prevention [CDC] 2017). The notations are also described in Section 3.0 of this report.

Limit threshold values marked by * are ≥ 10% lower explosive limit (LEL) but < 50% LEL. Limit threshold values marked by ** are > 50% LEL but < 100% LEL.

^{***} Limit threshold values marked by *** are ≥ LEL.

B.1.3 Considerations on Mitigative Measures

Based on the discussion and input provided about the chemicals used in TRISO fuel production and the processes involved, there are a few potentially process-specific mitigative measures that may be implemented. These measures address the specific hazards and operational conditions associated with TRISO-based fuel fabrication:

- Inert Atmosphere Management for Pyrolytic Carbon and Silicon Carbide Deposition: The use of flammable gases like C₂H₂, H₂, and CH₂CHCH₃ during the deposition of pyrolytic carbon and SiC layers requires rigorous maintenance of an inert atmosphere to prevent explosive mixtures. Unique mitigative measures could include enhanced monitoring of gas flow rates, inert gas purging systems, and interlocks to shut down the process if inert atmosphere integrity is compromised.
- Handling of Methyltrichlorosilane: Methyltrichlorosilane is highly reactive and can generate HCl and heat upon contact with moisture. Mitigative measures may include the use of moisture-proof containment systems, localized ventilation with scrubbers to neutralize acid vapors, and specialized training for handling this compound.
- <u>Dust Management for Graphite and Other Particulate Materials</u>: Fine graphite particles
 and other particulates generated during overcoating and compacting processes pose
 inhalation and explosion risks. Unique mitigative strategies could include advanced
 dust collection systems with HEPA filtration, enclosed processing equipment to limit
 worker exposure, and enhanced housekeeping protocols to minimize dust
 accumulation.
- Thermal Decomposition Products from Resins and Binders: During the carbonization and heat treatment of resins such as phenol-formaldehyde or phenol-HMTA, toxic or irritant fumes may be generated. Additional measures such as real-time gas monitoring and enhanced ventilation systems specific to these processing steps may be required.
- Emergency Preparedness for Chemical Spills and Releases: Chemicals such as HNO₃, uranyl nitrate, and NH₄OH require rapid containment and neutralization measures due to their corrosive and toxic nature. Facilities may need spill containment kits tailored to these specific chemicals and specialized training for workers to handle spills safely.

These unique considerations are tied to the specific properties of the chemicals and processes involved in TRISO fuel fabrication. While many standard mitigative measures outlined in NUREG/CR-6410 (NRC 1998) and NUREG-1520, Revision 2 (NRC 2015), apply broadly, these tailored measures address the process-specific hazards of TRISO fuel production.

B.2 Chemical Process Safety for Fabrication of Metallic-Based Fuels

The following provides an assessment of the chemical safety and process hazard considerations associated with metallic fuel fabrication as well as summarizes key threshold limit values for chemicals involved in these processes. A discussion is provided on mitigative measures to address specific hazards and operational conditions for metallic fuel fabrication. The assessment is organized by distinct tables and was performed using the methodology and approaches described in Section 3.0.

B.2.1 Chemical Safety Considerations

This section provides a summary of the chemical safety considerations relevant to metallic fuel fabrication. <u>Table B-8 Table B-8</u> outlines the physical and health hazards associated with chemicals identified in related processes.

Table B-9

Table B-9 identifies key process environments and the hazards associated with the chemicals used.

For metallic fuel fabrication, all associated tables cover the production of uranium metal through the magnesiothermic reduction of UF $_4$ using Mg under high temperature, inert atmosphere conditions. Additionally, for sodium-bonded metallic fuel fabrication, the tables address processes such as sodium bonding within cladding, vacuum-pressure casting of metallic fuel slugs, and related cleaning and inspection steps, emphasizing the use of sodium (Na) and associated process-specific chemicals like HNO $_3$ and tetrachloroethylene (C_2Cl_4).

Table B-8. Chemical Safety Considerations for Metallic Fuel Fabrication.

| Chemical Composition | Physical Hazard | Health Hazard |
|---|--|---|
| Uranium tetrafluoride UF ₄ | Uranium tetrafluoride is a non- combustible green crystalline solid that may release toxic fluoride vapors if heated or exposed to moisture. It reacts with acids, liberating hydrogen fluoride (HF), a highly corrosive gas. | Uranium tetrafluoride is harmful if inhaled, ingested, or absorbed through the skin. It can cause severe irritation or burns to the respiratory tract, eyes, and skin. Chronic exposure may result in kidney damage due to the chemical toxicity of uranium. |
| Magnesium Mg | Magnesium is a lightweight, silvery metal that is highly flammable in powder or finely divided form. It burns with an intense white flame, producing significant heat. Magnesium reacts with water and acids, releasing flammable hydrogen gas, which poses fire and explosion hazards. It may ignite spontaneously in air when finely divided. | Magnesium dust or fumes can irritate the respiratory tract if inhaled, potentially causing coughing or difficulty breathing. Prolonged or repeated exposure to magnesium dust may lead to irritation of the skin and eyes. Direct contact with burning magnesium can cause thermal burns. Chronic exposure to magnesium compounds in poorly ventilated areas may contribute to minor respiratory issues. |
| Nitric acid HNO₃ | Nitric acid is a highly corrosive, colorless to yellowish liquid. It is a strong oxidizing agent that reacts violently with many organic and inorganic substances, potentially causing fire or explosion hazards. It can produce toxic nitrogen oxide (NOx) fumes when heated or decomposed. Contact with metals may release flammable hydrogen gas. | Nitric acid is toxic if inhaled, ingested, or absorbed through the skin. It causes severe burns to the skin, eyes, and respiratory tract upon contact. Inhalation of fumes can lead to irritation, difficulty breathing, or pulmonary edema. Prolonged or repeated exposure can result in chronic respiratory issues and damage to mucous membranes. |
| Nitrogen oxides NO and NO ₂ | Nitrogen oxides are oxidizing gases. | Nitrogen oxides are toxic by inhalation and may cause severe respiratory irritation and pulmonary damage. High exposures can result in delayed-onset lung injury. |
| Hydrofluoric acid HF | Hydrofluoric acid is a colorless, corrosive liquid or gas with a strong, pungent odor. It is highly reactive, especially with glass, ceramics, and many metals, releasing flammable hydrogen gas upon contact. HF poses a significant fire and explosion hazard when in contact with incompatible materials. It can vaporize readily, releasing toxic fumes. | Hydrofluoric acid is extremely hazardous, causing severe burns to skin and eyes. It can penetrate tissue and damage underlying structures, including bones. Exposure through inhalation, skin contact, or ingestion may lead to systemic toxicity, potentially resulting in fatal cardiac arrhythmias or multi-organ damage. Symptoms may be delayed, and even small exposures require immediate medical attention. |
| Magnesium fluoride MgF ₂ | Magnesium fluoride is a white, crystalline solid that is non-flammable and stable under normal conditions. It is insoluble in water and has low | Magnesium fluoride may cause mechanical irritation to the eyes, skin, and respiratory system if inhaled as dust. Prolonged or repeated exposure |

| Chemical Composition | Physical Hazard | Health Hazard |
|---|---|--|
| | reactivity. Fine particles may become airborne, posing a minor dust explosion hazard in confined spaces. | to dust may lead to respiratory discomfort. Systemic toxicity is generally low, but proper protective equipment should be used to minimize contact. |
| Lithium carbonate Li ₂ CO ₃ | Lithium carbonate is a white, odorless powder that is stable under normal conditions. It is not flammable but may decompose at high temperatures, releasing toxic lithium oxide fumes. The fine powder can become airborne and pose a dust explosion hazard in confined spaces. | Lithium carbonate may cause irritation to the eyes, skin, and respiratory system upon exposure. Ingestion can result in gastrointestinal distress, including nausea, vomiting, and diarrhea. Prolonged exposure to high doses may affect kidney and central nervous system functions. Protective equipment is recommended to minimize exposure. |
| Potassium carbonate K ₂ CO ₃ | Potassium carbonate is a white, odorless crystalline solid. It is stable under normal conditions but reacts with acids to release carbon dioxide gas. Contact with water generates heat, which may pose a hazard in confined spaces. | Potassium carbonate is corrosive and can cause severe irritation or burns to the skin and eyes. Inhalation of dust or mist may lead to respiratory irritation, coughing, and shortness of breath. Ingestion can result in gastrointestinal irritation, nausea, vomiting, and abdominal pain. Proper personal protective equipment is recommended to minimize exposure. |
| Magnesium oxide MgO | Magnesium oxide is a white, odorless solid in powder or granular form. It is stable under normal conditions but may react with strong acids to release heat and form magnesium salts. Fine powders can pose a fire hazard in the presence of ignition sources. | Magnesium oxide dust may cause mechanical irritation to the eyes, skin, and respiratory tract. Prolonged or repeated inhalation of dust can lead to respiratory discomfort or chronic lung conditions, particularly in poorly ventilated areas. Direct contact may cause mild irritation to the skin or eyes. |
| Carbon dioxide CO ₂ | Carbon dioxide is a colorless, odorless, non-flammable gas that is heavier than air and can accumulate in confined spaces, potentially displacing oxygen and creating asphyxiation hazards. It can also cause pressure buildup in containers if improperly stored. | Carbon dioxide is a simple asphyxiant; exposure to high concentrations can cause dizziness, shortness of breath, loss of consciousness, or death due to oxygen displacement. Direct contact with solid carbon dioxide (dry ice) can cause severe frostbite. |
| Lithium fluoride LiF | Lithium fluoride is a white, crystalline solid that is stable under normal conditions. It is non-flammable but reacts with acids to release toxic hydrogen fluoride (HF) gas. It may also be corrosive to some metals. | Lithium fluoride can cause severe irritation to the eyes, skin, and respiratory tract. Prolonged or repeated inhalation of dust may lead to respiratory discomfort. If ingested, it can be harmful, causing nausea, vomiting, and abdominal pain. Direct skin or eye contact with LiF dust or solutions may result in irritation or burns. |

| Chemical Composition | Physical Hazard | Health Hazard |
|--|--|--|
| Parascandolaite KMgF₃ | Parascandolaite is stable under standard conditions but reacts with strong acids to release corrosive and toxic hydrogen fluoride (HF). Dust from this compound may be irritating to the respiratory system. | Parascandolaite may cause irritation to the eyes, skin, and respiratory tract upon exposure to dust or particles. The release of hydrogen fluoride upon reaction with acids poses a significant hazard, requiring careful handling to avoid accidental exposure. |
| Yttrium oxide Y ₂ O ₃ | Yttrium oxide is a white, odorless, non-flammable powder that is stable under normal conditions. Dust generated from the material can become airborne, potentially creating respiratory hazards. | Yttrium oxide dust may irritate the respiratory tract, eyes, and skin upon exposure. Prolonged or repeated inhalation of fine particles may pose a risk to lung health, leading to potential chronic respiratory conditions. |
| Zirconium dioxide ZrO ₂ | Zirconium dioxide is a white, odorless, non-flammable powder that is stable under normal conditions. Dust generated from the material can become airborne, potentially creating respiratory and explosion hazards in confined spaces. | Zirconium dioxide dust may irritate the respiratory tract, eyes, and skin upon exposure. Prolonged or repeated inhalation of fine particles may lead to chronic respiratory conditions. Direct contact with the eyes or skin can cause mild mechanical irritation. |
| Magnesium zirconium oxide MgZrO ₃ | Magnesium zirconium oxide is a white, odorless, non-flammable solid that is chemically stable under normal conditions. Dust from this material can become airborne, posing explosion risks in confined spaces if combined with flammable substances. | Inhalation of fine particles can irritate the respiratory system. Prolonged or repeated exposure to airborne dust may lead to chronic respiratory issues. Skin and eye contact may cause mild irritation, primarily due to the abrasive nature of the material. |
| Beryllium oxide BeO | Beryllium oxide is a white, odorless, crystalline powder that is stable under normal conditions but may form airborne particulates during handling. Dust is non-flammable but can become a respiratory hazard in enclosed areas. | Beryllium oxide is highly toxic if inhaled, as beryllium compounds can cause chronic beryllium disease (CBD) or lung cancer with prolonged exposure. It may irritate the eyes, skin, and respiratory system. Chronic exposure may result in systemic effects, including sensitization and immune response complications. |
| Sodium carboxymethyl cellulose C ₈ H ₁₅ NaO ₈ | Sodium carboxymethyl cellulose is a white to off-white powder that is stable under normal conditions. It is not flammable but may form dust-air mixtures that could become explosive in high concentrations. | This chemical is considered non-toxic but may cause mild eye, skin, or respiratory irritation upon contact or inhalation. Prolonged exposure to dust may result in discomfort or respiratory sensitization in susceptible individuals. |
| Uranyl nitrate UO ₂ (NO ₃) ₂ | This water-soluble uranium salt is a strong oxidizer. | This chemical is fatal if swallowed or inhaled and may cause damage to organs through prolonged or repeated exposure. |
| Tributyl phosphate (CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ O) ₃ PO | Tributyl phosphate is a clear, colorless to pale yellow liquid with a mild odor. It is not highly flammable but can emit toxic fumes, including phosphorus oxides, when heated or | Tributyl phosphate is harmful if swallowed, inhaled, or absorbed through the skin. It can cause irritation to the eyes, skin, and respiratory system. Prolonged or repeated |

| Chemical Composition | Physical Hazard | Health Hazard |
|---|---|---|
| | involved in a fire. Tributyl phosphate is stable under normal conditions but may react with strong oxidizers. | exposure may affect the kidneys and liver. Handling tributyl phosphate requires caution due to its potential for systemic toxicity. |
| Gaseous ammonia NH ₃ | Gaseous ammonia is a colorless, highly corrosive, and flammable gas with a pungent odor. It reacts violently with strong oxidizers, acids, halogens, and certain metals, potentially causing fires or explosions. Gaseous ammonia also reacts with water to form ammonium hydroxide, releasing significant heat that may lead to thermal burns or violent reactions in confined spaces. | Gaseous ammonia is toxic by inhalation, causing severe irritation or burns to the respiratory tract, eyes, and skin. High concentrations may result in respiratory distress, pulmonary edema, and systemic effects. Prolonged exposure can cause permanent tissue damage. |
| Ammonium diuranate ADU | Ammonium diuranate is a yellow solid that decomposes when heated, releasing ammonia gas and uranium oxides. It is moderately soluble in water and reacts with acids to produce toxic uranyl compounds. Improper storage or handling can lead to the release of uranium dust. | Ammonium diuranate is toxic if inhaled, ingested, or absorbed through the skin. It can cause severe irritation or burns to the respiratory tract, skin, and eyes. Prolonged or repeated exposure may result in kidney damage due to uranium's chemical toxicity. Ammonium diuranate also poses a radiological hazard due to the presence of uranium isotopes. |
| Triuranium octoxide U ₃ O ₈ | Triuranium octoxide is a stable black crystalline solid that is not flammable under normal conditions. It is chemically stable but can release uranium dust during handling, which is a physical and inhalation hazard. | Triuranium octoxide is toxic if inhaled, ingested, or absorbed through the skin. It can cause irritation to the respiratory tract, eyes, and skin. Prolonged or repeated exposure may result in kidney damage due to uranium's chemical toxicity. The compound also presents radiological hazards due to uranium isotopes. |
| Stannous chloride SnCl ₂ | Stannous chloride is a white crystalline solid that is hygroscopic and may release corrosive hydrogen chloride gas when exposed to moisture. It decomposes when heated, producing toxic fumes of hydrochloric acid and tin oxides. | Stannous chloride is harmful if inhaled, ingested, or absorbed through the skin. It may cause severe irritation or burns to the respiratory tract, eyes, and skin. Prolonged exposure can lead to systemic toxicity, potentially affecting the kidneys and liver. |
| Tetrachloroethylene C ₂ Cl ₄ | Tetrachloroethylene is a volatile, non- flammable liquid that can release toxic and irritating fumes when heated or exposed to fire. It is heavier than air and can accumulate in low-lying areas, posing suffocation hazards. | Tetrachloroethylene is harmful if inhaled and may cause dizziness, drowsiness, or central nervous system depression. Prolonged or repeated exposure can lead to liver and kidney damage. It is classified as a possible human carcinogen and can irritate the eyes, skin, and respiratory tract. |

| Chemical Composition | Physical Hazard | Health Hazard |
|---|--|---|
| Sodium Na | Sodium is a highly reactive and flammable solid. It reacts violently with water and moisture to produce hydrogen gas and heat, which can ignite spontaneously. Sodium can also react explosively with other reactive chemicals, such as acids, halogens, and oxidizers. Proper handling and storage in inert or dry atmospheres are essential. | Sodium is corrosive and can cause severe burns upon contact with skin, eyes, or mucous membranes. Inhalation of sodium fumes or reaction byproducts may cause respiratory irritation. Prolonged exposure can lead to more serious tissue damage due to its reactivity and corrosive nature. |
| Ammonium bicarbonate NH ₄ HCO ₃ | Ammonium bicarbonate is a white crystalline solid that decomposes when heated, releasing ammonia, carbon dioxide, and water vapor. It is incompatible with acids, bases, and strong oxidizing agents, potentially leading to the release of hazardous gases. Dust from the solid can become airborne, creating explosion hazards in confined spaces. | Ammonium bicarbonate may cause irritation to the skin, eyes, and respiratory tract upon exposure. Inhalation of ammonia released during decomposition can cause respiratory irritation and discomfort. Prolonged exposure to high concentrations of dust or decomposition products may lead to more severe respiratory effects. |
| Sodium chloride NaCl | Sodium chloride is a white crystalline solid, non-flammable, and stable under normal conditions. When heated to decomposition, it may release toxic gases such as hydrogen chloride and sodium oxides. Dust may become airborne in confined spaces, creating minor respiratory irritation hazards. | Sodium chloride may cause mild irritation to the skin and eyes upon contact. Inhalation of dust may irritate the respiratory tract, and ingestion of large amounts may cause gastrointestinal discomfort, including nausea and vomiting. Chronic exposure is not associated with significant health risks under normal handling conditions. |
| Argon Ar | When under pressure, this chemical may explode if heated. | This chemical is a simple asphyxiant. |
| Nitric sulfuric acid HNO ₃ + H ₂ SO ₄ | A highly corrosive and reactive acid mixture that generates intense heat when mixed with water or organics. Produces toxic fumes, particularly nitrogen oxides (NOx), and can cause severe burns. | Causes severe chemical burns to skin and eyes. Inhalation of fumes may result in irritation, pulmonary edema, or chronic respiratory issues. |
| Nitric hydrofluoric acid HNO ₃ + HF | Highly corrosive and reactive, releasing toxic vapors. Reacts with metals, ceramics, and glass, producing hazardous byproducts. | Causes severe burns to skin and eyes, with hydrogen fluoride capable of penetrating tissues and causing systemic toxicity (including nervous system, skeletal system). Inhalation can result in respiratory distress and cardiac arrhythmias. |
| Zircaloy-2 alloy with 5% beryllium | Releases beryllium-containing fumes during brazing or high temperature processes, which are hazardous if inhaled. Alloy particulates can be irritating. | Chronic exposure may lead to CBD or lung cancer. Direct contact may irritate the skin, and inhalation of fumes or dust requires protective measures. |

Table B-9. Chemical Process Hazards for Metallic Fuel Fabrication.

| Chemical Composition | Process Environment | Process Hazard |
|---|---|---|
| Uranium tetrafluoride UF₄ | Uranium tetrafluoride undergoes magnesiothermic reduction in a sealed reactor. The reaction begins at a preheated temperature of 570–620°C and produces molten uranium metal and magnesium fluoride slag. The reactor operates under an inert atmosphere to prevent contamination or oxidation. | The exothermic reaction generates significant heat and pressure, requiring robust containment. Pyrophoric uranium metal can ignite upon contact with air. Improper cooling or handling of the slag and ingot increases the risk of fire or explosion. |
| Magnesium Mg | Magnesium metal serves as a reductant in the magnesiothermic reduction of uranium tetrafluoride. The reaction is carried out in an oxygen-free environment to prevent premature ignition. | Magnesium is highly reactive, and its dust or fine particles are flammable. Contact with water or moisture generates hydrogen gas, posing fire and explosion risks. |
| Nitric acid HNO₃ | Nitric acid is used in cleaning uranium ingots to dissolve residual magnesium fluoride slag. The cleaning process often employs 35–50 wt% solutions at warm temperatures. | Nitric acid is highly corrosive and reacts with residual metals, releasing toxic gases. Spills or improper containment can cause severe burns to personnel and damage to equipment. |
| Nitrogen oxides NO and NO ₂ | Nitrogen oxides are generated during the dissolution of slag materials formed in the magnesiothermic reduction process when treated with nitric acid. | Nitrogen oxides are toxic oxidizing gases that may evolve rapidly during the exothermic reaction between slag components and nitric acid. Without sufficient ventilation, these gases may accumulate and pose serious inhalation and oxidative hazards. |
| Hydrofluoric acid HF | Hydrofluoric acid is used in the conversion of triuranium octoxide to uranium tetrafluoride, typically in conjunction with stannous chloride at approximately 400°C. | Hydrofluoric acid is extremely corrosive and toxic. Contact causes severe chemical burns and systemic toxicity (including nervous system, skeletal system). Vapors can damage respiratory systems and corrode nearby equipment. |
| Magnesium fluoride MgF ₂ | Magnesium fluoride is produced as a byproduct of uranium tetrafluoride reduction with magnesium. It is removed from uranium ingots using mechanical methods or dissolved in nitric acid baths. | Magnesium fluoride itself is stable but may retain traces of uranium, posing radiological hazards. Dust from handling may irritate the respiratory system. |
| Lithium carbonate Li ₂ CO ₃ | Magnesium fluoride itself is stable but may retain traces of uranium, posing radiological hazards. Dust from handling may irritate the respiratory system. | The reaction of lithium carbonate with magnesium fluoride generates carbon dioxide gas, which can build pressure in confined systems. Molten salts pose significant thermal hazards to workers. |
| Potassium carbonate K ₂ CO ₃ | Potassium carbonate is a component of eutectic salt mixtures used in slag cleaning baths. The mixtures operate at elevated temperatures to dissolve impurities effectively. | Exposure to molten potassium carbonate can cause severe burns. The chemical reaction produces heat and gases, requiring proper ventilation and safety precautions. |

| Chemical Composition | Process Environment | Process Hazard |
|---|---|--|
| Magnesium oxide MgO | Magnesium oxide forms during slag cleaning reactions involving magnesium fluoride and alkali carbonates. It is typically stable under process conditions. | Fine magnesium oxide dust can cause irritation to the eyes, skin, and respiratory system. Proper handling minimizes exposure risks. |
| Carbon dioxide CO ₂ | Carbon dioxide serves as a carrier gas during carbochlorination processes, where it transports chlorinating agents like carbon tetrachloride at 400–500°C. | Carbon dioxide is a simple asphyxiant, displacing oxygen in confined spaces and creating suffocation hazards. Overpressurization risks exist if systems are improperly vented. |
| Lithium fluoride LiF | Lithium fluoride is produced as a reaction byproduct in molten salt baths. It is collected and stored for potential reuse in other processes. | Lithium fluoride dust can cause mechanical irritation to the respiratory tract and eyes. Proper containment and personal protective equipment are required. |
| Parascandolaite KMgF₃ | Parascandolaite forms during molten salt cleaning processes that involve magnesium fluoride and alkali carbonates. It remains stable under normal conditions. | Contact with strong acids releases hydrofluoric acid gas, which is highly toxic and corrosive. Dust may irritate the respiratory system upon exposure. |
| Yttrium oxide Y ₂ O ₃ | Yttrium oxide is applied as a coating for crucibles and molds during high-temperature metallic fuel casting processes. | Dust from yttrium oxide can cause respiratory irritation if inhaled. Prolonged exposure may lead to chronic respiratory issues. |
| Zirconium dioxide ZrO ₂ | Zirconium dioxide is used as a protective coating for molds in vacuum-pressure casting processes, which operate at temperatures exceeding 1300°C. | Fine dust from zirconium dioxide poses respiratory hazards. Improper handling can lead to chronic lung conditions. |
| Magnesium zirconium oxide MgZrO ₃ | Magnesium zirconium oxide is utilized as a refractory material or coating in high-temperature casting processes. | Dust from magnesium zirconium oxide can irritate the respiratory tract and skin. The material's thermal stability reduces other hazards. |
| Beryllium oxide BeO | Beryllium oxide is used as a crucible liner in high-temperature melting processes for metallic fuel fabrication. | Inhalation of beryllium oxide dust is highly toxic and can cause CBD or lung cancer. Handling must be strictly controlled. |
| Sodium carboxymethyl cellulose C ₈ H ₁₅ NaO ₈ | This compound is used as a binder or coating material in casting and molding processes. | Fine dust can form explosive mixtures in air. Contact with skin or inhalation of dust may cause irritation. |
| Uranyl nitrate UO ₂ (NO ₃) ₂ | Uranyl nitrate is an intermediate in uranium recovery processes, which often involve solvent extraction and precipitation. | The compound is highly toxic and radioactive. Proper containment and handling protocols are essential to prevent exposure. |
| Tributyl phosphate (CH ₃ CH ₂ CH ₂ CH ₂ O) ₃ PO | Tributyl phosphate is used as a solvent in uranium recovery processes, often as part of liquid-liquid extraction in nitric acid media. The process operates at ambient to slightly elevated temperatures in enclosed systems. | Tributyl phosphate is flammable and can emit toxic fumes, including phosphorus oxides, when exposed to heat. Skin contact or inhalation can cause irritation, and prolonged exposure may affect the liver and kidneys. |

| Chemical Composition | Process Environment | Process Hazard |
|---|--|---|
| Gaseous ammonia NH ₃ | Gaseous ammonia is used in precipitation reactions to form ammonium diuranate from uranyl nitrate solutions. The process is typically conducted at ambient temperature and under controlled ventilation. | Gaseous ammonia is highly toxic and corrosive, causing severe irritation or burns to the respiratory system, skin, and eyes. Leaks can create fire and explosion hazards. |
| Ammonium diuranate ADU | Ammonium diuranate is formed as a precipitate during uranium recovery processes involving ammonium hydroxide. The reaction occurs at ambient temperatures. | Ammonium diuranate is toxic and poses radiological hazards due to its uranium content. Dust or particulates can become airborne during handling, increasing the risk of inhalation exposure. |
| Triuranium octoxide U ₃ O ₈ | Triuranium octoxide is produced by calcining ammonium diuranate at temperatures around 600°C. It is used as a stable intermediate in uranium processing. | Triuranium octoxide dust poses inhalation and radiological hazards. Prolonged exposure can result in chronic respiratory and kidney damage due to uranium's chemical toxicity. |
| Stannous chloride SnCl ₂ | Stannous chloride is used as a reducing agent in converting triuranium octoxide to uranium tetrafluoride. The process typically involves heating with hydrofluoric acid under controlled conditions. | Stannous chloride reacts with moisture to release hydrogen chloride gas, which is toxic and corrosive. Inhalation or contact with this chemical can cause respiratory and dermal irritation. |
| Tetrachloroethylene C ₂ Cl ₄ | Tetrachloroethylene is used as a degreaser during dry metallic fuel fabrication processes, particularly for cleaning metallic uranium components. Heated baths are employed for effective cleaning. | Tetrachloroethylene vapors are toxic and may cause central nervous system depression. Prolonged or repeated exposure can lead to liver and kidney damage. Accumulation of vapors in poorly ventilated areas poses suffocation risks. Handling hot degreasing baths introduces inhalation hazards. |
| Sodium Na | Sodium metal is used in fuel bonding processes for metallic fuel rods. It is typically handled in inert atmospheres due to its high reactivity. | Sodium reacts violently with water, releasing hydrogen gas and heat, which can ignite spontaneously. Improper handling poses significant fire and explosion risks. |
| Ammonium bicarbonate NH ₄ HCO ₃ | Ammonium bicarbonate is used in some fuel fabrication processes to control porosity during casting. The compound decomposes upon heating, releasing ammonia and carbon dioxide gases. | Decomposition can cause rapid gas expansion, leading to overpressurization in confined systems. Dust or gas exposure may cause respiratory irritation. |
| Argon Ar | Argon is used as an inert gas during metallic fuel casting, vacuum-pressure melting, and other high -temperature processes. | Argon displaces oxygen, posing asphyxiation hazards in confined spaces. Leaks or overuse in enclosed areas can endanger workers without proper monitoring systems. |
| Nitric sulfuric acid HNO ₃ + H ₂ SO ₄ | This acid mixture is used during the chemical milling of fuel element ends to remove excess uranium. The process | The mixture is highly corrosive and generates heat upon contact with organic materials or water, potentially |

| Chemical Composition | Process Environment | Process Hazard |
|---------------------------------------|--|--|
| | involves highly controlled environments to manage the exothermic reactions and prevent spills. | causing burns and toxic gas release. Improper handling poses risks of acid spills, exposure to fumes, and environmental contamination. |
| Nitric hydrofluoric acid HNO₃ + HF | This combination is used for etching metallic fuel components. The process involves controlled temperature conditions and corrosion-resistant equipment due to the mixture's extreme reactivity. | Highly toxic and corrosive, the mixture can release hazardous fumes, including nitrogen oxides and hydrogen fluoride, posing inhalation and skin exposure risks. Inadequate containment may result in severe burns or systemic toxicity. |
| Zircaloy-2 alloy with 5% beryllium | Used as a brazing material for metallic fuel components. Brazing involves heating in controlled atmospheres to ensure alloy stability and prevent oxidation. | High-temperature processes release beryllium-containing fumes, which are hazardous if inhaled. Chronic exposure may lead to CBD or lung cancer. Proper ventilation and protective equipment are critical. |

B.2.2 Exposure Guidelines and Limits for Consequence Severity Categorization

This section summarizes the threshold limit values for process chemicals related to the fabrication of metallic fuels. <u>Table B-10 Table B-10</u> presents key exposure limits and associated notations for chemicals used in these processes.

Table B-10 Threshold Limit Values for Process Chemicals Related to Fabrication of Metallic Fuels

| Flores et au Common de | Limit Thursday and Malassa | IDLH | Oldin Natation |
|---|---|---|---|
| Uranium tetrafluoride UF4 | Limit Threshold Values N/A | Concentration 10 mg/m³ (as U) | Skin Notation N/A |
| Magnesium Mg | TEEL-1 18 ppm TEEL-2 200 ppm TEEL-3 1,200 ppm | N/A | N/A |
| Nitric acid HNO ₃ | AEGL-1 0.16 ppm AEGL-2 24 ppm AEGL-3 92 ppm | 25 ppm | N/A |
| Nitrogen oxides NO and NO ₂ | AEGL-1 0.5 ppm AEGL-2 12 ppm AEGL-3 20 ppm | 100 ppm (NO) 13 ppm (NO ₂) | N/A |
| Hydrofluoric acid HF | AEGL-1 1 ppm AEGL-2 24 ppm AEGL-3 44 ppm | 30 ppm (as F) | Yes SYS(FATAL)-DIR(COR) ^(a) |
| Magnesium fluoride MgF ₂ | TEEL-1 4.7 ppm TEEL-2 55 ppm TEEL-3 320 ppm | N/A | N/A |
| Lithium carbonate Li ₂ CO ₃ | TEEL-1 1.0 ppm TEEL-2 11 ppm TEEL-3 68 ppm | N/A | N/A |
| Potassium carbonate K ₂ CO ₃ | TEEL-1 0.99 ppm TEEL-2 11 ppm TEEL-3 66 ppm | N/A | N/A |
| Magnesium oxide MgO | TEEL-1 18 ppm TEEL-2 73 ppm TEEL-3 440 ppm | N/A | N/A |
| Carbon dioxide CO ₂ | TEEL-1 30,000 ppm TEEL-2 40,000 ppm TEEL-3 50,000 ppm | 40,000 ppm | N/A |
| Lithium fluoride LiF | TEEL-1 9.4 ppm TEEL-2 100 ppm TEEL-3 640 ppm | N/A | N/A |
| Parascandolaite KMgF3 | N/A | N/A | N/A |
| Yttrium oxide Y ₂ O ₃ | TEEL-1 0.82 ppm TEEL-2 9.3 ppm TEEL-3 56 ppm | 500 mg/m³ (as Y) | N/A |
| Zirconium dioxide ZrO ₂ | TEEL-1 2.8 ppm TEEL-2 22 ppm TEEL-3 130 ppm | 25 mg/m³ (as Zr) | N/A |

| Element or Compound | Limit Threshold Values | IDLH Concentration | Skin Notation |
|---|---|-----------------------|---------------|
| Magnesium zirconium oxide MgZrO ₃ | N/A | N/A | N/A |
| Beryllium oxide BeO | TEEL-1 0.00041 ppm TEEL-2 0.024 ppm TEEL-3 0.098 ppm | 4 mg/m³ (as Be) | N/A |
| Sodium carboxymethyl cellulose C ₈ H ₁₅ NaO ₈ | N/A | N/A | N/A |
| Uranyl nitrate UO ₂ (NO ₃) ₂ | TEEL-1 0.99 mg/m ³ TEEL-2 5.5 mg/m ³ TEEL-3 33 mg/m ³ | 10 mg/m³ (as U) | N/A |
| Tributyl phosphate (CH ₃ CH ₂ CH ₂ CH ₂ O) ₃ PO | TEEL-1 15 mg/m ³ TEEL-2 230 mg/m ³ TEEL-3 1,400 mg/m ³ | 30 ppm | N/A |
| Gaseous ammonia NH₃ | AEGL-1 30 ppm AEGL-2 160 ppm AEGL-3 1,100 ppm | 300 ppm | N/A |
| Ammonium diuranate ADU | N/A | N/A | N/A |
| Triuranium octoxide U₃O ₈ | N/A | 10 mg/m³ (as U) | N/A |
| Stannous chloride SnCl ₂ | TEEL-1 1.2 ppm TEEL-2 8.4 ppm TEEL-3 83 ppm | N/A | N/A |
| Tetrachloroethylene C ₂ Cl ₄ | AEGL-1 35 ppm AEGL-2 230 ppm AEGL-3 1,200 ppm | 150 ppm | N/A |
| Sodium Na | ERPG-1 0.53 ppm ERPG-2 5.3 ppm ERPG-3 53 ppm | N/A | N/A |
| Ammonium bicarbonate NH ₄ HCO ₃ | TEEL-1 1.5 ppm TEEL-2 16 ppm TEEL-3 96 ppm | N/A | N/A |
| Sodium chloride NaCl | N/A | N/A | N/A |
| Argon Ar | TEEL-1 65,000 ppm TEEL-2 230,000 ppm TEEL-3 400,000 ppm | N/A | N/A |
| Sulfuric acid H ₂ SO ₄ | AEGL-1 0.050 ppm AEGL-2 2.2 ppm AEGL-3 40 ppm | 15 mg/m³ | N/A |
| Zircaloy-2 Alloy with 5% beryllium | N/A | 25 mg/m³ (as Zr) | N/A |
| | | 4 mg/m³ (as Be) | |

AEGL = Acute Exposure Guideline Level; ERPG = Emergency Response Planning Guideline; IDLH = Immediately Dangerous to Life or Health; N/A = not applicable; TEEL = Temporary Emergency Exposure Limit.

- (a) Refer to Table G.2 of Current Intelligence Bulletin 61, A Strategy for Assigning New NIOSH Skin Notations, for definitions associated with the NIOSH skin notation assignment (Centers for Disease Control and Prevention [CDC] 2017). The notations are also described in Section 3.0 of this report.
- * Limit threshold values marked by * are ≥ 10% lower explosive limit (LEL) but < 50% LEL.
- ** Limit threshold values marked by ** are > 50% LEL but < 100% LEL.
- *** Limit threshold values marked by *** are ≥ LEL.

B.2.3 Considerations on Mitigative Measures

Based on the discussion and input provided about the chemicals and processes used in the fabrication of metallic and sodium-bonded metallic fuels, several unique mitigative measures are noteworthy. These measures specifically address the hazards and operational conditions encountered in processes such as magnesiothermic reduction, vacuum-pressure casting, and sodium bonding.

- Pyrophoric Hazard Management for Uranium Metal and Fines: Metallic uranium and its byproducts, including fines generated during machining and casting, are highly pyrophoric, especially in the presence of air or moisture. Unique mitigative measures could include inert gas purging systems to maintain oxygen-free environments, specialized fire suppression systems for pyrophoric materials, and stringent housekeeping protocols to prevent accumulation of fines in work areas.
- Inert Atmosphere Control in High-Temperature Processes: Fabrication methods, such
 as vacuum-pressure casting and extrusion, require high temperatures (ranging from
 570°C to 1450°C) in environments free from oxygen to prevent oxidation and fire
 hazards. Mitigative measures may include the use of advanced inert gas systems (e.g.,
 argon or helium), real-time monitoring of atmospheric conditions, and automated
 shutdown mechanisms to prevent atmospheric breaches.
- Thermal Control and Safety During Reduction Processes: The magnesiothermic reduction of UF₄ involves exothermic reactions at temperatures of 1263°C and above, which necessitate robust thermal management. Enhanced thermal insulation, temperature monitoring systems, and emergency cooling systems may be employed to mitigate risks associated with overheating or uncontrolled reactions.
- Chemical Safety for Nitric Acid and Sodium Reactions: Processes involving HNO₃ (35–50 wt%) for slag removal and sodium bonding pose significant hazards, including corrosivity, exothermic reactions, and potential explosion risks when sodium reacts with water. Mitigative measures could include localized ventilation with acid scrubbing, emergency neutralization systems for spills, and segregated storage and handling protocols for reactive metals like sodium.
- Containment of Magnesium Fluoride Slag and Byproducts: The slag generated during reduction processes contains reactive components such as MgF₂, which must be handled carefully to avoid environmental and safety risks. Tailored mitigative measures may involve the use of corrosion-resistant containment materials, mechanical systems for slag removal, and secure disposal methods for contaminated byproducts.
- <u>Hazardous Gas and Vapor Control</u>: The use of volatile compounds like C₂Cl₄ for degreasing or the generation of hydrogen gas during reduction processes introduces risks of toxic exposure and flammability. Advanced ventilation systems, gas detection technologies, and automated interlocks for leak detection are essential mitigative strategies.

Emergency Preparedness for Metal Casting and Handling: The handling of molten
metals and ingots during vacuum-pressure casting presents risks of spills, burns, and
exposure to toxic fumes. Specialized training for workers, the provision of personal
protective equipment, and emergency response protocols tailored to molten metal
spills are critical.

These measures address the unique challenges associated with metallic and sodium-bonded metallic fuel fabrication while complementing the standard mitigative measures outlined in NUREG/CR-6410 (NRC 1998) and NUREG-1520, Revision 2 (NRC 2015).

B.3 Chemical Process Safety for Fabrication of Salt-Based Fuels

The following provides an assessment of the chemical safety considerations associated with salt fuel fabrication as well as summarizes key threshold limit values for chemicals involved in these processes. A discussion is provided on mitigative measures to address specific hazards and operational conditions for salt fuel fabrication. The assessment is organized by distinct tables and was performed using the methodology and approaches described in Section 3.0.

B.3.1 Chemical Safety Hazard Considerations

This section provides a summary of the chemical safety considerations relevant to salt fuel fabrication. <u>Table B-11 Table B-11</u> and <u>Table B-12 Table B-12</u> outline the physical and health safety considerations associated with chemicals identified in related processes. <u>Table B-13 Table B-13</u> and <u>Table B-14 Table B-14</u> identify key process environments and the hazards associated with the chemicals used. Details regarding the table's content and the methodology used in its development are provided in Section 3.0.

For fluoride-based salt fuel fabrication, <u>Table B-11 Table B-11</u> and <u>Table B-13 Table B-13</u> cover the production of UF₄ through two primary processes: the reaction of UO₂ with anhydrous HF at elevated temperatures and the direct reduction of UF₆ with H₂. For chloride-based salt fuel fabrication, <u>Table B-12 Table B-12</u> and <u>Table B-14 Table B-14</u> address the production of UCl₄ via carbochlorination of UO₂ and its subsequent reduction to UCl₃ using H₂.

Table B-11. Chemical Safety Considerations for Fluoride-Based Salt Fuel Fabrication.

| Chemical Composition | Physical Hazard | Health Hazard |
|--|---|--|
| Uranium hexafluoride UF ₆ | Uranium hexafluoride is a reactive and highly volatile solid that releases corrosive hydrogen fluoride gas when exposed to moisture. It is also an oxidizer and may react with combustible materials. | Uranium hexafluoride is toxic by inhalation and can cause severe irritation or burns to the respiratory tract, skin, and eyes. Prolonged exposure may result in kidney damage due to uranium toxicity. |
| Uranium tetrafluoride UF ₄ | Uranium tetrafluoride is a non-combustible green crystalline solid that may release toxic fluoride vapors if heated or exposed to moisture. It reacts with acids, liberating hydrogen fluoride, a highly corrosive gas. | Uranium tetrafluoride is harmful if inhaled, ingested, or absorbed through the skin. It can cause severe irritation or burns to the respiratory tract, eyes, and skin. Chronic exposure may result in kidney damage due to the chemical toxicity of uranium. |
| Uranium dioxide UO ₂ | Uranium dioxide is a non-combustible black powder or solid that is chemically stable under normal conditions. However, finely divided particles may pose a dust explosion hazard in certain environments. | Uranium dioxide is harmful if inhaled or ingested and may cause kidney damage due to uranium's chemical toxicity. Dust or powder can irritate the respiratory tract, eyes, and skin upon exposure. |
| Anhydrous hydrogen fluoride HF | Hydrogen fluoride is a colorless, highly corrosive gas or liquid that | Hydrogen fluoride is extremely toxic and corrosive. Inhalation, ingestion, or |

| Chemical Composition | Physical Hazard | Health Hazard |
|--|---|---|
| | fumes on contact with air. It reacts violently with water and many organic or inorganic substances, releasing toxic and corrosive vapors. | skin contact can cause severe burns, systemic toxicity (nervous system, skeletal system), and potentially fatal effects. It can penetrate deep into tissues, causing delayed damage to bones and organs such as the heart and kidneys. |
| Lithium fluoride LiF | Lithium fluoride is a high-melting inorganic salt that can emit toxic fumes if overheated. It is noncombustible but may react with strong acids. | Lithium fluoride is harmful if inhaled or ingested and may cause irritation to the eyes, skin, and respiratory tract. Chronic exposure to airborne particulates should be avoided. |
| Beryllium fluoride BeF ₂ | Beryllium fluoride is a hygroscopic, high-melting salt that is stable under normal conditions but may release hazardous fumes at high temperatures. | Beryllium fluoride is highly toxic by inhalation. It can cause severe respiratory irritation, chemical pneumonitis, and may contribute to chronic beryllium disease upon repeated exposure. |
| Beryllium Be | Metallic beryllium is a hard, brittle metal that can form dust during machining or crushing. It is noncombustible in bulk but may become reactive in finely divided form or at high temperatures. | Beryllium is highly toxic by inhalation. Chronic exposure can result in beryllium sensitization and chronic beryllium disease (CBD), a serious lung condition. It is also classified as a human carcinogen by IARC. |
| Beryllium oxide BeO | BeO is a high-melting, thermally stable ceramic used in high temperature environments. Fine powders may present dust explosion risks under specific conditions. | BeO is extremely hazardous when inhaled as dust or particulates. It can cause chronic beryllium disease, respiratory failure, and lung cancer. Strict airborne exposure limits apply; handling requires full containment and respiratory protection. |
| Anhydrous ammonia NH₃ | Ammonia is a colorless, highly corrosive, and flammable gas with a pungent odor. It reacts violently with strong oxidizers, acids, halogens, and certain metals, potentially causing fires or explosions. Ammonia also reacts with water to form ammonium hydroxide, releasing significant heat that may lead to thermal burns or violent reactions in confined spaces. | Ammonia is toxic by inhalation, causing severe irritation or burns to the respiratory tract, eyes, and skin. High concentrations may result in respiratory distress, pulmonary edema, and systemic effects. Prolonged exposure can cause permanent tissue damage. |
| Nitrogen N ₂ | When under pressure, this chemical may explode if heated. | This chemical is a simple asphyxiant. |

| Chemical Composition | Physical Hazard | Health Hazard |
|---|---|---|
| Hydrogen H ₂ | This chemical is extremely flammable, and when under pressure, may explode if heated. | No specific health hazards are documented. |
| Zirconium tetrafluoride ZrF ₄ | ZrF₄ is a non-combustible, thermally stable solid that may release irritating dust during handling. | ZrF ₄ dust may irritate the eyes, skin, or respiratory tract; prolonged inhalation may cause lung effects similar to zirconium exposure. |
| Nickel(II) fluoride NiF ₂ | NiF ₂ may form as a corrosion product during high temperature HF/H ₂ gas treatment in Inconel vessels and is corrosive to metals. | NiF ₂ is toxic if inhaled, causes severe skin burns and eye damage, and is classified as a suspected human carcinogen. |
| Ferric fluoride FeF ₃ | FeF ₃ may form as a corrosion product during purification of Flibe salts in Inconel vessels and is corrosive to metals. | FeF ₃ causes serious eye damage and may cause respiratory irritation upon inhalation. |
| Ferrous fluoride FeF ₂ | FeF2 may form as a corrosion product on metal vessel surfaces during HF-based processing of Flibe and is corrosive to metals. | FeF ₂ is harmful if inhaled and may cause skin and eye irritation. |

Table B-12. Chemical Safety Considerations for Chloride-Based Salt Fuel Fabrication.

| Chemical Composition | Physical Hazard | Health Hazard |
|---|---|--|
| Uranium trichloride UCl₃ | Uranium trichloride is a green crystalline solid that is hygroscopic and reacts with moisture to produce corrosive hydrochloric acid. It can release toxic and reactive vapors when heated or exposed to air. | Uranium trichloride is toxic if inhaled, ingested, or absorbed through the skin. It may cause severe irritation or burns to the respiratory tract, eyes, and skin. Prolonged exposure can result in kidney damage due to uranium's chemical toxicity. |
| Uranium tetrachloride UCl ₄ | Uranium tetrachloride is a green crystalline solid that is hygroscopic and reacts with water or moisture to release corrosive hydrogen chloride gas. It decomposes when heated, producing toxic and reactive vapors. | Uranium tetrachloride is toxic if inhaled, ingested, or absorbed through the skin. It may cause severe irritation or burns to the respiratory tract, eyes, and skin. Prolonged exposure can lead to kidney damage due to the chemical toxicity of uranium. |
| Carbon dioxide CO ₂ | Carbon dioxide is a colorless, odorless, non-flammable gas that is heavier than air and can accumulate in confined spaces, potentially displacing oxygen and creating asphyxiation hazards. It can also cause pressure buildup in containers if improperly stored. | Carbon dioxide is a simple asphyxiant; exposure to high concentrations can cause dizziness, shortness of breath, loss of consciousness, or death due to oxygen displacement. Direct contact with solid carbon dioxide (dry ice) can cause severe frostbite. |
| Carbon tetrachloride CCl ₄ | Carbon tetrachloride is a non- flammable liquid with a sweet odor that may form toxic gases upon decomposition, such as carbonyl dichloride and hydrogen chloride, when exposed to heat or flames. It can release harmful vapors, especially in enclosed spaces. | Carbon tetrachloride is highly toxic if inhaled, ingested, or absorbed through the skin. It can cause severe irritation to the respiratory tract, eyes, and skin. Prolonged or repeated exposure may result in liver and kidney damage and is classified as a probable human carcinogen. |
| Carbonyl dichloride COCl ₂ | Highly toxic gas with a suffocating odor resembling freshly cut hay. It is heavier than air and can accumulate in low-lying areas. Decomposes to release toxic chlorine gas when exposed to moisture. | Carbonyl dichloride is extremely toxic by inhalation and can cause severe respiratory irritation, pulmonary edema, and delayed lung damage. Symptoms may be delayed for several hours after exposure. Direct contact with eyes or skin can cause severe irritation and burns. |
| Uranium pentachloride UCl₅ | Uranium pentachloride is a yellow- green hygroscopic solid that reacts with moisture to produce corrosive hydrogen chloride gas. Decomposes upon heating to release toxic and reactive vapors. | Uranium pentachloride is toxic by inhalation, ingestion, and skin contact. It can cause severe irritation or burns to the respiratory tract, eyes, and skin. Prolonged exposure may result in kidney damage due to uranium's chemical toxicity. |

| Chemical Composition | Physical Hazard | Health Hazard |
|-----------------------------|--|--|
| Carbon monoxide CO | Carbon monoxide is a colorless, odorless, and highly flammable gas. It forms explosive mixtures with air and burns with a blue flame. It is lighter than air but can accumulate in enclosed spaces, creating fire and explosion hazards. | Carbon monoxide is highly toxic if inhaled, as it binds to hemoglobin, reducing oxygen transport in the blood. Symptoms of exposure include headache, dizziness, confusion, and nausea; high concentrations can cause unconsciousness, asphyxiation, and death. |
| Chlorine Cl ₂ | Chlorine is a greenish-yellow gas with a pungent odor that is highly reactive and oxidizing. It can form explosive mixtures with hydrogen and reacts violently with organic materials, ammonia, and finely divided metals. | Chlorine is highly toxic if inhaled, causing severe irritation to the respiratory tract, eyes, and skin. Acute exposure can result in coughing, chest pain, difficulty breathing, and pulmonary edema. Prolonged exposure or high concentrations may lead to permanent lung damage or death. |
| Hydrogen H ₂ | This chemical is extremely flammable, and when under pressure, may explode if heated. | No specific health hazards are documented. |

Table B-13. Chemical Process Hazards for Fluoride-Based Salt Fuel Fabrication.

| Chemical Composition | Process Environment | Process Hazard |
|---|--|--|
| Uranium hexafluoride UF ₆ | Uranium hexafluoride is handled as a volatile gas and converted to uranium dioxide in a controlled furnace environment or directly reduced with hydrogen gas in a high-temperature chemical reactor. | |
| Uranium tetrafluoride UF4 | Uranium tetrafluoride is formed by reacting uranium dioxide with hydrogen fluoride in a kiln or by reducing uranium hexafluoride with hydrogen gas in a high-temperature reactor. Both methods require careful temperature control to ensure process efficiency. | Uranium tetrafluoride reacts with moisture or acids to release hydrogen fluoride, posing toxic and corrosive hazards. Accumulation of uranium tetrafluoride within reactors may create operational inefficiencies and potential criticality risks in certain configurations. |
| Uranium dioxide UO ₂ | Uranium dioxide is handled as an intermediate solid product formed during the reduction of uranium hexafluoride. It is then reacted with hydrogen fluoride in a kiln at elevated temperatures to produce uranium tetrafluoride. | Handling of uranium dioxide can produce fine dust that poses inhalation hazards. Long-term exposure may result in kidney damage due to the chemical toxicity of uranium. |
| Anhydrous hydrogen fluoride HF | Hydrogen fluoride is used as a reactive gas in high-temperature systems to produce uranium tetrafluoride from uranium dioxide. It must be carefully introduced and contained within the system to avoid exposure. | Hydrogen fluoride is extremely toxic and corrosive, causing severe burns, systemic toxicity, and delayed organ damage upon exposure. Releases can result in significant inhalation and dermal hazards. |
| Lithium fluoride LiF | Lithium fluoride is combined with beryllium fluoride to form Flibe, a eutectic carrier salt used in fluoride- based molten salt fuels. The powders are handled in inert atmospheres to avoid oxidation and are subjected to thermal processing at temperatures ranging from 250°C to 700°C. | High-temperature handling of lithium fluoride may result in exposure to hot surfaces, molten salts, or fluoride vapors. Inert gas atmospheres are required to prevent oxidation. Appropriate thermal controls and ventilation are essential. |
| Beryllium fluoride BeF ₂ | Beryllium fluoride is used together with lithium fluoride in the preparation of Flibe carrier salts. It is handled in powdered form and processed under inert atmosphere at elevated temperatures, including degassing (~250°C) and purification steps up to 700°C using hydrofluorination gas mixtures. | health hazards, including beryllium |
| Beryllium Be | Used as a reducing agent during desulfidation of Flibe salts at elevated temperatures (e.g., ~700°C). Metallic beryllium reacts with sulfates to form BeO and sulfide ions. | Handling at high temperatures may release beryllium fumes or particulates. Reactions must be performed under controlled inert atmosphere to prevent oxidation. |

| Chemical Composition | Process Environment | Process Hazard |
|---|--|---|
| | | Generated BeO particulates present serious inhalation hazards. |
| Beryllium oxide BeO | Forms in-situ during beryllium desulfidation reactions or may be present as contamination in solid residues. May also be used as a crucible or coating material in high-temperature salt environments. | BeO formation in poorly ventilated systems can lead to hazardous dust accumulation. Disturbance of solid residues or maintenance on equipment coated with BeO requires strict respiratory controls due to its extreme toxicity. |
| Anhydrous ammonia NH₃ | Ammonia is dissociated at high temperatures using catalytic reactions to produce hydrogen gas, which is then introduced into the system to reduce uranium hexafluoride to uranium tetrafluoride. | Ammonia is highly toxic and reacts violently with acids and oxidizers, posing fire or explosion risks. Inhalation can cause severe respiratory damage, and improper handling increases exposure hazards. |
| Nitrogen N ₂ | Nitrogen is used as an inert gas during high-temperature operations to prevent unwanted reactions and maintain a controlled atmosphere within the system. | Nitrogen can displace oxygen in confined spaces, leading to asphyxiation hazards. Inadequate ventilation increases the risk of oxygen displacement and worker exposure. |
| Hydrogen H ₂ | Hydrogen is used as a reducing agent at elevated temperatures and pressures in chemical reactors during the conversion of uranium hexafluoride to uranium tetrafluoride. | increases the risk of uncontrolled |
| Zirconium tetrafluoride ZrF ₄ | ZrF ₄ is introduced during molten fluoride salt blending at elevated temperatures (>500°C) under inert conditions. | Fine particulates may become airborne during handling; moisture ingress can cause hydrolysis, and hot ZrF ₄ vapors may corrode equipment. |
| Nickel(II) fluoride NiF ₂ | This compound may form as corrosion products during HF/H ₂ gas phase purification of Flibe salts at 525–700°C in Inconel or other nickelbased alloy vessels. | Formation of this fluoride may indicate degradation of vessel materials and contribute to accumulation of metal impurities in salt. |
| Ferric fluoride FeF3 | This compound may form as corrosion products during HF/H ₂ gas phase purification of Flibe salts at 525–700°C in Inconel or other nickel-based alloy vessels. | Formation of this fluoride may indicate degradation of vessel materials and contribute to accumulation of metal impurities in salt. |
| Ferrous fluoride FeF ₂ | This compound may form as corrosion products during HF/H ₂ gas phase purification of Flibe salts at 525–700°C in Inconel or other nickel-based alloy vessels. | Formation of this fluoride may indicate degradation of vessel materials and contribute to accumulation of metal impurities in salt. |

Table B-14. Chemical Process Hazards for Chloride-Based Salt Fuel Fabrication.

| Chemical Composition | Process Environment | Process Hazard |
|---|--|--|
| Uranium tetrachloride UCl ₄ | Uranium tetrachloride is produced by carbochlorination, reacting uranium dioxide with carbon tetrachloride in a carbon dioxide gas stream at 400–500°C. The reaction also produces byproducts such as uranium pentachloride, carbonyl dichloride, carbon monoxide, and chlorine. | The process involves highly toxic and reactive chemicals. Carbon tetrachloride and carbonyl dichloride are toxic and pose inhalation and environmental hazards. Chlorine and other byproducts are corrosive and hazardous, requiring strict containment and venting systems. Accumulation of uranium pentachloride in the product may necessitate additional reduction steps with hydrogen, which introduces risks of flammability and explosive mixtures. |
| Uranium trichloride UCl₃ | Uranium trichloride is produced by reducing uranium tetrachloride with hydrogen gas at temperatures below 300°C in a controlled environment. This reaction helps convert uranium pentachloride impurities in uranium tetrachloride into the desired uranium trichloride product. | The process uses hydrogen, which is highly flammable and poses explosion hazards. Uranium tetrachloride and uranium pentachloride are corrosive and react with moisture to release hydrogen chloride, creating inhalation and dermal exposure risks. Careful temperature and pressure controls are essential to ensure product quality and safety. |
| Carbon dioxide CO ₂ | Carbon dioxide serves as a carrier gas for transporting carbon tetrachloride vapors during the carbochlorination of uranium dioxide. The process operates at atmospheric pressure and temperatures ranging from 400–500°C, with 450°C being optimal. | |
| Carbon tetrachloride CCl ₄ | Carbon tetrachloride is vaporized and introduced with carbon dioxide into a high-temperature reaction system operating at 400–500°C. The vaporized carbon tetrachloride reacts with uranium dioxide to form uranium tetrachloride, while minimizing uranium pentachloride formation. | and carcinogenic. Exposure to vapors can cause severe respiratory and liver damage. When heated, it decomposes to produce carbonyl |
| Carbonyl dichloride COCl ₂ | Carbonyl dichloride is generated as a byproduct during carbochlorination, particularly when carbon tetrachloride decomposes at elevated temperatures. | inhalation, causing delayed respiratory damage, pulmonary edema, and severe irritation to the eyes and skin. Accidental releases pose significant health hazards. |
| Uranium pentachloride UCl₅ | Uranium pentachloride forms as an unintended byproduct during uranium tetrachloride production when reaction temperatures exceed the | Uranium pentachloride reacts with moisture to release hydrogen chloride, which is toxic and corrosive. Accumulation in reactors can |

| Chemical Composition | Process Environment | Process Hazard |
|-----------------------------|--|---|
| | 450°C optimum. Reduction of uranium pentachloride to uranium tetrachloride or uranium trichloride is typically achieved below 300°C with hydrogen gas. | complicate operations, requiring additional reduction steps. |
| Carbon monoxide CO | Carbon monoxide is produced as a byproduct in the carbochlorination process and can accumulate in poorly vented systems. | Carbon monoxide is highly flammable and toxic. It binds to hemoglobin, reducing oxygen transport in the blood, leading to dizziness, confusion, or death at high concentrations. |
| Chlorine Cl ₂ | Chlorine is produced as a byproduct during uranium tetrachloride formation from uranium dioxide and carbon tetrachloride at elevated temperatures. | Chlorine is a toxic and reactive gas. Exposure can cause severe respiratory irritation, pulmonary edema, and chemical burns. Leaks or spills can result in significant inhalation hazards. |
| Hydrogen H ₂ | Hydrogen is introduced as a gas under controlled pressures to reduce uranium tetrachloride to uranium trichloride at temperatures below 300°C. | Hydrogen is highly flammable and poses explosion risks, particularly in systems with poor ventilation or loss of inert atmospheres. Uncontrolled reactions can lead to catastrophic failures. |

B.3.2 Exposure Guidelines and Limits for Consequence Severity Categorization

This section summarizes the threshold limit values for process chemicals related to the fabrication of salt fuels. <u>Table B-15</u> presents key exposure limits and associated notations for chemicals used in these processes.

Table B-15. Threshold Limit Values for Process Chemicals Related to Fabrication of Salt Fuels.

| Element or Compound | Limit Threshold Values | IDLH Concentration | Skin Notation |
|---|---|-----------------------|---|
| Uranium hexafluoride UF ₆ | AEGL-1 0.25 ppm AEGL-2 0.67 ppm AEGL-3 2.5 ppm | 10 mg/m³ (as U) | N/A |
| Uranium tetrafluoride UF ₄ | N/A | 10 mg/m³ (as U) | N/A |
| Uranium dioxide UO ₂ | ERPG-1 0.68 ppm ERPG-2 10 ppm ERPG-3 30 ppm | 10 mg/m³ (as U) | N/A |
| Anhydrous hydrogen fluoride HF | AEGL-1 0.82 ppm AEGL-2 20 ppm AEGL-3 36 ppm | 30 ppm (as F) | Yes SYS(FATAL)-DIR(COR) ^(a) |
| Lithium fluoride LiF | TEEL-1 9.4 ppm TEEL-2 22 ppm TEEL-3 130 ppm | 250 mg/m³ (as F) | N/A |
| Beryllium fluoride BeF ₂ | TEEL-1 0.00041 ppm ERPG-2 0.013 ppm ERPG-3 0.052 ppm | 4 mg/m³ (as Be) | N/A |
| Beryllium Be | TEEL-1 0.00015 ppm ERPG-2 0.068 ppm ERPG-3 0.1 ppm | 4 mg/m³ (as Be) | N/A |
| Beryllium oxide BeO | TEEL-1 0.00041 ppm TEEL-2 0.024 ppm TEEL-3 0.098 ppm | 4 mg/m³ (as Be) | N/A |
| Anhydrous ammonia NH₃ | AEGL-1 21 ppm AEGL-2 110 ppm AEGL-3 770 ppm | 300 ppm | N/A |
| Uranium trichloride UCl ₃ | N/A | 10 mg/m³ (as U) | N/A |
| Uranium tetrachloride UCl ₄ | N/A | 10 mg/m³ (as U) | N/A |
| Carbon dioxide CO ₂ | TEEL-1 30,000 ppm TEEL-2 40,000 ppm TEEL-3 50,000 ppm | 40,000 ppm | N/A |
| Carbon tetrachloride CCl ₄ | TEEL-1 1.2 ppm AEGL-2 13 ppm AEGL-3 340 ppm | 200 ppm | N/A |
| Carbonyl dichloride COCl ₂ | TEEL-1 0.027 ppm AEGL-2 0.30 ppm AEGL-3 0.75 ppm | 2 ppm | N/A |

| | | IDLH | |
|---|--|---------------------|----------------------|
| Element or Compound | Limit Threshold Values | Concentration | Skin Notation |
| Uranium pentachloride UCl₅ | N/A | 10 mg/m³ (as U) | N/A |
| Carbon monoxide CO | TEEL-1 75 ppm AEGL-2 83 ppm AEGL-3 330 ppm | 1,200 ppm | N/A |
| Chlorine Cl ₂ | AEGL-1 0.5 ppm AEGL-2 2 ppm AEGL-3 20 ppm | 10 ppm | N/A |
| Nitrogen N2 | TEEL-1 796,000 ppm TEEL-2 832,000 ppm TEEL-3 869,000 ppm | N/A | N/A |
| Hydrogen H ₂ | TEEL-1 65,000 ppm*** TEEL-2 230,000 ppm*** TEEL-3 400,000 ppm*** | N/A | N/A |
| Zirconium tetrafluoride ZrF ₄ | N/A | 25 mg/m³ (as Zr) | N/A |
| Nickel(II) fluoride NiF ₂ | TEEL-1 ^(b) 1.7 mg/m ³ TEEL-1 ^(b) 19 mg/m ³ TEEL-1 ^(b) 110 mg/m ³ | 250 mg/m³ (as F) | N/A |
| Ferric fluoride FeF ₃ | TEEL-1 6.1 mg/m ³ TEEL-2 22 mg/m ³ TEEL-3 130 mg/m ³ | 250 mg/m³ (as F) | N/A |
| Ferrous fluoride FeF ₂ | N/A | 250 mg/m³ (as F) | N/A |

AEGL = Acute Exposure Guideline Level; ERPG = Emergency Response Planning Guideline; IDLH = Immediately Dangerous to Life or Health; N/A = not available; TEEL = Temporary Emergency Exposure Limit.

(b) This TEEL value is for Nickel fluoride, tetrahydrate (NiF₂·4H₂O).

B.3.3 Considerations on Mitigative Measures

Based on the discussion and input provided about the chemicals used in fluoride- and chloride-based salt fuel production and the associated processes, a few potentially unique mitigative measures are worth mentioning. These measures specifically address the hazards and operational conditions related to the production of UF₄, UCl₃, and UCl₄.

- Inert Atmosphere Management for Hydrogen-Based Reduction Processes: The use of H₂ gas during the reduction of UF₆ to UF₄ and UCl₄ to UCl₃ requires stringent inert atmosphere control to prevent explosive mixtures. Unique mitigative measures could include continuous monitoring of hydrogen flow rates, inert gas purging systems, and automated interlocks to immediately terminate operations if inert atmosphere integrity is compromised.
- Handling and Containment of Hydrogen Fluoride (HF): HF is toxic and highly corrosive, posing significant risks during its use in converting UO₂ to UF₄. Mitigative measures may

⁽a) Refer to Table G.2 of Current Intelligence Bulletin 61, A Strategy for Assigning New NIOSH Skin Notations, for definitions associated with the NIOSH skin notation assignment (Centers for Disease Control and Prevention [CDC] 2017). The notations are also described in Section 3.0 of this report.

Limit threshold values marked by * are ≥ 10% lower explosive limit (LEL) but < 50% LEL.

Limit threshold values marked by ** are > 50% LEL but < 100% LEL. Limit threshold values marked by *** are ≥ LEL.

include the use of corrosion-resistant materials for equipment, localized exhaust ventilation systems with acid scrubbing, and emergency spill containment kits tailored for HF.

- Management of Chlorinating Agents and Byproducts: The carbochlorination process for producing UCl₄ from UO₂ involves the use of carbon tetrachloride (CCl₄) or similar chlorinating agents, which can generate toxic byproducts such as carbonyl dichloride (COCl₂) and chlorine (Cl₂). Mitigative strategies could include advanced gas containment systems, real-time monitoring of chlorinating agent usage, and neutralization systems for toxic vapors.
- Thermal Control During High-Temperature Processes: The elevated temperatures required for reactions such as the reduction of UCl₄ to UCl₃ or UO₂ to UF₄ necessitate robust thermal management systems to avoid overheating and uncontrolled reactions. Enhanced thermal monitoring and the use of heat-resistant materials may be required.
- Emergency Preparedness for Chemical Spills and Releases: The use of hazardous chemicals such as HF, CCl₄, and ammonia (NH₃) requires comprehensive emergency preparedness plans. Tailored containment measures, such as spill containment kits, and specialized worker training are critical to minimize exposure risks and support rapid response in case of a release.

These measures are specifically tailored to address the unique hazards associated with the fluoride- and chloride-based salt fuel fabrication processes. While many standard mitigative measures outlined in NUREG/CR-6410 (NRC 1998) and NUREG-1520, Revision 2 (NRC 2015), apply broadly, these additional considerations support adequate mitigation of the specific risks of these processes.

B.3.4 Considerations on Chemical Process Safety for Industrial Carrier Salts

The primary carrier salt for use in liquid-fueled MSRs with UF_4 or, potentially thorium fluoride (ThF_4) fuel, as well as solid-fueled MSRs with TRISO-based fuel, is commonly referred to as "FLiBe" or "Flibe". Flibe is a mixture of lithium fluoride (LiF) and beryllium fluoride (BeF $_2$) at a nominal 2:1 mole ratio. This is the same salt mixture used as the intermediate coolant in the MSRE. It is likely that a separate industrial facility will be used for Flibe preparation, which would not be operated under a license per 10 CFR Part 70. However, a summary of fabrication and chemical process safety aspects for Flibe production are discussed if a fuel cycle facility were to incorporate these operations.

Flibe is prepared by mixing high purity BeF₂ and LiF powders per the necessary molar ratio. For thermal spectrum MSRs and some fast spectrum MSRs, high purity 7 Li is required as the other naturally occurring isotope 6 Li has a high neutron absorption cross section (particularly in the thermal spectrum range). BeF₂ is chemically toxic but is desired as it has the lowest thermal neutron cross section of the fluoride salts ($\sigma \sim 0.010$ barn = 10^{-26} cm²) (Roper et al. 2022).

The powders are handled in inert environments (e.g., glove boxes, inert furnaces) to mitigate oxidation during processing. The powders are loaded into metal vessels (e.g., stainless steel, Inconel) and may be initially degassed at 250°C (Anderl et al. 2004). The procured powders may contain oxygenated impurities, as well as water, which are removed to mitigate precipitation and impacts to heat transfer during reactor operations (Shaffer 1971).

The powders are heated to 525–700°C under gas flow mixtures of He/HF/H₂ or He/HF to reduce inherent oxides by hydrofluorination (Shaffer 1971; Hara et al. 2006; Smolik et al. 2004). A 1:10 ratio of HF/H₂ has been described as suitable for the former gas mixture (Anderl et al. 2004), which is consistent with prior experience from the MSRE, as shown in Figure B-1 (Shaffer 1971).

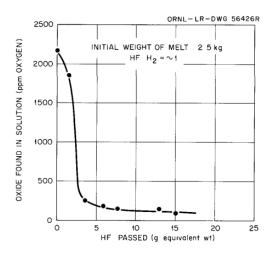


Figure B-1. Measured Oxide Content in LiF-BeF₂ (63–37 mol.%) Following Treatment with HF-H₂ Mixtures at 700°C (Shaffer 1971).

Hydrofluorination of oxides occurs through the following general reaction:

$$O^{2-} + 2HF(g) \rightleftharpoons 2F^{-} + H_2O(g)$$
 (43)

The structural material of construction for the reaction vessel is an important consideration as the hydrofluorination reaction in the gas phase leads to the formation of an impervious layer of metal fluorides on the vessel surface. These metal fluorides dissolve into the salt melt, which may limit the life of the vessel (Shaffer 1971). MSRE operations used Inconel as a structural material, which exhibited mild corrosion from operations. Shaffer (1971) proposed chromium and iron leaches from the metal surfaces of the vessel, although the rate of corrosion may be limited by the relatively low rate of diffusion of these elements in the metal.

The use of metallic reducing agents has been described as an alternate approach for oxygen/oxide removal from the salt (Shaffer 1971). Gaseous effluents from the treatment process are removed by an off-gas system. The rate of oxide dissolution and removal may be characterized through water measurements from the gas effluent (Shaffer 1971).

Sulfur impurities are removed to very low levels due to their ability for corrosive attack on nickel-based alloys. These impurities are found in the starting material primarily as sulfates (SO_4^{2-}). The use of hydrogen in the treatment process allows for reduction of the sulfates to sulfide ion, which then reacts with HF to produce volatile hydrogen sulfide (H_2S) (Shaffer 1971). The use of 1:10 ratio of HF/H₂, as previously discussed, may be adequate for sulfur removal, as shown in Figure B-2. The process step follows the general reaction (44).

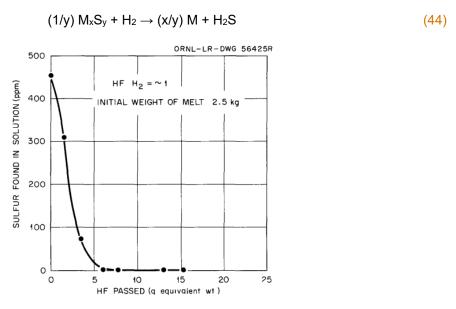


Figure B-2. Measured Sulfur Content in LiF-BeF₂ (63–37 mol.%) Following Treatment with HF-H₂ mixtures at 700°C (Shaffer 1971).

The desulfidation step may also need to consider adequate selection of structural materials for the reaction vessel. Sulfates, its thermal decomposition products, SO_3 and SO_2 , as well as the H_2S generated, would react with nickel or copper to form metal sulfides and oxides at process temperatures of 600 to 800°C (Shaffer 1971). The rate of reduction of sulfate ions may be increased by the introduction of beryllium metal into the vessel, per the following reaction (Shaffer 1971):

$$SO_4^{2-}$$
 (soln) + $4Be^0$ (cryst) $\rightleftharpoons 4BeO$ (cryst) + S^{2-} (soln) (45)

followed by sulfide removal with HF, per the following reaction:

$$2HF(q) + S^{2-}(soln) \rightleftharpoons H_2S(q) + 2F^{-}(soln)$$
 (46)

Corrosion of nickel in the reaction vessel may be mitigated or prevented by control of the H_2S to H_2 ratios (Shaffer 1971). The concentration of structural metal fluoride impurities (e.g., nickel(II) fluoride [NiF₂], ferric fluoride [FeF₃], or ferricII) fluoride [FeF₂]) in the salt would likely need to be controlled to mitigate later corrosion of structural materials in the reactor.

The molten Flibe mixture is then sieved to separate solid impurity precipitates during the purification step. In an industrial process, this step may be implemented through a heated transfer line equipped with a porous stainless steel filter (<60 µm pore size) (Anderl et al. 2004). Flibe is a non-combustible solid at room temperature with a melting point of 459°C (858°F) and a boiling point of 1430°C (2610°F).

Beryllium is a potential carcinogen, primarily impacting lung function, and in 29 CFR 1910.1024, OSHA classifies the hazards of beryllium as causing acute or chronic lung effects upon inhalation. Acute exposure can lead to severe pneumonitis, whereas chronic exposure leads to granulomas in the lungs, causing long-term respiratory dysfunction. Symptoms may appear years post-exposure, worsening over time. Contact dermatitis is common in beryllium-exposed occupations, but data on the general population is lacking. BeF₂ poses significant systemic risks due to its solubility and mobility in the body, while metallic beryllium, usually protected with insoluble oxide, poses less threat unless freshly cut. LiF₂ can cause skin irritation and serious ocular damage, as well as may cause respiratory irritation. Exposure to corrosion products due to Flibe production operations would also be considered.

Operations and associated procedures involving Flibe would consider the hazards associated with occupational contact or exposure during maintenance and potential accidents such as salt spills. Maintenance activities (e.g., repair or replacement of pumps or valves, calibration of instrumentation in contact with the salt) would implement protocols that avoid contact with the skin. Operations with Flibe at elevated temperature may increase reactivity hazards. Engineering controls may be implemented to mitigate occupational exposure to the Flibe at elevated temperatures, such as piping insulation or double walled piping, high air flow general ventilation, and physical separation, such as the use of pipe corridor exclusion areas (Cadwallader and Longhurst 1999).

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