Technical Letter Report

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Aqueous and Pyrochemical Reprocessing Chemical Safety: Technical Descriptions to Aid Regulatory Considerations

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Prepared in response to Task 3 in User Need Request NMSS-2024-003 by:

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EXECUTIVE SUMMARY

This report provides technical information regarding select topics of chemical safety relevant to the operations of fuel reprocessing. The information identified is intended to support NRC's licensing reviews of spent fuel reprocessing facilities. Chemical safety is largely concerned with the prevention and mitigation of hazardous chemical conditions, which may be anticipated or unanticipated. The two greatest contributors to chemical safety are thorough process knowledge and stringent process control.

Aqueous reprocessing is a much more mature industry than pyrochemical reprocessing. Consequently, there is a larger body of industrial chemical safety knowledge and experience associated with aqueous reprocessing than with pyrochemical reprocessing. Aqueous reprocessing plants have been operating for decades in many different countries. The U.S. experience with pyrochemical reprocessing is largely limited to the engineering-scale work performed at the Argonne National Laboratory and the Idaho National Laboratory from the mid-1980s to the present. Other countries have also pursued research into pyrochemical reprocessing at similar engineering scales.

Due to the high radiation levels associated with spent nuclear fuels, reprocessing is performed in heavily radiation-shielded nuclear facilities called canyons or hot cells. In the U.S., canyons are associated with aqueous reprocessing, and hot cells are associated with pyrochemical reprocessing, although a future pyrochemical reprocessing plant may utilize a canyon. Process chemicals that are not contaminated with fission product radionuclides are called cold chemicals, and those that are contaminated are called hot chemicals. Safety practices within a reprocessing plant must consider the chemical safety aspects of both the cold and hot chemicals and the radiological safety aspects of the hot chemicals. For example, licensed nuclear facilities must consider chemical accident scenarios that release toxic chemicals or radiological materials.

NRC has regulatory responsibility for chemical hazards associated with nuclear material processing when the chemical hazard is associated with (e.g., UF_6) or derived from licensed material (e.g., UF_6 oxidized to HF), when the chemical hazard is intimately mixed with the licensed material (e.g., a solution of uranium nitrate in nitric acid), or when a chemical hazard could impact the ability of plant personnel to control license material operations (e.g., toxic chemical release into a control room). In the case of NRC-licensed nuclear facilities, chemical processes may involve occupational safety under the purview of both the NRC and the Occupational Safety and Health Administration (OSHA).

Radiological materials do not accumulate in the aqueous process as they do in the pyrochemical process. In the aqueous process, select actinides are recovered in product streams, and the remaining actinides and fission products are recovered in waste raffinate streams. When desired, the entire process can be flushed with clean solvents, thereby displacing nearly the entire inventory of radionuclides from the process equipment. The same is not true of the pyrochemical process where certain actinides and fission products accumulate in the process salts, until such time that the salts must be processed and the fission products disposed of as wastes.

Criticality safety is an important consideration wherever fissile materials are involved. Reprocessing is a chemical process involving fissile materials; therefore, chemical safety and criticality safety are intertwined and safety reviews should be coordinated. Means of maintaining criticality safety include administrative and engineering practices such as rigorous materials control and accountancy protocols and procedures, as well as criticality-safe designs. The inventories of fissile materials can be tightly limited based on their location, type, form, and quantity. In some instances, the masses of individual fissile isotopes are normalized and expressed as an equivalency mass of ^{235}U or plutonium. By these means, the masses of a diverse inventory of fissile radionuclides within the nuclear facility can then be expressed in terms of a single equivalent mass.

A head-end[a] step of aqueous reprocessing is the dissolution of spent fuel in concentrated nitric acid solutions. In the case of oxide fuel, the metal cladding is typically not dissolved and is recovered as metal waste. In the case of metallic fuel, the entirety of the metal cladding and fuel is dissolved. The chemical separations that follow recover both the actinides and the fission products as oxidized materials, not metallic materials. In contrast, pyrochemical reprocessing can accept either oxide or metallic spent fuel and recover the actinides as metals. These metal products may include uranium, alloys of uranium and zirconium, and alloys of uranium and transuranics. These metal products are often in the form of high surface area deposits that are later consolidated into ingot form. These metals are known to be pyrophoric, particularly when they are in high surface area forms such as reduced metals and electrorefined metals prior to casting operations. But even in cast forms, these metals may be pyrophoric. Therefore, pyrophoric hazards are associated with pyrochemical reprocessing operations performed in argon-atmosphere hot cells, where the loss of hot cell containment can lead to the loss of the argon atmosphere and introduce air into the hot cell.

Chemical safety is of course concerned with preventing the exposure of personnel to harmful process chemicals. In addition, chemical safety is concerned with the prevention and mitigation of hazardous chemical conditions, anticipated or unanticipated, which may cause harm to personnel and property. Examples of unanticipated energetic chemical reactions were the explosions associated with PUREX “red oil” and the nitric acid dissolution of certain fuel alloys containing zirconium.

[a] The term head-end refers to the initial mechanical, chemical, or thermal steps in a nuclear fuel reprocessing plant that prepares spent fuel for materials recovery operations.

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FOREWORD

Three complementary reports were prepared for the Nuclear Regulatory Commission:

- *Aqueous and Pyrochemical Reprocessing Off-Gas and Ventilation Systems: Technical Descriptions to Aid Regulatory Considerations*, INL/RPT-25-85408
- *Topics Related to Pyrochemical Reprocessing: Technical Descriptions to Aid Regulatory Considerations*, INL/RPT-25-85431
- *Aqueous and Pyrochemical Reprocessing Chemical Safety: Technical Descriptions to Aid Regulatory Considerations*, INL/RPT-25-87767.

The first report describes key issues associated with volatile radionuclides during both aqueous and pyrochemical reprocessing and provides a technical basis for any future NRC guidance pertaining to off-gas and ventilation systems at a reprocessing facility. The key topics include the chemistry of release into off-gas ventilation systems, the capture from off-gas ventilation systems, Federal regulations governing the release to the atmosphere, technical descriptions of existing hot cell facilities, and an extensive bibliography on related publications.

The second report expands the technical descriptions of pyrochemical reprocessing into subjects beyond the reference case discussed in the first report. These subjects include the application of pyrochemical reprocessing to various fuel types, the unit operations of voloxidation and oxide reduction, the technology of fluoride volatility, salt waste management, and the consequences of aged fuels. The report identifies expected safety-related aspects of existing potential technologies to support potential near-term reprocessing applications.

The third report provides a deeper assessment of key chemical process safety issues associated with both aqueous and pyrochemical reprocessing. These key issues include chemical excursions, pyrophoric materials, and chemical safety.

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CONTENTS

FIGURES

TABLES

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ACRONYMS

ATR	Advanced Test Reactor
CEA	French Alternative Energies and Atomic Energy Commission
CHC	Criticality Hazards Control
CIC	Core internal changeout
CMC	Closed metal confinement
COEX	Co-extraction
CSE	Criticality Safety Engineer
CSO	Criticality Safety Officer
DOE	U.S. Department of Energy
DOG	Dissolver off-gas
DSA	Documented safety analysis
DSC	Differential scanning calorimetry
EPA	Environmental Protection Agency
EPR	Electron paramagnetic resonance
FBC	Fuel Bottle Container
FBR	Fluidized bed reactor
FMH	Fissile Material Handler
GASR	Gas assay, sample and recharge
HFEF	Hot Fuels Examination Facility
HLW	High-level waste
INL	Idaho National Laboratory
LLW	Low-level waste
LWR	Light-water reactor
MAGNOX	Magnesium non-oxidizing
MAR	Material-at-risk
MCFR	Molten chloride fast reactor
MDD	Modified direct denitration
MSRE	Molten Salt Reactor Experiment
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
PEM	Plutonium equivalent mass
PSM	Process Safety Management

PUREX	Plutonium Uranium Reduction Extraction
RCRA	Resource Conservation and Recovery Act
RI	Responsible Individual
TFM	Total fissile material
TRISO	Tri-structural isotropic
TRU	Transuranic
ZIRCEX	Zirconium Extraction

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Aqueous and Pyrochemical Reprocessing Chemical Safety

Technical Descriptions to Aid Regulatory Considerations

1. INTRODUCTION

This report provides technical information regarding select topics of chemical safety relevant to the operations of fuel reprocessing. The information identified is intended to support NRCs licensing reviews of spent fuel reprocessing facilities. Chemical safety is largely concerned with the prevention and mitigation of hazardous chemical conditions, which may be anticipated or unanticipated. The two greatest contributors to chemical safety are thorough process knowledge and stringent process control. Nevertheless, in the history of reprocessing, there have been unanticipated occurrences, most significantly the explosive thermal excursions experienced with red oil and the nitric acid dissolution of fuel alloys containing uranium and zirconium.

With regards to chemical process safety, a facility design will adequately protect the health and safety of workers and the public during normal operations and credible accident conditions from the chemical risks of licensed material and from hazardous chemicals produced from licensed material. It should also protect against facility conditions that could affect the safety of licensed materials and thus present an increased radiation risk (e.g., release of a chemical that could incapacitate operators and preclude their entry to an area of the facility where licensed materials are handled). For example, when nitric acid is being used to dissolve spent fuels inside a shielded canyon (e.g., H-Canyon, Savannah River Site), the exposure limit of personnel to nitric acid would likely be of limited concern because personnel will not be inside the canyon due to the high radiation environment inside the canyon. On the other hand, when nitric acid solutions are prepared outside the canyon for pumping into the canyon, then the exposure limit of personnel to nitric acid may be of greater concern because of the potential for the chemical to impair operators and their ability to perform their jobs. However, if containment of the canyon environment were to be breached, the main concern for personnel safety would be the resultant exposure to radiological materials and not the resultant exposure to non-radiological chemicals.

From the perspective of an NRC chemical safety review, consequences of the loss of utilities are considered. Additionally, natural phenomena hazards such as tornadoes, hurricanes, and earthquakes, which can cause infrastructure damage leading to hazardous chemical conditions, may be part of the review.

Aqueous and pyrochemical reprocessing have different criticality concerns, different process chemistries, different methods for materials control and accountancy, and different facility designs. Due to the large disparity between their relative levels of deployment, issues of chemical safety for aqueous reprocessing are much more widely known and disseminated in literature than those for pyrochemical reprocessing. This consequence of history means that many aspects of pyrochemical reprocessing remain at low technology readiness levels and that certain aspects of chemical safety have not been fully assessed.

Another important distinction between the two technologies is the accumulation of radiological materials. Radiological materials accumulate in the pyrochemical process equipment, particularly in the molten salts used in the oxide reduction cell and the electrorefining cell. Radiological materials do not accumulate in the aqueous process equipment. This is because the organic and aqueous solutions are passed through the process, discharging the radiological materials into product and waste streams that leave the process. In contrast, fission products and transuranics accumulate in the pyrochemical salts, and there comes a limit where the salts must be managed by some combination of chemical processing and waste disposal. There are competing factors that will cause this limit, such as increasing liquidus

temperature (i.e., loss of solubility of certain constituents within the salt), increasing decay heat load (i.e., too much heat generation within the salt from fission product decay), increasing salt volume, and increasing inventories of various radionuclides that are limited by administrative safety considerations.

The mechanism for the accumulation of fission products in the oxide reduction and electrorefiner cells involves exchange chemistry with lithium chloride (LiCl) and uranium trichloride (UCl_3), respectively. Lithium chloride can exchange with cesium and strontium in the spent fuel, while uranium trichloride can exchange with the alkali, alkaline earth, lanthanide, and transuranic metals in the spent fuel. Lithium chloride is the least stable chloride in the oxide reduction salt, and uranium trichloride is the least stable chloride in the electrorefiner salt.

The report begins with describing how radiological risks are managed in the Idaho National Laboratory (INL) Fuel Conditioning Facility, which is the best example of a pyrochemical reprocessing facility in the DOE complex and perhaps the world. The report then describes select topics related to chemical process safety for pyrochemical and aqueous reprocessing operations.

2. MATERIAL LIMITS WITHIN THE FUEL CONDITIONING FACILITY

Pyrochemical reprocessing operations are performed in the Fuel Conditioning Facility (FCF) as described in the complementary reports referenced in the Foreword. This section describes some of the strategies used to administratively regulate per DOE requirements the disposition and handling of fissile, radiological, and pyrophoric materials within the FCF and its hot cells. Similar strategies could potentially be considered for a commercial pyroprocessing facility to ensure adequate protection of workers and the public.

2.1. Criticality Safety

This section provides a brief discussion on criticality safety to highlight the most significant difference between aqueous and pyrochemical reprocessing, which is the presence and absence of water. It is noted that chemical safety can be impacted by or can impact chemical/physical phenomena in other safety areas, such as criticality; therefore, safety reviews should be coordinated. Pyrochemical reprocessing is called *dry processing* in some literature to accentuate that no water is involved. Water and other hydrogenous substances are, of course, neutron moderators. Molten salt solutions can accommodate concentrations of fissile materials that are much higher than what is possible in aqueous solutions due to the absence of moderator.

A criticality event:

- results in the accidental release of nuclear fission energy that occurs when fissile, moderator, and/or reflector materials are assembled in certain masses, proportions, and geometric configurations.
- produces a burst of radiation and heat that is potentially lethal to personnel in the vicinity and can potentially cause significant damage to the facility.
- is usually a single event because the release of energy usually disrupts the configuration that caused the criticality, but cyclic criticalities have occurred in cases where the configuration has reassembled.
- can generally be prevented by administrative controls that rely on high-accuracy materials control and accountancy protocols, engineering controls, and human reliability programs.

Neutron moderators are materials that absorb some of the neutron energy, causing the neutron energy to be reduced. In the parlance of engineering, a neutron moderator converts fast neutrons into slower neutrons (i.e., toward the thermal spectrum of neutrons). Fissile materials present larger capture cross sections to thermal neutrons than to fast neutrons, meaning that thermal neutrons have a better chance of causing fission. Therefore, moderators decrease the mass of fissile material needed for criticality by slowing down the neutrons.

Neutron reflectors are distinguished from neutron moderators by the degrees to which the material absorbs or reflects the neutron energy. A perfect moderator will absorb much of the neutron energy in the process of soft recoil, and a perfect reflector will absorb very little of the neutron energy in the process of hard recoil. The reflected neutron has a second chance of causing fission. Therefore, reflectors decrease the mass of fissile material needed for criticality by effectively increasing the neutron flux by reflectance.

Hydrogenous substances such as water and hydrocarbons are very effective moderators. Water and hydrocarbons are used extensively during aqueous reprocessing. Therefore, the main engineering controls during aqueous reprocessing are to limit the fissile concentrations in these solutions and maintain criticality-safe configuration geometries of piping and tankage. Pyrochemical reprocessing takes a very different approach. The examples that follow are based on current operations within FCF.

2.2. Fissile Material Zones

The main administrative controls are to limit the masses of fissile materials in well-defined fissile material handling zones and eliminate moderators as much as possible from the process environment.

Figure 1 is a schematic diagram of the hot cells in the FCF, which shows the *air cell* (rectangular hot cell with an air atmosphere) and *argon cell* (circular hot cell with an argon atmosphere). The air cell is divided into fissile material handling zones labeled "A," and the argon cell is divided into zones labeled "P." Examples of rules regarding these zones include the following:

- The General Building Zone includes all areas outside of the air and argon atmosphere hot cells.
- The General Building Zone fissionable material limit is a maximum of 0.220 kg of total fissile material (TFM), which may contain a maximum of 0.220 kg plutonium equivalent mass (PEM).
- Additional rules are found in the documentation for General Building Zone; however, much of this information is non-public.

- Zone A8 is in front of Window A8 in the air cell.
- During EBR-II Fuel Bottle Container (FBC) handling operations, the fissionable material content of Zone A8 shall not exceed a maximum of 16 closed FBCs. Each FBC is limited to 0.800 kg TFM, which may contain a maximum of 0.010 kg PEM.
- Additional rules are found in the documentation for Zone A8.

- Zone P98 is in front of Window 1 in the argon cell.
- The fissionable material content of Zone P98 shall not exceed 10.0 kg of ^{235}U equivalent mass (U5M) with no restrictions on type and form.
- Additional rules are found in the documentation for Zone P98.

Where,

$$TFM = {}^{235}U\ mass + Np\ mass + Am\ mass + Pu\ mass$$

$$U5M = {}^{235}U\ mass + Np\ mass + Am\ mass + 4({}^{233}U\ mass + Pu\ mass)$$

These rules continue for all the zones listed in Figure 1 and take into account the type, form, amount, packaging, and configuration of the fissile materials in each zone.[b] The rules are established for very specific process operations within FCF and are reviewed and updated as conditions change. Fissile materials are tracked within the zones by a combination of process modeling software, database software, process sampling and analyses, and physical inventory accountancy.

2.3. Fissile Material Handling

There are additional administrative controls regarding the roles and responsibilities—and training—of the operations staff that are authorized to handle fissile materials within the FCF. Examples of rules regarding fissile material handling include the following:

- Fissionable and Criticality Hazards Control (CHC) material shall be handled only by personnel certified as Fissile Material Handler (FMH) or by designated trainees under the direct supervision of a certified FMH.
- Proposed process changes, equipment modifications, or proposed experiments must be analyzed for compliance with the FCF criticality safety criterion and formally approved prior to implementation.
- Prior to use inside the hot cells, all container types must be reviewed for use by the Criticality Safety Officer (CSO).

b. Type refers to the element and isotope. Form refers to the physical form, such as metal, oxide, salt, solution, etc.

- Zone boundaries may be moved with approval of the CSO, Criticality Safety Engineer (CSE), and Responsible Individual (RI).
- More rules follow.

These rules mandate a system of communications, and checks and balances, among the operations staff to ensure the safe handling and storage of fissile materials. It is not enough to solely rely on the rules for fissile material limits within the facility zones.

2.4. Material-At-Risk

There are additional rules regarding the exposed inventories of potentially hazardous materials based on considerations of releases beyond the physical boundaries of the hot cell containment. Material-at-risk (MAR) is an administrative designation given to select material types and forms. MAR is material available to be acted upon by physical stresses resulting from postulated FCF accident scenarios, thereby potentially leading to harmful human exposure to the material or its combustion products. Postulated accident scenarios in the FCF include such things as fires, pyrophoric metal fires, molten metal spills, molten salt spills, solidified salt powder spills, breaching of the hot cell containment boundary, or an earthquake, which could potentially involve all these events.

For example, uranium dendrites recovered from the uranium electrorefiner are comprised of high surface area uranium metal that is coated in electrorefiner salt. This material is MAR in three respects. The uranium metal is *radiological and pyrophoric MAR*, and the salt is *radiological MAR*. In another example, clean sodium metal is *pyrophoric MAR*, while bond-sodium recovered from spent EBR-II driver fuel is *radiological and pyrophoric MAR*. In another example, clean salts such as lithium chloride (LiCl) and potassium chloride (KCl) are not MAR because they are neither radiological nor pyrophoric, while salt from the electrorefiner is *radiological MAR*. MAR limits can change based on the operations stance of the facility. In FCF, MAR limits are reduced as the facility transitions between Operational Mode and Standby Mode. Operational Mode means that fissile material handling operations are being performed. Standby Mode means that fissile materials handling operations have been curtailed, which is usually done as a safety precaution while facility maintenance activities are performed.

A closed metal confinement (CMC) container is an approved container type that provides a high likelihood of protecting contained metal from exposure to air. Pyrophoric materials contained in the CMC container are not considered MAR.

2.5. Plutonium Equivalent Grams

Plutonium equivalent kilograms (kPEG) is a calculated value used to specify a single MAR limit for dose consequence purposes in facilities where various nuclide spectrums exist and are used at various times. For example, in the FCF argon cell, the MAR limit is 13.7 kPEG for exposed pyrophoric materials and 88.3 kPEG for non-pyrophoric salts. There are numerous other designations of MAR limits within FCF. These MAR limits are based on an analysis of the source term, which is the amount of radioactive material released during the postulated accident scenarios and is calculated to model downwind radiological doses. kPEG quantities apply to radiological MAR. There can also be limits applied to non-radiological MAR.

Calculation strategies for kPEG values of different process chemicals and materials are presented by Andrus [1]. The calculation of kPEG is more subjective and not as straight forward as the calculations of TFM and U5M. The calculation of kPEG considers both the radiological properties of the material, as well as the airborne dispersive properties of the material for the postulated accident scenario. kPEG is a measure of the airborne dose risk to downwind populations following the postulated accident scenario.

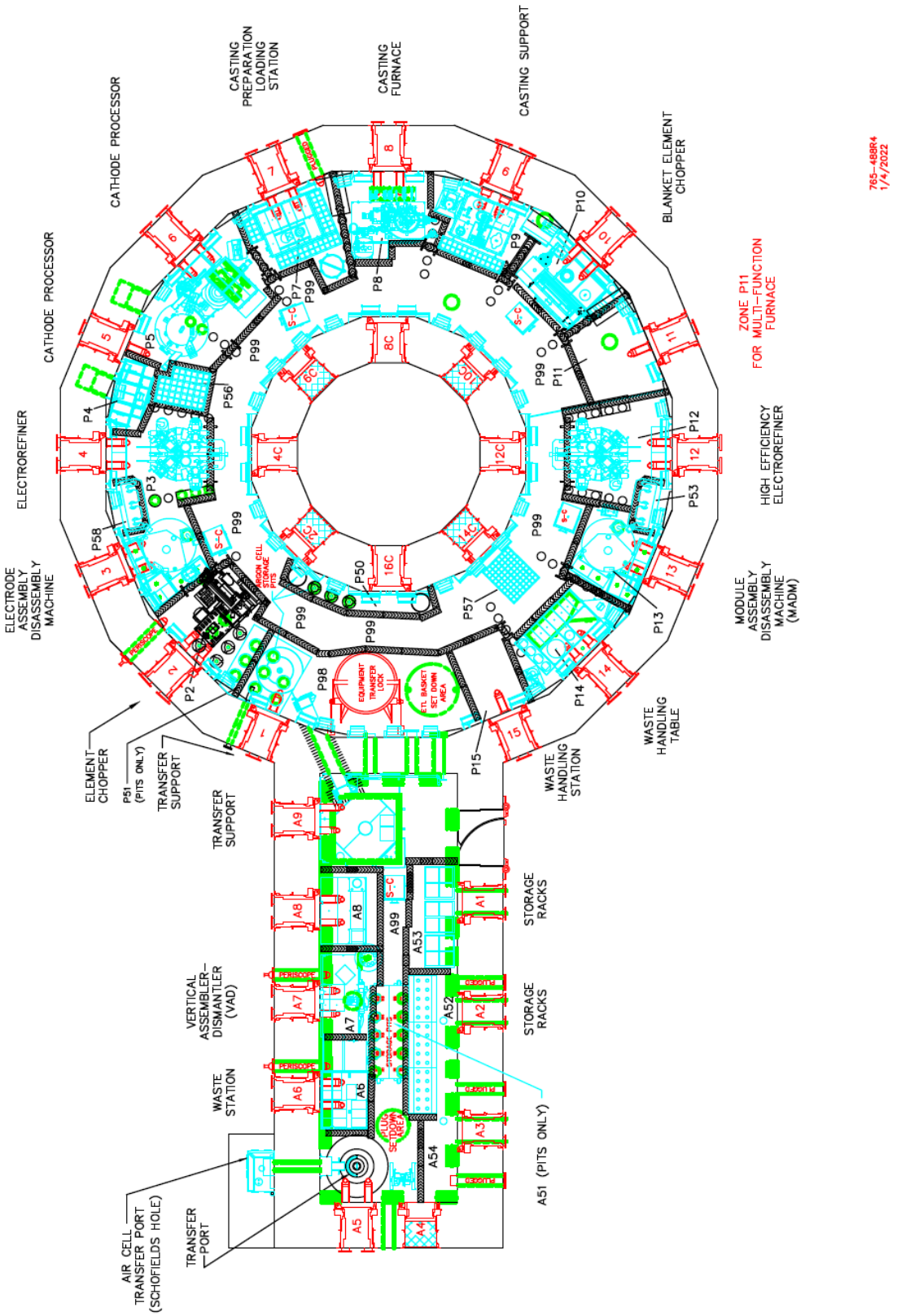

Figure 1. Schematic diagram of the Fuel Cycle Facility hot cells showing the partitioning of zones. Source: DOE.

2.6. Transuranic Gloveboxes

The FCF is in the process of installing transuranic gloveboxes for aqueous reprocessing research as shown in Figure 2 and pyrochemical reprocessing research as shown in Figure 3. The glovebox shown in Figure 3 is a mini hot cell, complete with tele-manipulators. Depending on the radiation levels within the glovebox, either the glove ports are used (low radiation), or the manipulators are used (high radiation). A summary of potentially hazardous chemicals for these facilities is presented in Table 1. This table only references potentially hazardous chemicals since criticality, radiological, and pyrophoric materials are considered under different safety criteria as described earlier. Similar rules will apply to these gloveboxes, as currently apply to the hot cells, with respect to Fissile Material Zones, and limits on TFM, U5M, PEG, and MAR. There are numerous other chemicals used in these facilities, but they are excluded from Table 1 due to their diminutive quantities. A complete list of chemicals approved for use in the aqueous glovebox is given in Section 6.

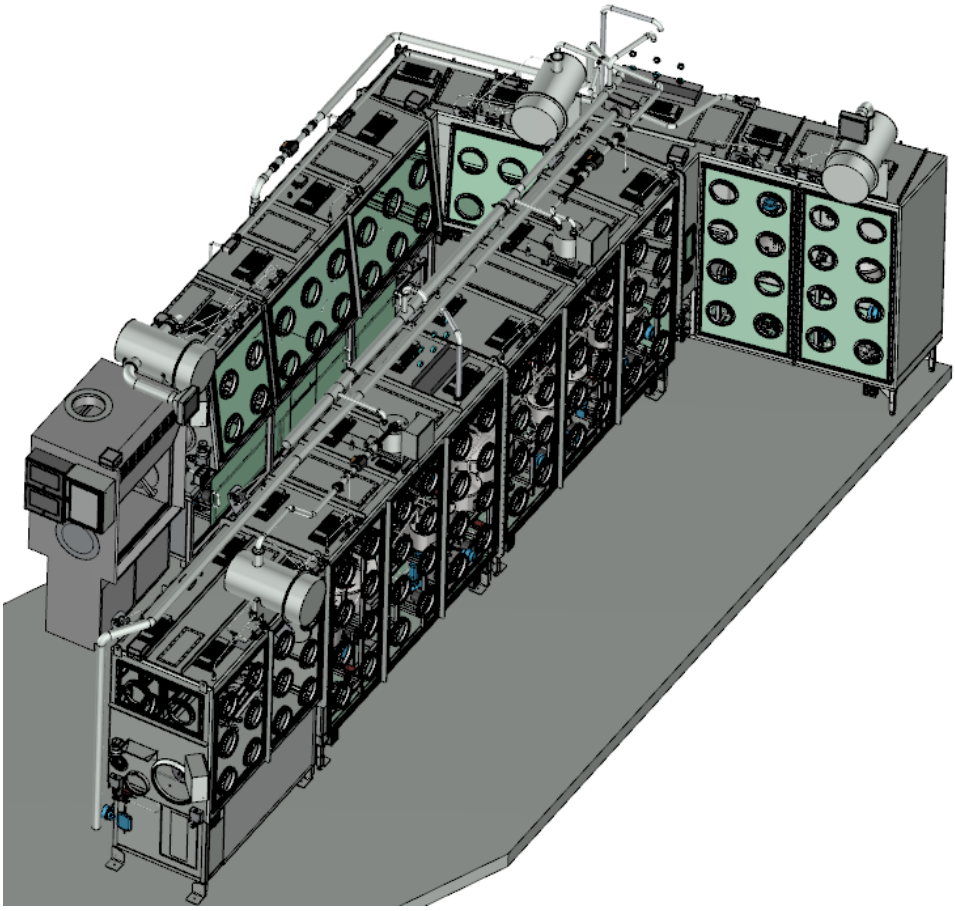

Figure 2. Schematic diagram of a glovebox for aqueous separations research. Source: DOE.

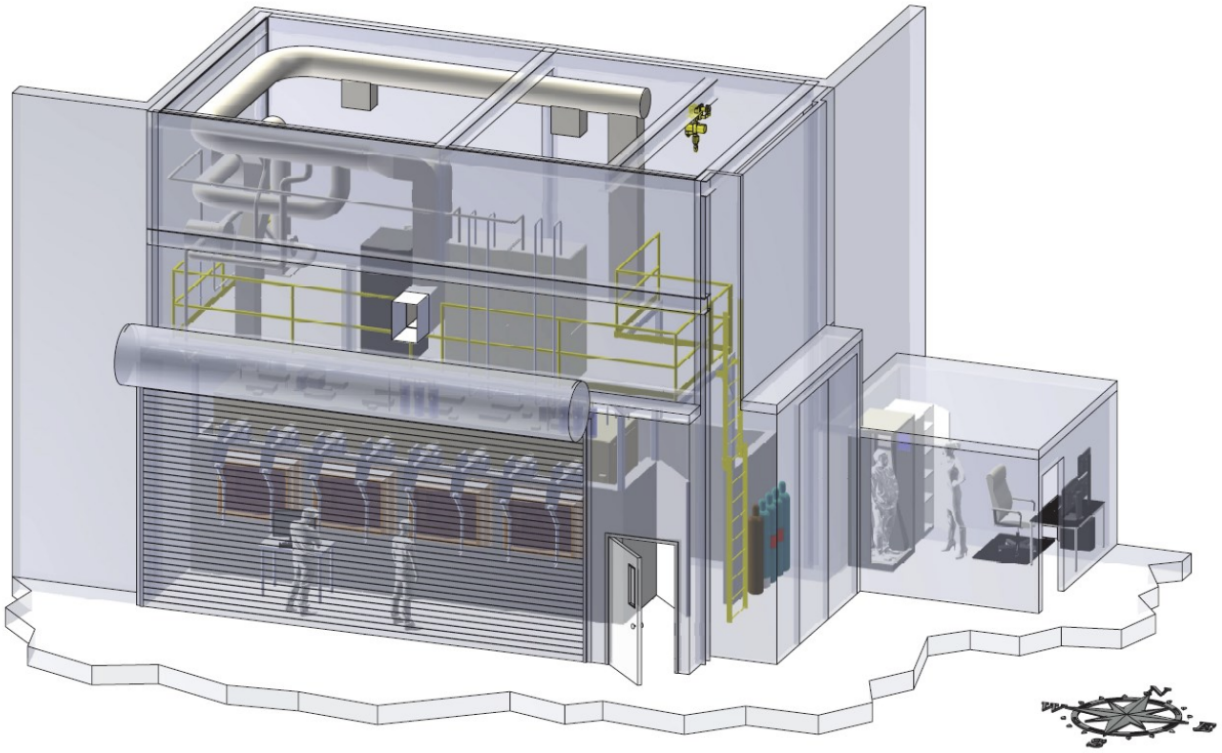

Figure 3. Schematic diagram of a glovebox for pyrochemical separations research. Source: DOE.

Table 1. Summary of potentially hazardous chemicals.

Chemical Names	CAS#	Purpose
Aqueous Glovebox (Figure 2)		
2-Ethylhexylphosphonic Acid Mono-2-Ethylhexyl Ester	14802-03-0	Solvent extraction (minor actinide/lanthanide separations).
Ammonium Hydroxide	1336-21-6	Solvent washing, off-gas scrubbing.
Ferrous Sulfamate	14017-39-1	Pu reductant in solvent extraction.
Hydrazine	302-01-2	Nitrous acid scavenger for Pu reduction in solvent extraction.
Hydrofluoric Acid	7664-39-3	Dissolution of fuel
Hydroxylamine Nitrate	13465-08-2	Pu reductant in solvent extraction.
Kerosene (Lamp Oil)	8008-20-6	Solvent extraction.
Dodecane	112-40-3	Alternative to kerosene.
Nitric Acid	7697-37-2	Solvent extraction.
Sodium Carbonate	497-19-8	Dissolution, solvent extraction, NO_x scrubbing.
Tributyl Phosphate	126-73-8	Solvent washing, neutralization of acidic solutions.
Xylene	1330-20-7	Solvent extraction (U/Pu separations).
Pyrochemical Glovebox (Figure 3)		
Chlorine Gas	7782-50-5	Salt purification.
Fluorine Gas	7782-41-4	Salt purification.
Hydrogen Gas	1333-74-0	Salt purification.
Hydrogen Chloride Gas	7647-01-0	Salt purification.
Hydrogen Fluoride Gas	7664-39-3	Salt purification.
Nitrogen Trifluoride Gas	7783-54-2	Salt purification.
Various Chloride and Fluoride Salts		Added as needed.

2.7. Summary of Materials Limits

There are two fundamentally different sets of rules that govern the material limits within the FCF hot cells. The first set of rules are meant to prevent a criticality event. These rules consider the type, form, amount, packaging, and configuration of the fissile materials in designated materials handling zones. The

second set of rules are meant to protect the surrounding population in the event of a postulated accident scenario that could release radiological and non-radiological hazardous materials into the atmosphere. These rules consider the hazards of radiological materials in terms of mass equivalency quantities such as kPEG, TFM, or U5M.

In other words, the overarching strategy is to identify the hazards associated with materials or families of materials and limit the amounts of those materials in the hot cell or limit the amounts of those materials exposed to the atmosphere within the hot cell. These limits are based on considerations of criticality safety or the potential for radiological dose to the surrounding population.

3. PYROCHEMICAL REPROCESSING

This section addresses chemical process safety considerations associated with pyrochemical reprocessing. Unlike aqueous reprocessing, pyrochemical reprocessing has never been used at a commercial scale to support the fuel cycles of operating reactors. Pyrochemical reprocessing has only been demonstrated for research purposes. The information presented here is based on experience from operations at the FCF and the Hot Fuels Examination Facility (HFEF) argon hot cells.

Pyrochemical reprocessing is envisioned as being performed within hot cells. The radiation shielding and containment systems of the hot cells protect personnel from exposure to radiation and chemical hazards. Precautionary measures involve radiological controls and work practices designed to protect personnel as described earlier in this report.

3.1. Pyrophoric Materials

Pyrophoric materials are those defined as capable of spontaneously igniting when exposed to air, without an external ignition source. However, this definition is not as simple as it may at first appear. Many circumstantial factors influence pyrophoricity, which makes the subject complex. For example, in the above definition:

- *Material* is concerned not only with the chemical formula but also its form (e.g., solid, liquid, gas), surface area, quantity, shape, temperature, and surroundings.
- *Capable* means there is sometimes a degree of probability. It is possible that slight changes to the conditions can affect whether the material will ignite.
- *Spontaneously* means that under the given conditions, no additional action is needed to initiate ignition other than exposure of the material to air.
- *Ignite* means that the reaction is self-sustaining once initiated and may continue until either the fuel or the oxidizer is consumed, or the reaction is somehow passivated. Generally, the pyrophoric material is the *fuel* and oxygen is the *oxidizer*.
- *Exposed* means that the conditions surrounding the material have changed bringing the material into contact with air. The rate of this change can occur slowly, rapidly, or anywhere in between.
- *Air* is ambient air and subject to environmental conditions of barometric pressure, temperature, humidity, and velocity.

The discussion above makes the point that, under certain conditions, materials that are generally considered pyrophoric may not be pyrophoric and materials that are generally not considered pyrophoric may be pyrophoric. Sodium hydride (NaH) is an example of the former. It is extremely pyrophoric, but if it is exposed very slowly to air, it may oxidize but not ignite. Aluminum metal is an example of the latter. It is used in many applications with no chance of being pyrophoric, but if it is in a form that has high surface area and clean metal surfaces, it may ignite when exposed to air.

Because it is not always possible to predict pyrophoric behaviors, experimental investigations are sometimes necessary to determine the pyrophoric characteristics of materials under anticipated process conditions and upset conditions. In other words, if a material can conceivably be pyrophoric, then it should be considered pyrophoric until proven otherwise.

In pyrochemical reprocessing, pyrophoricity is most often associated with reactive metals that include, but are not limited to, sodium, zirconium, uranium, and plutonium. For the application of reprocessing, pyrochemical flowsheets are designed to recover purified uranium. However, zirconium and plutonium, if they are recovered, would likely be recovered as uranium/zirconium, uranium/plutonium, or uranium/plutonium/zirconium alloys. Pyrochemical reprocessing does not seek to recover purified plutonium metal for fuel fabrication, and the minor actinides tend to follow the recovered plutonium.

Furthermore, applying an exacting engineering-based definition to describe what is and what is not pyrophoric material or a pyrophoric event is difficult because there are many variables involved. The most reliable predictors will be based on experience and testing.

3.1.1. Oxide Reduction

Photographs of stainless steel cathode baskets used for the electrochemical reduction of oxide fuel to metal are shown in Figure 4. This figure shows the basket loaded with approximately 3 kg of crushed light-water reactor (LWR) oxide fuel before oxide reduction (left) and after oxide reduction and salt distillation (right). Because of its high surface area, the reduced uranium metal product is considered pyrophoric.

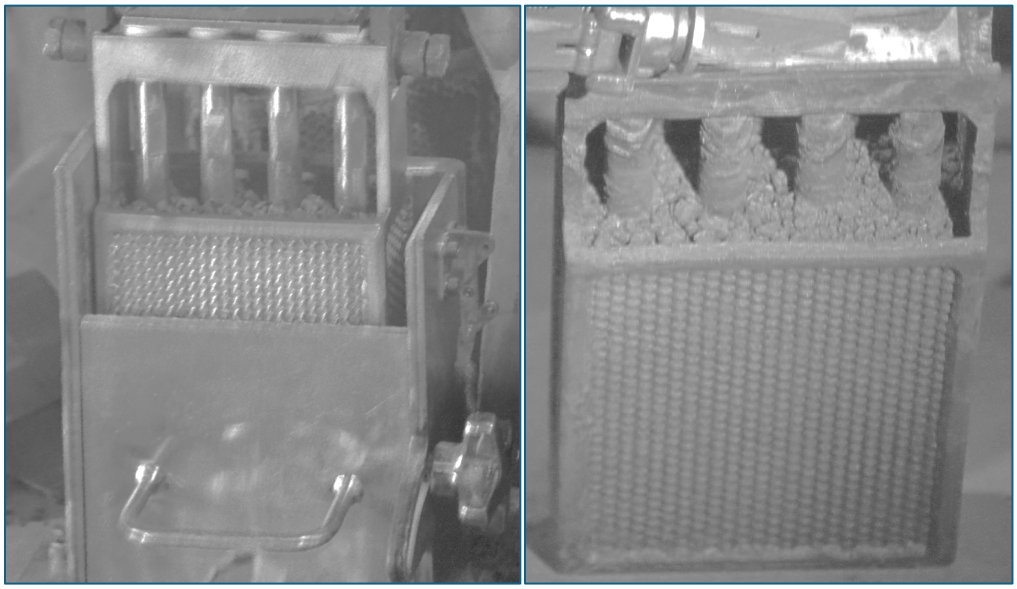

Figure 4. Photographs of oxide fuel processing. Oxide fuel in cathode basket pre-oxide reduction (left). Reduced metal in cathode basket post-oxide reduction and post-salt distillation (right).

3.1.2. Uranium Electrorefining

The reduced uranium metal product shown in Figure 4 and chopped sodium-bonded metal fuel are both suitable feed materials for uranium electrorefining.

Photographs of cathode deposits from the Mk-IV electrorefiner are shown in Figure 5. The photograph on the left shows a deposit of purified uranium metal. The morphology of this deposit is fine structured dendrites, resulting in a very high surface area metal. As pictured, the deposit was removed from the electrorefiner salt and cooled to the ambient temperature of the hot cell, which was in the vicinity of 34°C. Therefore, the deposit has a thin coating of solidified salt. The photograph on the right is similar, with the exception that the deposit is a uranium/zirconium alloy. As a result of the presence of zirconium, the morphology of the alloy deposit was more finely structured than the uranium deposit. Because of their high surface areas, both metallic deposits are considered pyrophoric.

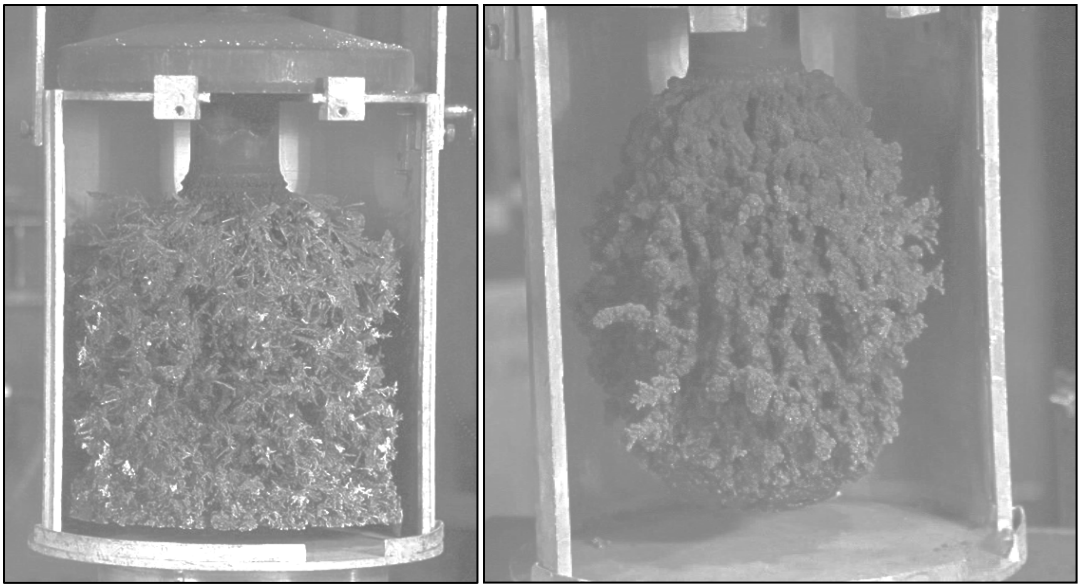

Figure 5. Photographs of cathode deposits from the Mk-IV electrorefiner. Purified uranium (left) and uranium/zirconium alloy (right). The diameters are approximately 22 cm.

Photographs of a solid uranium ingot and casting dross are shown in Figure 6 and Figure 7, respectively. The uranium ingot was formed by melting and consolidating the electrorefined uranium shown in Figure 5. Casting dross is a brittle mixture of uranium metal, uranium oxide, crucible materials, and crucible coating materials that can be crushed into a powder. Dross forms on the top surfaces of the uranium ingots during the casting process. Dross does not fully disengage from the ingots. These uranium ingots are considered pyrophoric. However, because the uranium ingots have a much lower surface area compared to the dross, the uranium ingots are considered less pyrophoric than the dross.

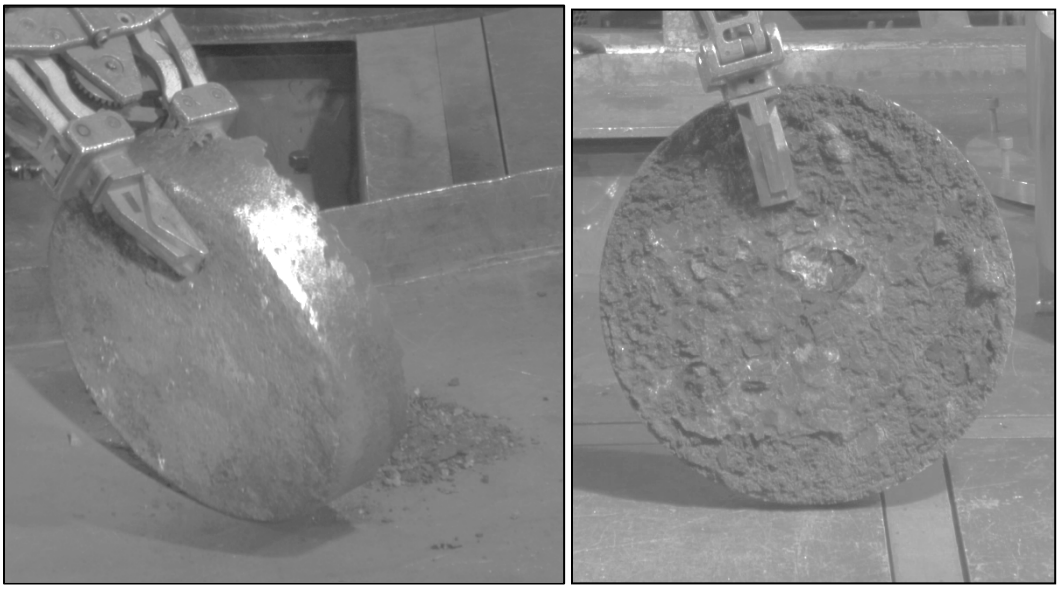

Figure 6. Photographs of solid ingots of electrorefined uranium from casting operations. Bottom of ingot (left). Top of ingot (right). Dross collects on the tops of the ingots during casting operations. The diameter of the ingot is approximately 20 cm.

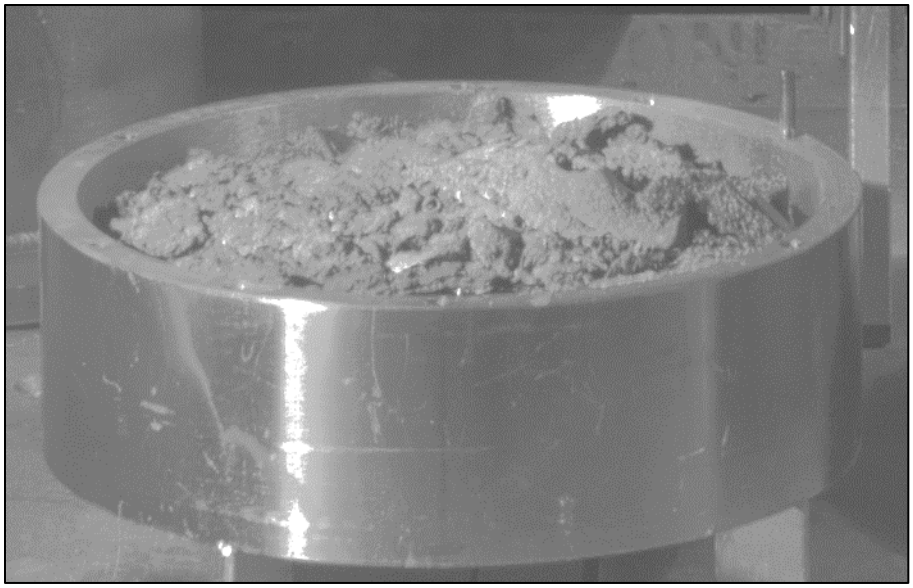

Figure 7. Photograph of dross collected during uranium casting operations. The inside diameter of the container is approximately 20 cm.

Photographs of cladding hulls and metal waste ingots are shown in Figure 8 and Figure 9, respectively. Cladding hulls are what remains of the chopped fuel in the anode baskets of the Mk-IV electrorefiner after most of the uranium metal has been removed by the electrorefining process. The cladding hulls contain residual uranium and zirconium and an appreciable fraction of the transition metal fission products. Cladding hulls are considered pyrophoric by virtue of the high surface area of the residual metals. Like the cathode deposits shown in Figure 5, cladding hulls are removed from the salt and have a thin coating of solidified salt. The cladding hulls are consolidated into metal waste ingots that are predominantly an alloy of stainless steel and zirconium. The metal waste ingots are not considered pyrophoric due to their composition and low surface area. However, dross from the metal waste ingot casting operations is considered pyrophoric.

Figure 8. Photographs of cladding hull waste. Cladding hulls in the anode basket after the uranium was removed (left) and cladding hulls removed from the anode basket (right). The cladding hulls are approximately 6 mm in diameter.

Figure 9. Photograph of cladding hulls consolidated into metal waste ingots by casting operations. The metal waste ingots are approximately 40 cm in diameter.

A uranium/plutonium alloy can be recovered from the electrorefiner salt using the liquid cadmium cathode technology, which is shown in Figure 10. In this application, the electrode starts as a pool of cadmium whose chemistry allows uranium and plutonium to be recovered together from the salt into the cadmium. The recovered uranium/plutonium alloy is accompanied by minor actinides, mostly neptunium and americium, and lanthanides, mostly cerium and neodymium. The chemistry of the liquid cadmium cathode prohibits the collection of purified plutonium. This behavior contrasts with the deposit of purified uranium shown in Figure 5, which contains very little plutonium. After deposition is complete, the cadmium cathode is processed in a furnace to distill the salt and cadmium away from the

uranium/plutonium metal and consolidate the uranium/plutonium metal into an ingot. The dendrites, cast ingots, and dross are all considered pyrophoric. Cadmium is not pyrophoric, but it is a Resource Conservation and Recovery Act (RCRA) metal.

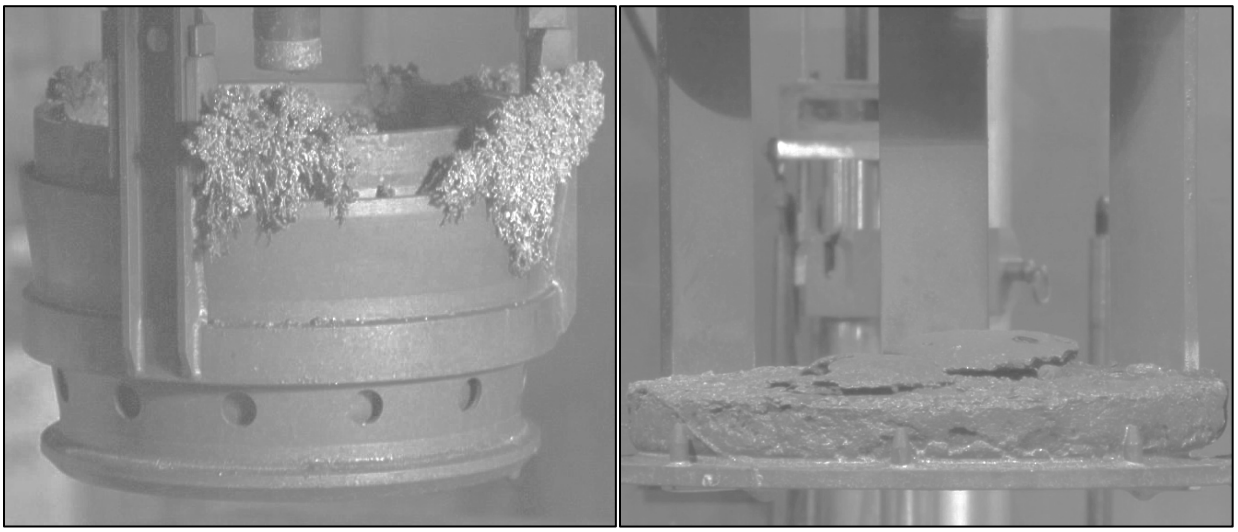

Figure 10. Photographs of the liquid cadmium cathode used in the Mk-V electrorefiner. Liquid cadmium cathode with metal dendrites (left). Uranium/plutonium alloy ingot after casting operations (right).

The metal casting operations discussed above are all performed in graphite crucibles of different sizes and configurations that are lined with either zirconia (ZrO_2) or yttria (Y_2O_3) castable ceramics. Graphite, zirconia, and yttria are not pyrophoric, but after being used for casting operations, these materials can absorb reactive metals that are pyrophoric. Photographs of reguli casting are shown in Figure 11.

Figure 11. Photographs of the casting of electrorefined uranium into reguli weighing 7 kg. Graphite casting crucible coated with zirconia (left). This crucible has multiple compartments for casting reguli. Uranium reguli (right).

Sodium-bonded metal fuels from Experimental Breeder Reactor II (EBR-II) are shown in Figure 12. Fuels contained in stainless steel cladding are not pyrophoric, provided the cladding is intact. However,

these fuel elements are pyrophoric once the cladding is breached thereby potentially exposing the sodium and fuel alloy to air. Notice the spiral failure of the breached fuel elements in Figure 13. This failure mechanism is observed when corrosion begins at a small breach in the cladding. The bond-sodium and fuel swell as they slowly oxidize. The internal pressure causes the cladding to fail in this spiral manner. In Figure 13, the powder among the failed cladding is oxidized fuel debris, which is considered pyrophoric.

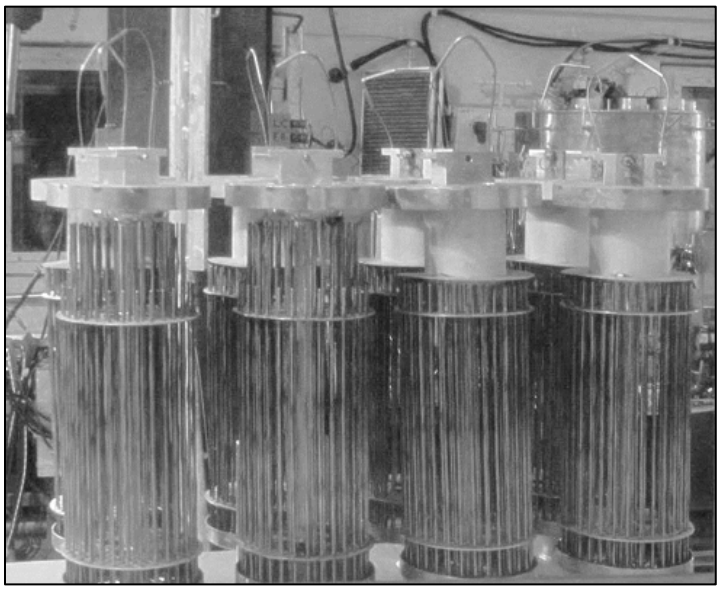

Figure 12. Photograph of EBR-II fuel elements that are intact and loaded into storage carousels. These fuel elements contain sodium-bonded uranium/zirconium alloy fuel.

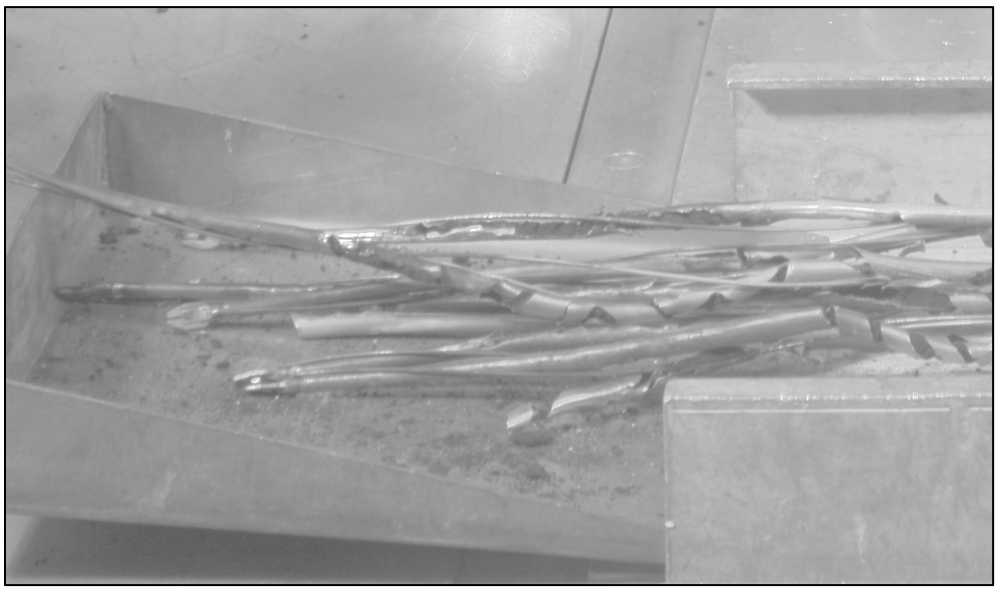

Figure 13. Photograph of EBR-II fuel elements that are breached and corroded. Notice the split cladding and fuel debris.

3.1.3. Bond-Sodium

Sodium metal is present in a family of fuels called sodium-bonded metal fuels. The bond-sodium serves the purpose of improving the thermal conductivity between the fuel and the stainless steel

cladding. There are a few examples of oxide and ceramic fuels utilizing bond-sodium in their designs, but these have been limited to fuel performance research activities. Select fission products are known to accumulate in the bond-sodium. These fission products include cesium, strontium, rubidium, barium, and iodine.

If the chopped metal fuel is loaded into an anode basket, which is then loaded into the electrorefiner salt, then these metals (i.e., sodium, cesium, rubidium, barium, and strontium) will report to the electrorefiner salt as metal chlorides. However, some pyrochemical reprocessing flowsheets propose separating these metals from the chopped fuel by distillation before the chopped fuel enters the electrorefiner salt. Keeping these metals out of the electrorefiner salt has certain benefits, such as generating less electrorefiner salt waste and decreasing the amount of reagent uranium chloride (UCl_3) needed to maintain the concentration of uranium chloride in the electrorefiner salt. However, distillation produces reactive metal alloy waste that must be neutralized. To complicate matters further, some of the fission product iodine is suspected to report to the bond-sodium as cesium iodide (CsI). If this distillation operation is used, the reactive metal distillate will be pyrophoric.

EBR-II fuel elements have a plenum section above the fuel section to accommodate the buildup of fission product gases within the fuel elements to prevent over-pressurization and failure of the cladding. The plenum sections are not chopped and do not report to the anode baskets. The plenum sections are a separate waste form that contains some of the bond-sodium. Due to the bond-sodium, plenum sections are pyrophoric.

There are several chemical processes proposed for salt waste management. These include the separation of fission product metals from salts in the oxide reduction and electrorefiner cells. Some of these processes have the potential to generate materials that are pyrophoric. These processes should be examined for their unique chemical hazards on a case-by-case basis.

3.1.4. Materials Transfer from an Inert Atmosphere into Air

In the FCF and HFEF argon-atmosphere hot cells at the Idaho National Laboratory (INL), the oxygen and moisture concentrations are each normally maintained below approximately 50 ppm. In other words, the hot cell environments are extremely inert and dry. There are additional aspects of pyrophoricity that should be considered when exposing materials created in the hot cell to air. For example, imagine two bins filled with metal turnings, one created in air and one created in argon. The turnings created in air would have immediately begun to oxidize as they were created. In a sense, only a small fraction of these turnings is oxidizing at any one time. In contrast, the turnings created in argon would not have oxidized. Upon moving this bin into air, all the turnings in the bin would, in-mass, begin oxidizing resulting in an event that is much more likely to be pyrophoric.

3.1.5. Materials Holdup in Process Equipment

Holdup in process equipment is material that accumulates over time within the process equipment. High-temperature processes are particularly prone to holdup because of the vapor pressures of the materials being processed. Examples are the headspaces above the salts in the oxide reduction and electrorefining cells, fuel element chopping equipment, and the heatshields and splash shields in salt distillation furnaces and metal casting furnaces. Figure 14 is a photograph of the heat shields from a salt distillation furnace. Holdup, as salt and metal splatter, can become entrained in the heat shields. The pyrophoricity of materials in holdup should be considered.

Figure 14. Photograph of the heat shields from a salt distillation furnace.

3.1.6. Extinguishing Metal Fires

Pyrophoric reactions can produce tremendous amounts of heat, cause the dispersion of burning and flammable materials, and generate toxic gases.

Metal fires are among the most difficult types of fires to extinguish. Fire suppressants like water (H_2O), carbon dioxide (CO_2), and Halon ($CBrClF_2$) will act as oxidizers and make the fire worse. Metal fires are extinguished by blocking the ingress of oxidizers to the combustion source. Commercial fire-retardant products are available for this application that rely on powdered mixtures of polymers, salts, and sometimes graphite, which are poured over the combustion source where the retardant melts to provide a barrier to the ingress of air. Effective strategies to reduce the risk of metal fires are to store pyrophoric materials in safety-class containers and to administratively limit the amounts of pyrophoric materials that are exposed at any given time.

Safety class structures systems and components (SSCs) are those for which credit must be taken, either preventive or mitigative, to meet the risk evaluation guidelines for the offsite public. Safety significant SSCs are those for which the preventive or mitigative functions are major contributors to defense-in-depth (i.e., the prevention of uncontrolled radioactive or other hazardous material releases) and/or worker safety.

A metal fire within an argon-atmosphere hot cell would only be anticipated upon the failure of the hot cell containment boundary. The pyrophoricity of all materials leaving the hot cell should be considered.

3.1.7. Pyrophoricity Summary

Several materials produced during pyrochemical reprocessing operations in an argon-atmosphere hot cell may be pyrophoric if exposed to air.

Table 2. Summary of pyrophoric materials in pyrochemical reprocessing.

Pyrophoric Material	Notes
Uranium, Zirconium, Plutonium Dendrites	High surface area increases the risk of pyrophoricity.
Uranium, Zirconium, Plutonium Ingots	Low surface area decreases the risk of pyrophoricity, but these materials can still be pyrophoric.
Uranium, Zirconium, Plutonium Casting Dross	High surface area increases the risk of pyrophoricity.
Breached Sodium-Bonded Fuels	Exposure of sodium and fuel alloys increases the risk of pyrophoricity.
Chopped Sodium-Bonded Fuels	Exposure of sodium and fuel alloys increases the risk of pyrophoricity.
Cladding Hulls	High surface area of residual metals increases the risk of pyrophoricity.
Metal Waste Ingots	Low surface area decreases the risk of pyrophoricity.
Metal Waste Casting Dross	High surface area increases the risk of pyrophoricity.
Reactive Metal Distillate	Pyrophoric due to metals such as sodium, cesium, and strontium.
Plenum Sections of Sodium-Bonded Fuels	Pyrophoric due to bond-sodium content.
Holdup in Process Equipment	Potentially pyrophoric due to composition and high surface area.

3.2. Chemical Hazards

There are unique chemical hazards associated with pyrochemical reprocessing.

3.2.1. Hygroscopic Salts

Pyrochemical processes utilize various chloride and fluoride salt systems. A list of select salts are shown in Table 3. In their use as high purity chemical reagents, exposure to air is avoided. The most benign salt on the list is sodium chloride (NaCl), which is used as a food product. Nevertheless, even when this salt is used as a high purity chemical reagent, it would not be exposed to air.

To varying degrees, all the salts in Table 3 will react with oxygen and moisture in air. Therefore, to avoid the introduction of impurities into the salts, great lengths are taken to avoid exposure of the salts to air. For example, lithium chloride (LiCl) is the most hygroscopic salt on the list. Given sufficient time, lithium chloride exposed to air will turn into a pool of saltwater. This behavior of lithium chloride is shown in Figure 15. After a long exposure to air at 40°C and 20% relative humidity, the initial solid puck of salt turned into a pool of saltwater.

Table 3. Reagent salts that are commonly used in pyrochemical processes.

Salt Name	Formula
Lithium Chloride	LiCl
Sodium Chloride	NaCl
Potassium Chloride	KCl
Cadmium Chloride	$CdCl_2$
Uranium (III) Chloride	UCl_3
Uranium (IV) Chloride	UCl_4
Lithium Fluoride	LiF
Potassium Fluoride	KF
Beryllium Fluoride	BeF_2
Zirconium Fluoride	ZrF_4
Thorium Fluoride	ThF_4
Uranium (III) Fluoride	UF_3
Uranium (IV) Fluoride	UF_4

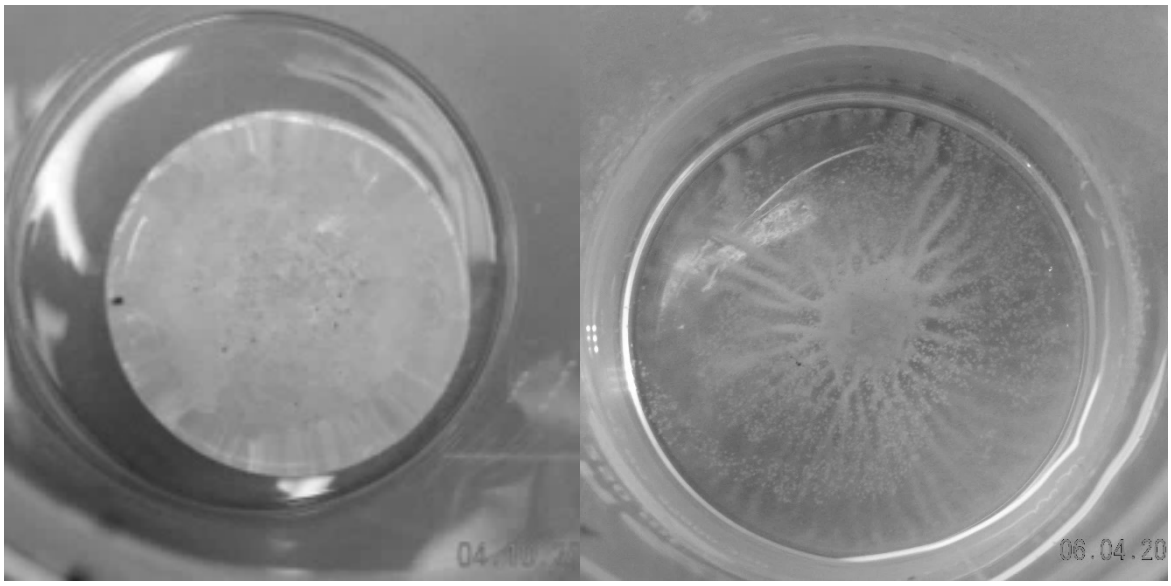

Figure 15. Photographs of a puck of LiCl salt exposed to air at 40°C and 20% relative humidity. The initial salt puck (left). The resulting pool of saltwater after 1,150 hour of exposure (right). Initial mass of LiCl was approximately 40 g.

Other salts exposed to air can partially oxidize to form metal oxychlorides or metal oxyfluorides. Complete oxidation of the metals can release the chlorine as chlorine (Cl_2) or hydrogen chloride (HCl) gases, or the fluorine as fluorine (F_2) or hydrogen fluoride (HF) gases. A few examples of oxidation and hydrolysis reactions are shown in Table 4.

Table 4. Examples of oxidation and hydrolysis reactions.

Salt	Oxidation Reactions	Hydrolysis Reactions
UCl_3	$3\ UCl_3 + 4\ O_2 = U_3O_8 + 4.5\ Cl_2$	$3\ UCl_3 + 8\ H_2O = U_3O_8 + 9\ HCl + 3.5\ H_2$
UCl_3	$2\ UCl_3 + O_2 = 2\ UOCl_2 + Cl_2$	$2\ UCl_3 + 2\ H_2O = 2\ UOCl_2 + H_2 + 2\ HCl$
$ZrCl_4$	$ZrCl_4 + O_2 = ZrO_2 + 2\ Cl_2$	$ZrCl_4 + 2\ H_2O = ZrO_2 + 4\ HCl$
UF_4	$3\ UF_4 + 4\ O_2 = U_3O_8 + 6\ F_2$	$3\ UF_4 + 8\ H_2O = U_3O_8 + 12\ HF + 2\ H_2$
UF_4	$2\ UF_4 + O_2 = 2\ UOF_2 + 2\ F_2$	$UF_4 + H_2O = UOF_2 + 2\ HF$
ZrF_4	$ZrF_4 + O_2 = ZrO_2 + 2\ F_2$	$ZrF_4 + 2\ H_2O = ZrO_2 + 4\ HF$

Oxidation and hydrolysis reactions of salts exposed to air are much more complex than the idealized reactions in Table 4 would suggest. Many different reactions are possible, and many different phases can form. The important point to consider here is that oxidation and hydrolysis reactions can release an explosive gas, hydrogen (H_2), and corrosive gases such as chlorine (Cl_2), hydrogen chloride (HCl), fluorine (F_2), and hydrogen fluoride (HF).

As discussed above, oxidation and hydrolysis reactions can result in the oxidation of actinides. These actinide oxides, oxychlorides, or oxyfluorides will have very low solubility limits in the chloride and fluoride salts. Therefore, the oxidation products can precipitate from the salts as solids and accumulate on the bottoms of the vessels containing the molten salts. This can lead to a loss of nuclear materials accountancy and can pose a concern for criticality safety.

Another important consideration is the hygroscopic nature of salts that can result in the accumulation of significant quantities of water, which is a neutron moderator. Design considerations for pyrochemical facilities specifically limit the amounts of moderators inside hot cell facilities and nuclear materials storage facilities. Criticality safety may take into consideration the effects of salts being exposed to air while the salts are at high temperatures within the process equipment and at ambient temperatures within storage containers. It may also be necessary to consider the potential for the accumulation of water by hygroscopic salts leading to a criticality event.

3.2.2. Steam Explosion

The contact between water and high-temperature molten salt can cause a steam explosion. The water entering the salt can rapidly turn into steam and the resulting volume expansion of the steam can expel the steam along with the molten salt in a catastrophic event. This falls into the category of an accident scenario that may need to be considered in a safety analysis.

A steam explosion can also occur from unrecognized sources of water. Anything contacting the molten salt must be absolutely dry. This applies to, but is not limited to, process equipment, furnace refractory materials, crucible materials, electrode materials, and chemical additives. There are other mechanisms for liberating and evolving gases at high temperatures that could also pose a danger. For example, upon heating, carbonates can evolve carbon dioxide (CO_2), hydrides can liberate hydrogen (H_2) gas, and hydrates can liberate water vapor.

There are salt purification technologies that rely on sparging reactive gases into molten salts for the purpose of removing metallic impurities, moisture, and oxygen. These gases include chlorine (Cl_2), hydrogen chloride (HCl), fluorine (F_2), hydrogen fluoride (HF), and nitrogen trifluoride (NF_3). These systems must never result in the expulsion of molten salt.

3.2.3. Reactive Gases

Metal fires were discussed earlier in the context of pyrophoricity via reactions with air. The whole understanding of pyrophoricity changes when the atmosphere is no longer air but an oxygen-enriched atmosphere. Material that would never ignite in air may very well ignite in an oxygen-enriched atmosphere. Furthermore, it should be recognized that chlorine and fluorine gases can react with many materials to support combustion in a manner similar to oxygen (i.e., exothermic reactions with gaseous products formation).

3.2.4. Radiolysis of Fluoride Salts

Solidified salts at ambient temperatures have demonstrated radiolysis effects. Perhaps the first discovery of these effects was following the end of the Oak Ridge National Laboratory (ORNL) Molten Salt Reactor Experiment (MSRE). The radiolysis effect liberated fluorine (F_2) gas from the solidified fuel salt, which recombined with uranium tetrafluoride (UF_4) to form gaseous uranium hexafluoride (UF_6). This reaction and transport mechanism enabled fuel salt enriched in ^{233}U to migrate to, and deposit at, unexpected locations within the off-gas systems.

The following was described by Icenhour regarding the MSRE experience [2]:

> The MSRE was operated at ORNL from 1965 to 1969 to test the concept of a high-temperature, homogeneous, fluid-fueled reactor. When the reactor was shut down, the fuel salt ($LiF\text{-}BeF_2\text{-}ZrF_4\text{-}^{233}UF_4$) was drained into two tanks at the reactor site, where it still remains today. ^{233}U, containing about 220 ppm of the impurity isotope ^{232}U, was used in the final fuel charge. The presence of high radiation readings in some of the reactor piping systems and the results from the analysis of gas samples led to the determination in 1994 that the ^{233}U had migrated throughout the piping system as UF_6. Additionally, it was discovered that UF_6 and F_2 had leaked past a faulty valve and deposited onto a charcoal bed. These discoveries resulted in the initiation of an extensive remediation program to remove and recover the ^{233}U from the reactor.

The following was described by Peretz regarding the MSRE experience [3]:

> Over the years, indications were noted of migration of radioactive materials in the piping connected to the drain tank cell and the off-gas system. In particular, increased radiation levels were observed in the north electrical service area adjacent to the drain tank cell. In addition to electrical penetrations, this service area houses components of the helium addition system that had been used to pressurize the drain tanks for salt transfers. Maintenance activities on the off-gas system indicated the presence of alpha activity. Gamma scans indicated the presence of ^{208}Tl, a product of the decay of ^{232}U. The annual annealing procedure was halted after December 1989 in part because of concerns that this procedure may have aided the migration of radioactive material out of the drain tank cell.
>
> In March 1994, a gas sample was taken from the auxiliary off-gas system, which was connected to the gas space above the drain tanks. Expectations were that fluorine might be detected in part per million quantities. An analysis of the gas [see Table 5 below] revealed that fluorine composed about half of the gas sample. Even more unexpectedly, UF_6 was a major component of the gas stream. At a partial pressure of 69 mm Hg, the amount of UF_6 identified was just below the 79 mm Hg saturation pressure of UF_6 at the sampling temperature of 21°C (69.8°F).

Table 5. Results from analysis of MSRE off-gas samples taken in 1994. Source: [3].

Component	Partial Pressure (mm Hg)
F_2	350
Inert Gases	305
UF_6	69
MoF_6	10
CF_4	5
HF	0.74
N-F Compounds	Trace

> The auxiliary off-gas system was in communication with the vapor space above the drain tanks; this provided a migration path for UF_6 and F_2 that had been liberated from the salt. A detailed review of the off-gas system was undertaken to identify all locations to which uranium might have migrated. It was also recognized that the auxiliary charcoal bed was in communication with the drain tanks because a valve had failed in the open position. Radiation and thermal surveys were used to identify a uranium deposit in the auxiliary charcoal bed. These data indicated that 2.6 kg of uranium was deposited in a 1-ft section of bed near the inlet pipe. It was also discovered that reactions of fluorine with carbon at low temperatures can result in the formation of potentially reactive carbon-fluorine compounds. Laboratory investigations determined the likely stoichiometry of these compounds to be that of C_2F. On the basis of volume estimates of the piping and vessels in communication with the drain tanks and the measured concentration of UF_6 in the off-gas, at least 1.8 kg of uranium is believed to exist as vapor in the vessels and piping. Because the measured UF_6 concentration is so close to the saturation pressure, solid deposits of UF_6 may exist in the off-gas system. Thus, the amount of uranium present in the system could exceed 1.8 kg.

A simplified description of the radiolysis effect is that gamma radiation is effective at breaking the bonds between lithium and fluorine in lithium fluoride (LiF) and between beryllium and fluorine in beryllium fluoride (BeF_2), thereby liberating fluorine gas ($F_2(g)$) and creating reduced lithium metal and beryllium metal. The following reaction illustrates how gamma radiation can interact with LiF in solidified salt at ambient temperatures. The gamma radiation (shown as eV energy) breaks the bond leading to lithium and fluorine liberated in the crystalline lattice. The fluorine migrates and pairs with another fluorine to form fluorine gas:

$$LiF + eV = Li\bullet + F\bullet = Li\bullet + \frac{1}{2}F_2(g).$$

A similar mechanism can act upon beryllium fluoride:

$$BeF_2 + eV = Be\bullet + 2F\bullet = Be\bullet + F_2(g).$$

The liberated fluorine, as elemental fluorine or fluorine gas, can act upon UF_4 to form $UF_6(g)$:

$$UF_4 + 2F\bullet = UF_6(g).$$

The $UF_6(g)$ renders the uranium mobile within the system [4].

3.2.5. Radiolysis of Chloride Salts

Radiolysis effects of chloride salts are not as well-studied as fluoride salts. This is largely because the ORNL MSRE used molten fluoride salts, and a molten chloride salt reactor has yet to be operated.

The following was described by Phillips [5]:

> This report documents the results of the gamma ray irradiation of NaCl-UCl_3 eutectic salt in the gamma tube at the advanced test reactor spent fuel pool, and analysis of capsules by the gas sample assay and recharge system. NaCl-UCl_3 salt capsules were irradiated at temperatures of 75°C, 131°C, 150°C, 300°C and 600°C shortly after the core internal changeout (CIC) of the Advanced Test Reactor (ATR) in April of 2021, for a duration of 2638 hours. The ATR gamma radiolysis test was completed successfully. Based on the gas assay, sample and recharge (GASR) analysis results, the quantity of Cl_2 gas released from NaCl-UCl_3 under the test conditions was non-detectable, and therefore, it is likely that releases of Cl_2 gas during long term storage of used molten chloride fast reactor (MCFR) fuel under similar conditions will be insignificant. To further elucidate the radiolysis effect on the NaCl-UCl_3 salts and reach a more definitive conclusion, advanced analyses such as scanning electron microscopy energy dispersive x ray spectroscopy (SEM-EDS), electron paramagnetic resonance (EPR), and differential scanning calorimetry (DSC) are recommended to analyze the capsule wall and salt samples.

However, this study only suggests that within the confines of the experimental limits, chlorine gas was not detected. This study does not suggest that chloride salts are immune to radiolysis effects that can liberate chlorine gas.

3.2.6. Radiolysis Discussion

Radiolysis will affect fluoride and chloride salts differently. In the example above for fluoride salts, fluorine liberated from the salt by radiolysis resulted in the formation of $UF_6(g)$, which, in turn, provided a mechanism for uranium migration throughout the system. In comparison, chloride salts do not have a high vapor pressure counterpart to UF_6 under ambient conditions. A predominance area diagram of the U-Cl-F system at 25°C is shown in Figure 16 [6]. Fluorine chemical potential is represented along the ordinate axis as the partial pressure of fluorine gas. Chlorine chemical potential is represented along the abscissa as the partial pressure of chlorine gas. At high fluorine chemical potentials, there is a stability field for UF_6. At the high chlorine chemical potentials, there is a stability field for UCl_4. These two halide salts have very different properties.

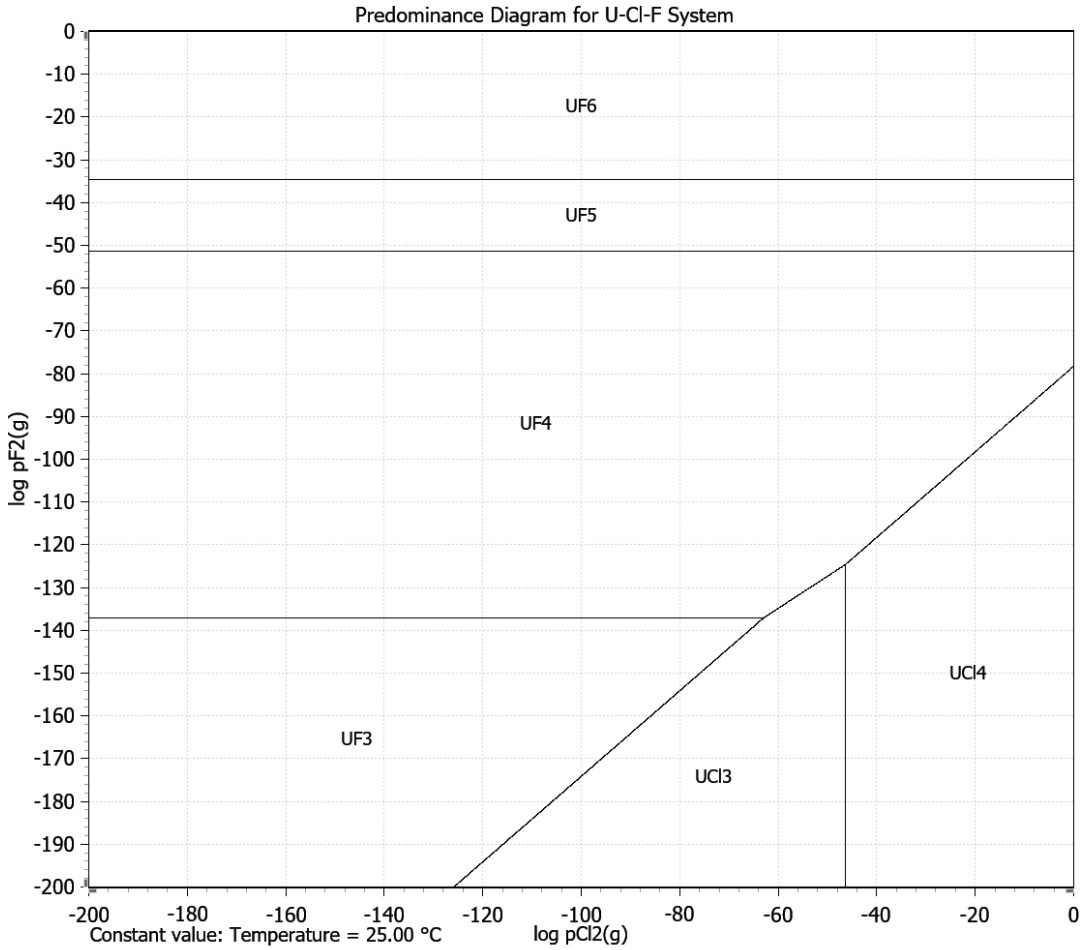

Figure 16. Predominance area diagram for the U-Cl-F system at 25°C. Pressure in units of bar.

The vapor pressures of UF_6(g) above UF_6(s), and UCl_4(g) above UCl_4(s) are shown in Figure 17. Clearly, the vapor pressure of UF_6 is several orders of magnitude greater than that of UCl_4. In this example, radiolysis of fluoride fuel salt can result in the migration of uranium as a volatile uranium fluoride species. However, radiolysis of chloride fuel salt provides no similar mechanism for the formation of a volatile uranium chloride species.

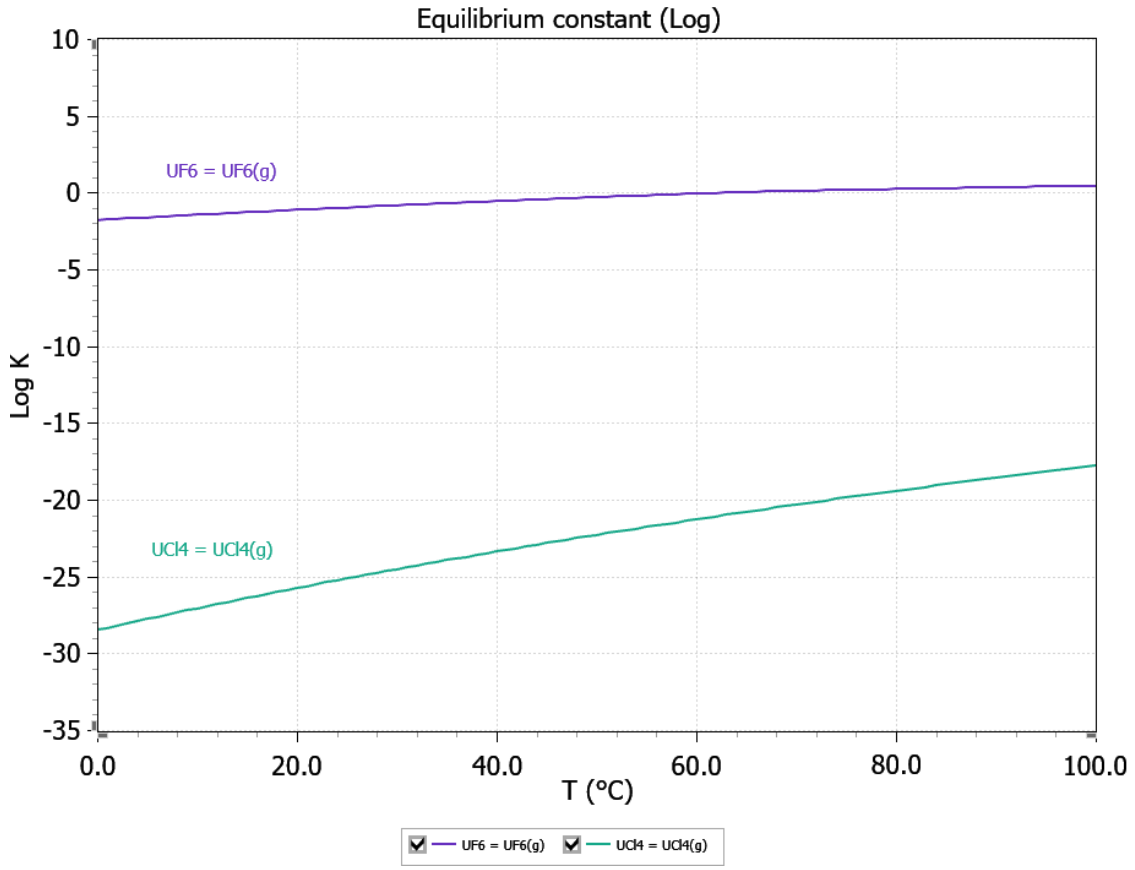

Figure 17. Vapor pressure diagram of UF_6(g) and UCl_4(g) as a function of temperature. Pressure in units of bar.

3.2.7. Uranium (III) Chloride Production

Pyrochemical reprocessing flowsheets will include electrorefining of uranium in molten chloride salt. During this process, many chemical separations occur. At the anode basket, impure uranium metal is oxidized into the salt as uranium cations (U^{3+}), which migrate through the salt to the cathode. At the cathode, the uranium cations are reduced from the salt to form a deposit of purified uranium metal. Impurity metals that are more electronegative than uranium are not oxidized and remain in the anode basket as metals. These materials are called *anode sludge* or *anode residue*. Impurity metals that are more electropositive than uranium are oxidized and accumulate in the salt as metal chlorides. Metals that accumulate in the salt do so at the expense of the uranium cation concentration. Uranium cations are needed in the salt to support electrorefining. Therefore, to maintain a constant concentration of uranium cations, uranium (III) chloride must be periodically added.

This makeup uranium chloride can be made in situ in the salt, or it can be made externally and added to the salt. The in situ production of uranium chloride can be done by adding cadmium chloride to the salt while uranium metal is present. The external production of uranium chloride requires chemical chlorination, which can be done with chlorinating reagents such as cadmium chloride, ammonium chloride, chlorine gas, or hydrogen chloride gas.

3.3. Hot Cell Operations

Once in use, the interiors of hot cells and canyons[c] are prone to radioactive contamination of many types and forms. One of the key considerations of facility design is the ability to remotely repair or replace every mechanical system associated with the functionality of the facility. These mechanical systems include those that support the hot cell and those that support the process within the hot cell. All mechanical systems will eventually require repair, replacement, and/or disposal. To facilitate these activities, the facility may need to provide the ability to decontaminate, or at least lessen the contamination of, articles that are to be repaired or disposed of as waste. Decontamination is necessary to properly manage the exposure of personnel to radiation during these activities. Hot cell facilities may be (1) equipped with suited entry repair areas, where personnel can enter a room to perform hands-on activities, (2) equipped with gloveboxes, where personnel can perform hand-on activities through glove ports, or (3) equipped with tele-manipulator stations for fine repair work.

Another design consideration is the failure mode of process equipment. For example, vessels used for electrochemical operations and crucibles used for casting operations will occasionally fail, resulting in the loss of containment of molten salts and metals. Process equipment for these operations must be designed to tolerate and recover from such events. Additionally, processes such as voloxidation, oxide reduction, dehalogenation, and salt purification use or liberate process gases that are highly corrosive. These gases must be managed to prevent facility damage.

3.4. Hot Cell Wastes

Pyrochemical reprocessing operations produce several types of waste. These wastes include items such as fission product laden salt, uranium casting dross, activated fuel assembly hardware, and contaminated process equipment. The distinctions between high-level waste (HLW) and low-level waste (LLW) are explained in Table 6.

Table 6. Summary of attributes of high-level and low-level wastes.

Parameter	High-Level Waste	Low-Level Waste
Radioactivity	High radiation levels. Requires significant radiation shielding.	Low radiation levels. May require moderate shielding or distance.
Decay Heat	Significant decay heat. Requires active or passive heat management.	Negligible decay heat. Does not require heat management.
Composition	Mostly long-lived radioisotopes. Fission products and transuranics separated from the spent fuels.	Mostly short-lived radioisotopes. Activated hardware and contaminated process scrap.
Disposal	Requires permanent isolation for hundreds or thousands of years.	Requires isolation for decades to a few hundred years.

c. The following descriptions are generalities. Hot cells can be small or large facilities. Work is often performed visually by sighting through windows and performing tasks using tele-manipulators mounted through the walls or suspended on overhead cranes. Canyons are usually associated with large facilities. Work is often performed visually by sighting with cameras and performing tasks using tele-manipulators suspended on overhead cranes. Both types of facilities are heavily radiation shielded. For this report, the terms hot cells and canyons are used interchangeably.

Parameter	High-Level Waste	Low-Level Waste
Volume	Small volume compared to low-level wastes.	Large volume compared to high-level wastes.
Additional Distinction	Less severe is intermediate-level waste.	Less severe is very low-level waste.
Examples	Salt from the oxide reduction cell, salt from the electrorefiner cell, and anode residue.	Activated fuel hardware. Contaminated scrap, crucibles, equipment, and tools.

The distinctions between contact-handled transuranic (CH-TRU) waste and remote-handled transuranic (RH-TRU) waste are explained below:

> TRU waste is waste that contains alpha particle-emitting radionuclides with an atomic number greater than that of uranium (92), half-lives greater than 20 years, and concentrations greater than 100 nanocuries per gram of waste. TRU waste is classified according to the radiation dose rate at a package surface. Contact-handled (CH) TRU waste has a radiation dose rate at a package surface of 200 millirem per hour or less; this waste can be safely handled directly by personnel. Remote-handled (RH) TRU waste has a radiation dose rate at a package surface of 200 millirem or greater per hour but not more than 1,000 rem per hour; this waste must be handled remotely (i.e., with machinery designed to shield the handler from radiation). Alpha radiation is the primary factor in the radiation health hazard associated with TRU waste. Alpha radiation is not energetic enough to penetrate human skin but poses a health hazard if it is taken into the body (e.g., inhaled or ingested). In addition to alpha radiation, TRU waste also emits gamma and/or beta radiation, which can penetrate the human body and requires shielding during transport and handling. RH-TRU waste has gamma and/or beta radiation emitting radionuclides in greater quantities than exist in CH-TRU waste [7].

In summary:

- CH-TRU waste is transuranic waste that has a measured radiation dose rate at the container surface of 200 millirems per hour or less and can be safely handled without special equipment when placed in containers.
- RH-TRU waste is transuranic waste that has a measured radiation dose rate at the container surface of between 200 mrems per hour and 1,000 rems per hour and, therefore, must be shielded for safe handling.
- CH-TRU and RH-TRU are defense related waste. HLW and LLW are not defense related waste.
- CH-TRU may share the characteristics of a LLW, and RH-TRU may share the characteristics of an HLW. Nevertheless, because of the “defense waste” distinction, CH-TRU and RH-TRU wastes are not called HLW or LLW, and HLW and LLW are not called CH-TRU or RH-TRU wastes.

4. CHEMICAL PROCESS SAFETY IN AQUEOUS REPROCESSING

The major unit operations in aqueous reprocessing include fuel decladding, dissolution, chemical separations via solvent extraction, solidification, off-gas treatment, and waste handling. The Plutonium Uranium Reduction Extraction (PUREX) process is the most technologically mature reprocessing method used globally and primarily relies upon the solvent extraction chemistry of tributyl phosphate (TBP) with nitric acid media to facilitate the separation of uranium and plutonium from fission products in used nuclear fuel. Detailed descriptions of these unit operations and the corresponding flowsheets may be found in complementary reports mentioned in the Foreword (i.e., INL/PRT-25-85431 and INL/RPT-25-85408). This report focuses specifically on the chemical process safety considerations associated with these unit operations. There is some variability in the unit operations depending on the type of fuel being reprocessed and the separation objectives for final products and waste forms; subsequent chemical hazards of the most common variants will also be discussed. It is also important to note that the majority of the unit operations occur within a hot cell environment due to the radiological hazards of used nuclear fuel; bulk chemical reagents pose chemical hazard risks to operators, and some chemical accident scenarios have significant consequences for in-cell operations.

4.1. Cold Chemical Reagents

Aqueous processing plants consuming significant amounts of chemical reagents pose several chemical safety considerations for bulk handling. Nitric acid, utilized for dissolution of nuclear fuel and for the makeup of various feed solutions to the PUREX process, represents the largest chemical consumption in a reprocessing plant. Concentrated nitric acid is typically procured commercially as 70% by weight HNO_3 and is both a corrosive liquid and an oxidizer. Exposure hazards exist for external contact, inhalation, and ingestion. Bulk nitric acid must be stored in chemically compatible vessels constructed from stainless steels (commonly 304 or 316L alloys). Tributyl phosphate (TBP) is utilized as the organic for the PUREX process. The TBP is combined with a hydrocarbon diluent such as kerosene or dodecane. TBP is categorized as a carcinogen and is harmful if ingested. It is considered an irritant if it is in contact with skin. TBP is combustible at elevated temperatures and will produce toxic fumes containing phosphorus oxides [8]. Therefore, it must be stored in a cool, dry, and well-ventilated area away from incompatible materials such as oxidizing agents [9]. Significant quantities of additional PUREX process chemicals include reducing agents, solvent washing solutions, and solidification precipitation additives. Chemicals need to be stored in cool, dry, and well-ventilated locations. The chemicals should be in chemically compatible storage containers and in areas based on hazard class [10]. A list of potentially used or generated chemicals in the pursuit or study of aqueous reprocessing is presented in Section 6.

4.2. Fuel Dissolution

Traditional Dissolution Processes. PUREX and all other derivatives of aqueous reprocessing require the dissolution of nuclear fuel to liquid solutions amenable to chemical separations. Dissolution methods, associated chemical reagents, and hazards/accident scenarios will vary depending on the fuel type; major methods will be described here including a brief description of alternative head-end processes that may be used for advanced reactor fuel forms. First, the most common form of dissolution utilizes concentrated nitric acid and has been utilized commercially for both uranium oxide and uranium metal fuels. Commercial LWR fuels comprised of uranium oxide pellets in zirconium alloy cladding are commonly reprocessed using the “chop and leach” method, where the fuel is mechanically sheared into small pieces to expose the fuel, which is subsequently dissolved in nitric acid solution. The zirconium alloy cladding hulls are not soluble in nitric acid solution; the cladding hulls are typically recovered from the dissolver, rinsed, and compacted into a final waste form. Dissolution processes are exothermic reactions, and reaction kinetics are largely driven by available surface area of the fuel and increased temperature. Dissolution typically occurs at near-boiling temperatures (90–95°C) to improve reaction kinetics. Chopping the fuel aids to increase the available surface area, and dissolver vessels are typically heated

using steam jackets and/or steam coils in the vessel design. Depending on the scale/throughput of the reprocessing plant, dissolution may be batchwise or continuous. Batchwise dissolvers will be charged with discrete batches of nuclear fuel that is fully dissolved, drained, and the process repeated. Continuous dissolvers are more common at commercial scale, such as those employed at La Hague in France (Orano SA) and Rokkasho in Japan (Japan Nuclear Fuels Limited, JNFL). Continuous dissolvers are based on a rotary wheel concept, where chopped nuclear fuel is loaded into baskets that slowly rotate through nitric acid solution. Rotary-style [11] and batch-style [12] dissolvers are shown in Figure 18. Chemical reagents and nuclear fuel are added continuously to achieve higher throughput. Dissolved fuel in the PUREX process typically targets a final concentration of 1.26 mol/L uranium and 3 mol/L nitric acid, although this may vary depending on the specific flowsheet. Generally, high nitrate concentrations of 2–4 mol/L improve extractability by TBP during solvent extraction, and high uranium concentrations help reduce the volume of HLW while minimizing the size of solvent extraction equipment [13].

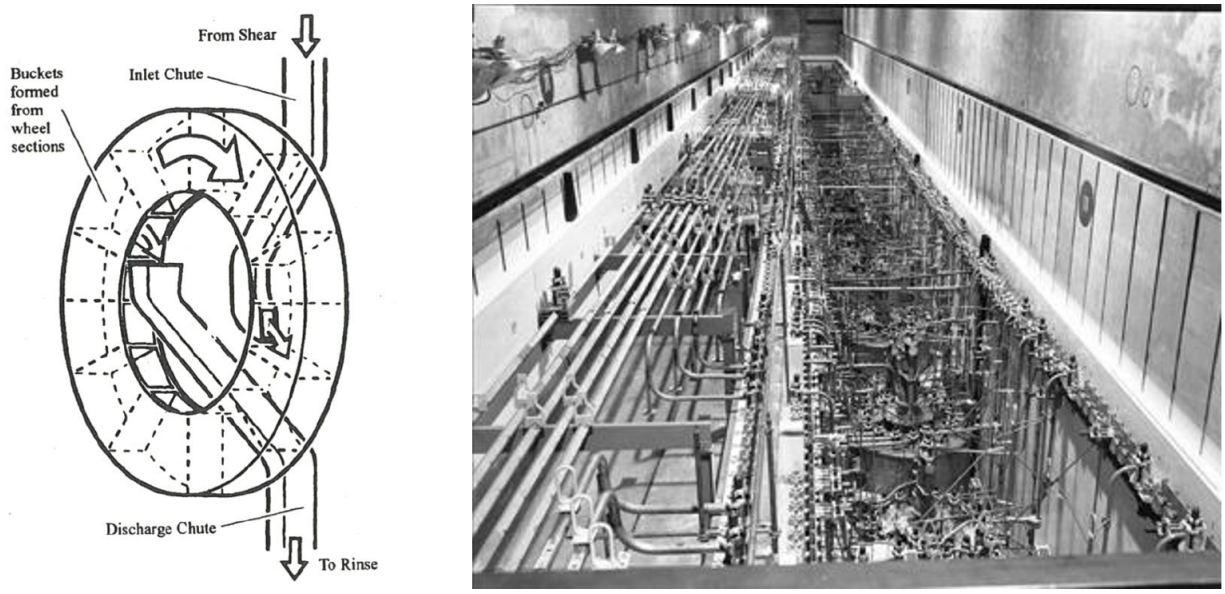

Figure 18. Schematic diagram of a rotary-style dissolver for continuous operations (left) and a photograph of batch-style dissolvers in H-Canyon (right).

From a chemical hazard perspective, the largest hazard is the dissolver off-gas (DOG), which contains highly toxic oxides of nitrogen (NO and NO_2) evolved from the dissolution of nuclear fuel in nitric acid. Off-gas system chemical hazards and descriptions will be discussed separately in a subsequent section of this report. The next significant hazard is nitric acid. Reprocessing plants consume bulk quantities of concentrated nitric acid in dissolution typically ranging from 10 to 15.55 mol/L (50 to 70 weight percent), which is both a strong oxidizer and corrosive chemical. While dissolution operations occur within the confines of a hot cell, nitric acid solutions are commonly stored and/or prepared in a cold chemical area where the potential for personnel exposure is increased.

Chemical Decladding. As opposed to the "chop and leach" method, some fuel assembly cladding materials may be chemically dissolved rather than mechanically removed. This primarily includes aluminum-clad nuclear fuel. Magnesium non-oxidizing (MAGNOX) fuel cladding is comprised of magnesium alloyed with small quantities of aluminum and beryllium. Historically, MAGNOX has been mechanically declad followed by chemical decladding to remove residual cladding material. In chemical decladding, the cladding is dissolved away from the uranium fuel using a caustic solution of sodium hydroxide and aluminum nitrate at elevated temperatures. Also, historically, mercury has been utilized as a catalyst to remove protective aluminum oxide layers present on some aluminum-clad fuels. After chemical decladding, the uranium fuel that is left behind is dissolved as described above in nitric acid

solution. This method is more specific to research reactor fuels or MAGNOX fuel derivatives but is included here for completeness due to the additional chemical hazards introduced with concentrated sodium hydroxide and aluminum nitrate.

Dissolution of Zirconium Alloy Fuels. The dissolution of uranium/zirconium metal alloys in nitric acid has historically resulted in chemical excursions or explosions [14, 15, 16, 17]. These explosions were attributed to the presence of the uranium-zirconium epsilon phase (UZr_3) that becomes exposed during dissolution of the matrix alloy in nitric acid [18]. The nitric acid is effective at dissolving the uranium and zirconium matrix alloy but is ineffective at dissolving the epsilon phase intermetallic. The epsilon phase forms finely divided inclusions in the matrix alloy, providing a high surface area as the matrix alloy is dissolved. When a sufficient quantity of epsilon phase is exposed, the material may rapidly oxidize, and rapid gas evolution may lead to an explosion [16]. The addition of hydrofluoric acid (to the nitric acid solution) will promote the dissolution of the epsilon phase. An appropriate molar ratio of fluorine-to-zirconium (F:Zr) ensures that the hydrofluoric acid is not entirely consumed and the exposed quantity of epsilon phase is maintained below levels at which an explosive condition may exist [16]. The following are possible oxidation reactions:

Oxidation by nitric acid

$$UZr_3 + 8/3\ NHO_3 = UO_2 + 3\ ZrO_2 + 4/3\ N_2(g) + 4/3\ H_2(g)$$

Oxidation by water

$$UZr_3 + 8\ H_2O = UO_2 + 3\ ZrO_2 + 8\ H_2(g)$$

Oxidation by air

$$UZr_3 + 4\ O_2 = UO_2 + 3\ ZrO_2.$$

However, the reaction mechanisms are likely to be more complex than these simple reactions indicate. The actual reaction mechanism may also involve the formation of sub-stoichiometric oxides that form on the surface of the UZr_3 particles, providing an unstable mixture of metal and oxygen that can react rapidly. The UZr_3 epsilon phase is also associated with zirconium-clad uranium oxide fuels where UZr_3 can form along the interface between the cladding and the fuel [19].

HF has been used in combination with nitric acid to dissolve the entirety of alloyed nuclear fuel assemblies that otherwise would not dissolve in nitric acid alone. However, HF introduces additional hazards and chemical reagents into the process. Exposure to HF requires immediate and specialized first aid, as the fluoride ion readily binds with calcium or magnesium in human tissue and bone, leading to tissue death or fatal cardiac effects. HF also requires specialized storage vessels and processing equipment due to its corrosivity; HF will typically be stored in fluoride-resistant polymer containers, while processing equipment will typically be constructed of high-nickel content alloys suitable for HF applications (e.g., Monel, Hastelloy). Lastly, free fluoride concentration in dissolved nuclear fuel solutions must be managed carefully to prevent precipitation of uranium fluoride (UF_4) or zirconium fluoride (ZrF_4) species and to minimize corrosion of downstream processing equipment. Aluminum nitrate ($Al(NO_3)_3$) and/or zirconyl nitrate ($Zr(NO_3)_4$) can be added to complex free fluorides post-dissolution, stabilizing the solution to prevent precipitation and binding free fluoride ions. Both aluminum nitrate and zirconyl nitrate are chemical irritants and must be handled according to their hazard class.

Alternative Processes for Advanced Fuels. Lastly, a brief discussion of alternative head-end processes for alloyed and/or advanced nuclear fuels is included due to the unique chemical process safety considerations they may pose. First, a dry head-end process utilizing halide volatility has been demonstrated on aluminum and zirconium-clad nuclear fuels. INL has significant expertise conducting research and pilot plant operations with the Zirconium Extraction (ZIRCEX) process based on chloride volatility. In this process, nuclear fuel is contacted with hydrogen chloride gas (HCl) or chlorine gas (Cl_2) at elevated temperature in a fluidized bed reactor (FBR), selectively volatilizing zirconium (as $ZrCl_4$) or

aluminum (as $AlCl_3$) as chloride salt vapors, leaving behind uranium and non-volatile fission products. The reaction is extremely exothermic, and for this reason, FBRs are a preferred reactor type due to their ability for near-isothermal operations. ZIRCEX provides the benefit of reducing high-level waste volumes by avoiding dissolution of the entire fuel assembly in nitric acid and hydrofluoric acid—or avoiding chemical decladding for aluminum fuels. However, use of hydrogen chloride gas or chlorine gas introduces the potential for significant chemical hazards, as both are acutely toxic and strongly corrosive. Bulk reagent storage of these gases also invokes Process Safety Management (PSM) standards set by OSHA (Occupational Safety and Health Administration). Halide volatility can also be conducted using fluorine gas or hydrofluoride gas, both of which are also regulated under PSM standards. Note that oxides of nitrogen are also under PSM, which evolve during traditional dissolution operations and may be used in oxidation reactions for alternative methods such as ZIRCEX or fumeless dissolution.

As a final point, many advanced reactor concepts under development are high-temperature gas reactors, which utilize tri-structural isotropic (TRISO) fuel. TRISO fuel contains a small kernel of uranium oxide (UO_2) or uranium oxycarbide (UOC), surrounded by four layers, which include a porous carbon buffer layer, an inner pyrolytic carbon layer, a silicon carbide layer, and an outer pyrolytic carbon layer. This layered structure enables superior fission product retainment and prevents the potential for melting under accident scenarios, thus termed accident tolerant fuel (ATF). TRISO particles are compacted within a graphite matrix to make hexagonal or spherical fuel assemblies, respectively for prismatic core design or pebble bed reactors, which are completely unique when compared to traditional LWR fuel assemblies. While TRISO serves as one of the most robust fuel types, it does not lend itself well to reprocessing due to the bulk quantity of graphite present and layered construction. However, the use of higher ^{235}U enrichments such as high-assay low-enriched uranium (HALEU), nominally 19.75% ^{235}U, may shift the economics of material recovery from TRISO fuel. Waste minimization/management of the graphite matrix may also be a motivator for TRISO reprocessing. Head-end steps may include crushing and burning, followed by leaching in nitric acid solution. Advanced proprietary methods for chemical removal of graphite and silicon carbide have also been developed. Aqueous reprocessing plants that use TRISO fuel forms as a feedstock may introduce additional chemical hazards that are not bound by traditional acidic dissolution processes.

4.3. Solvent Extraction

In aqueous reprocessing, solvent extraction is used to separate and recover materials of interest, mainly plutonium and uranium. Solvent extraction works by mixing two immiscible fluids (organic and aqueous phases) to selectively extract the materials of interest from one phase to the other phase and then separate the phases from each other. This is accomplished by running multiple stages of solvent extraction equipment, such as pulse columns, mixer-settlers, or centrifugal contactors, in a continuous countercurrent operation.

Pulse columns are shown in Figure 19 [20]. A vertical tube contains a stack of perforated plates that facilitate contact between the organic and aqueous phases. The lighter organic phase enters from the bottom and moves toward the top of the column. The heavier aqueous phase enters from the top and moves toward the bottom of the column. During this movement, chemical exchange occurs between the two phases.

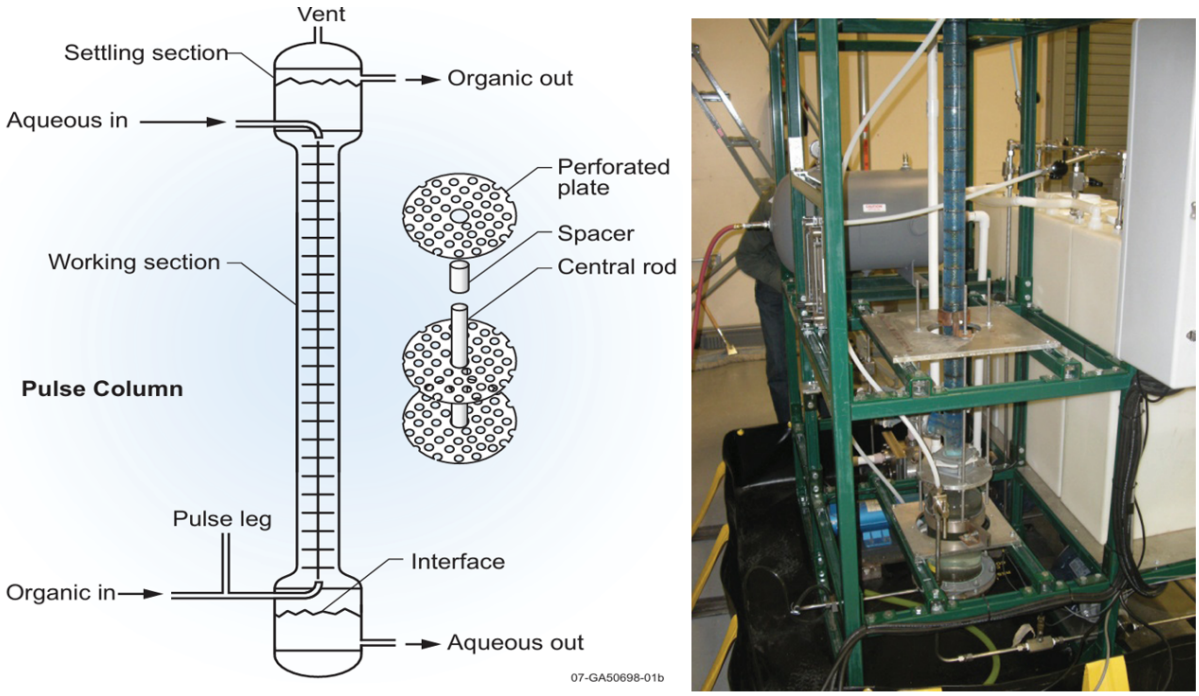

Figure 19. Schematic diagram of a pulse column (left) and a photograph of a glass pulse column (right) showing the dark organic phase rising and the clear aqueous phase sinking.

A mixer-settler is shown in Figure 20 [20]. The organic and aqueous phases enter the mixing chamber of the process where a high-energy impellor aggressively mixes the two phases to facilitate contact between the organic and aqueous phases. The combined solution passes from the mixing chamber into the settling chamber by way of a weir channel. The conditions in the settling chamber are quiescent to allow separation between the organic and aqueous phases, each of which exit the process through a separate outlet.

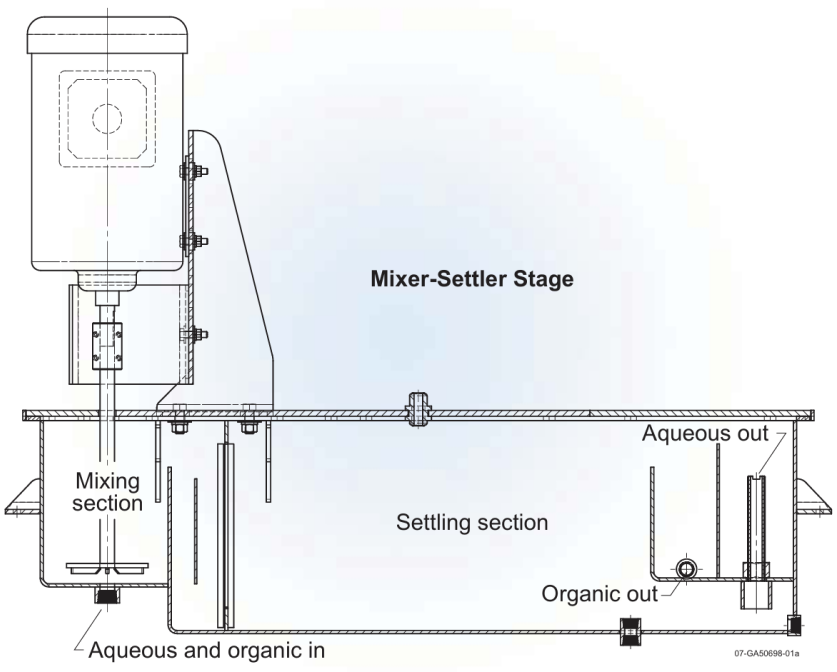

Figure 20. Schematic diagram of a mixer-settler.

Centrifugal contactors are shown in Figure 21 [20]. In a centrifugal contactor, the organic phase enters and exits the process through dedicated ports, as does the aqueous phase. Aggressive mixing of the two phases occurs on the outside of the centrifuge cylinder, while density-based separation of the two phases occurs on the inside of the centrifuge cylinder. In other words, the organic and aqueous phases enter the process separately, are aggressively mixed in the process, and exit the process separately.

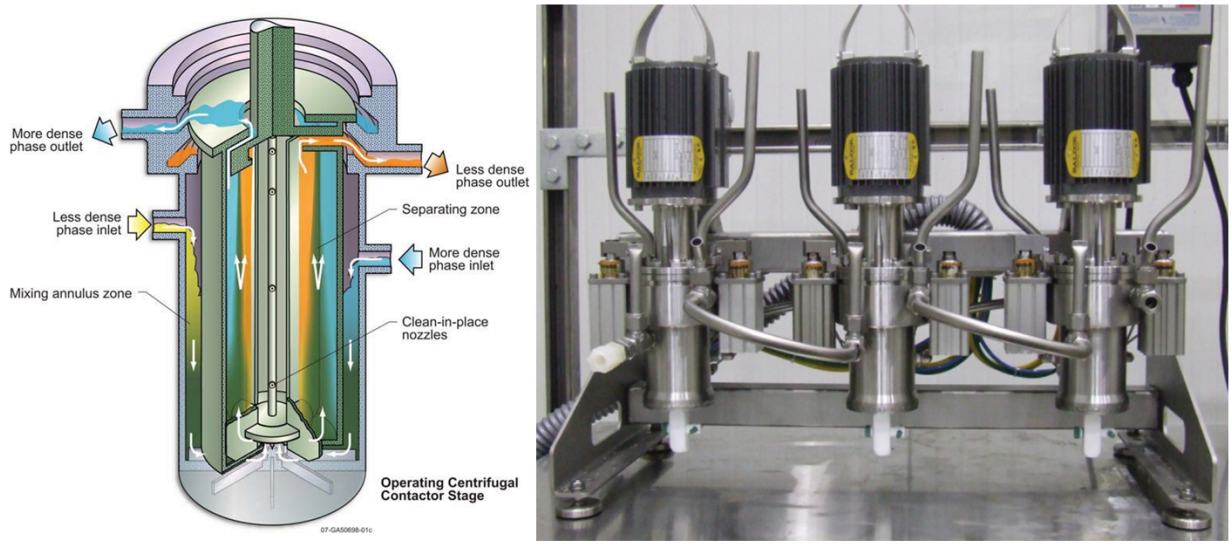

Figure 21. Schematic diagram of a centrifugal contactor (left) and photograph of three centrifugal contactors in a series (right).

These stages are used to build a flowsheet, which is focused on extracting the material of interest, scrubbing unwanted materials out of the phase, and then stripping out the material of interest to produce a purified product stream. The most well-researched and implemented flowsheet for aqueous reprocessing

is the PUREX process. The PUREX process utilizes 20 to 40 vol% tributyl phosphate (TBP) in a hydrocarbon diluent, like kerosene or n-dodecane, as the organic phase and varying concentrations of nitric acid as the aqueous phases [9, 13]. In addition to tributyl phosphate, a hydrocarbon diluent, and nitric acid, other chemicals may be used to aid in the separation process including reductant systems for plutonium and uranium separation. This will be covered further in the report.

High (molar) to low (dilute) concentrations of nitric acid solutions are utilized in the solvent extraction process. Nitric acid is highly corrosive and a strong oxidizer. This can cause severe burns to skin if not washed or flushed quickly. In addition, there is the potential for elevated airborne concentrations of nitric acid vapor, mainly due to its high vapor pressure, which is harmful to the respiratory tract if inhaled [21]. Nitric acid can be flammable when it reacts with reducing agents such as acetone (CH_3COCH_3), disulfuric acids ($H_2S_2O_7$), ammonium permanganate (NH_4MnO_4), and potassium permanganate ($KMnO_4$). Nitric acid can be explosive if it reacts with acetic acid (CH_3COOH). If heated, it will emit NO_x fumes, which are corrosive and can be harmful if inhaled [21].

TBP is categorized as a carcinogen and is harmful if ingested. It is considered an irritant if it is in contact with skin. This chemical is combustible at elevated temperatures and will produce toxic fumes containing phosphorus oxides [8]. A hazard of tributyl phosphate is the generation of red oil. Red oil can form if TBP, decomposed to its byproducts, contacts nitric acid and is heated. Additional information regarding red oil generation and mitigation is discussed further by Liu [22].

4.3.1. Plutonium Reductant Systems

In the PUREX process, plutonium is partitioned from uranium using reductants such as ferrous sulfamate (FS, $Fe(NH_2SO_3)_2$), hydroxylamine nitrate (HAN, $H_4N_2O_4$), hydrazine (N_2H_4), acetohydroxamic acid (AHA, $CH_3CONHOH$), or uranous nitrate U(IV). Each of these reductants reduce the oxidation state of plutonium from Pu(IV) to Pu(III), thus making it unfavorable for complexation by TBP in the organic phase, partitioning it selectively from uranium to the aqueous phase.

4.3.1.1. Ferrous Sulfamate

Ferrous sulfamate utilizes a ferrous ion to reduce Pu(IV) to Pu(III), which is shown in the following reaction [23]:

$$Fe^{2+} + Pu^{4+} \rightarrow Pu^{3+} + Fe^{3+}.$$

In addition, sulfamate is used as a *holding reductant* to aid in limiting the generation of nitrite, which can cause the unwanted oxidation of Fe(II) and Pu(III). The ferrous sulfamate reductant chemistry is shown by the following reactions:

$$NH_2SO_3^- + NO_2^- \rightarrow N_2 + SO_4^{2-} + H_2O$$

$$Fe^{2+} + NO_2^- + 2H^+ \rightarrow Fe^{3+} + NO + H_2O$$

$$Pu^{4+} + NO_2^- + 2H^+ \rightarrow Pu^{3+} + NO + H_2O.$$

Ferrous sulfamate is one of the first chemical plutonium reductants used in large-scale reprocessing facilities, specifically in the mid-1950s at the Savannah River Plant [23]. Although effective, there are several hazards for utilizing the reductant. Due to the required reductant to be in excess, it contributes to increased volume in radioactive waste and increased complexities for waste form immobilization. In addition, it accelerates the corrosion of stainless steel equipment [24]. In terms of health hazards, it is an eye, skin and respiratory tract irritant and can be harmful if ingested [25]. Currently, ferrous sulfamate is not largely used as a plutonium reductant due to other available reductants.

4.3.1.2. Hydroxylamine Nitrate (HAN)

HAN reduces Pu(IV) via the following reaction [26]:

$$2NH_3OH^+ + 4Pu^{4+} \rightarrow 4Pu^{3+} + N_2O \uparrow + H_2O + 6H^+$$

$$2NH_3OH^+ + 2Pu^{4+} \rightarrow 2Pu^{3+} + N_2 \uparrow + 2H_2O + 4H^+.$$

According to these reactions, gaseous species of N_2O and N_2 are generated. The first equation is favored under condition of excess plutonium, while the second equation is favored under conditions of excess HAN. HAN can also reduce Fe (III) to Fe(II) in similar reactions as shown below:

$$2NH_3OH^+ + 4Fe^{3+} \rightarrow 4Fe^{2+} + N_2O \uparrow + H_2O + 6H^+$$

$$2NH_3OH^+ + 2Fe^{3+} \rightarrow 2Fe^{2+} + N_2 \uparrow + 2H_2O + 4H^+.$$

Under certain conditions in the presence of nitrous acid (HNO_2), an autocatalytic reaction can occur that rapidly oxidizes the HAN to produce N_2O. There have been several documented accidents in large-scale DOE plutonium processing facilities, some of which have been linked to the presence of iron as a catalyst in the autocatalytic degradation of HAN, which caused over-pressurization excursions due to inadequate venting. There are several intermediate reactions hypothesized in the autocatalytic degradation of HAN, but the net iron-catalyzed chemical reaction may be expressed as:

$$4NH_3OH^+ \rightarrow 3N_2O \uparrow + 7H_2O + 2HNO_2 \ (Fe\ catalyzed).$$

Most adverse events with the use of HAN have been caused by one common element: the accidental concentration of HAN and nitric acid solutions leading to uncontrolled reactions. Due to the large-scale accidents occurring at DOE facilities, DOE investigated the accidents and provided the following recommendations [26]:

- Incorporate conservative safety-envelope limits into appropriate safety documents, standards, and procedures recognizing the uncertainties in available data.
- Passivate the surfaces of HAN-nitric acid solution tanks and piping.
- Store unused HAN in the original, sealed manufacturer's shipping container. If only portions are used, avoid contamination of the material and reseal the container to preclude evaporation.
- Manage the chemical makeup and addition system by:
  - Defining mixing sequences and procedures.
  - Making up only the amount required.
  - Eliminating direct addition of concentrated acid.
  - Maintaining chemicals within specification.
  - Maintain heating conditions to process specifications.
  - Draining and flushing the system to a neutral pH and refilling with water for extended downtimes.
  - Confirming that tanks assumed operationally empty contain no heel and then draining and flushing.
  - Disposing of unneeded chemicals.
- Ensure an effective system pressure relief.
- Train engineering and operating personnel on the potential hazards along with possible off-normal conditions and mitigations necessary to remain within safety limits.
- Evaluate the use of alternate reductants.

Many large-scale plutonium processing facilities used nominal concentrations of HAN and nitric acid within the range of 0.3 mol/L and 0.1 mol/L, respectively. According to the Nuclear Regulatory Commission (NRC) safety evaluation for the Mixed Oxide Fuel Fabrication Facility in Aiken, SC, the proposed HAN safety strategy summarized in Table 7 was developed [27].

Table 7. Safety strategy for HAN/Nitric at Mixed Oxide Fuel Fabrication Facility.

Principle Structures, Systems, and Components	Safety Function	Parameter	Design Basis
Process Safety Requirements Subsystem	Maintain Temperature Below Safe Limits	Temperature	<100°C (122°F)
Chemical Safety Requirements	Maintain Maximum Nitric Acid Concentration	Concentration of HNO_3	<6 M
	Maintain Maximum HAN concentration	Concentration of HAN	<2.5 M
	Limiting residence time of nitric acid and HAN	Time	As low as reasonable (several months)

To minimize residence time and potential for concentration, residual HAN solutions may be neutralized through the addition of sodium nitrite, thereby eliminating the potential autocatalytic reaction scenario. Empirical correlations have also been developed to estimate the stability of HAN-nitric acid solutions in the presence of an iron catalyst, which may be found in literature [28].

4.3.1.3. Hydrazine

Hydrazine is widely used in combination with another reductant, mainly for the utilization of the chemical as a holding reductant. The importance of hydrazine as a holding reductant is likened to the use of sulfamate in the ferrous sulfamate reductant system; it is used to ensure the stability of Pu(III) and interact with nitrous acid to prevent unwanted species oxidation. Hydrazine is combined with other reductant systems such as HAN, ferrous nitrate, or ferrous sulfamate. Hydrazine itself poses several chemical hazards including being a carcinogen, corrosive, flammable, and reactive. Even though hydrazine is widely seen as a holding reductant, the reaction between hydrazine and nitrous acid forms hydrazoic acid, which is hazardous and potentially explosive. The reaction can be seen below in two steps [24, 29]:

$$N_2H_5^+ + HNO_2 \rightarrow k_1HN_3 + N_2O + H^+$$

$$HN_3 + HNO_2 \rightarrow k_2N_2 + N_2O + H_2O.$$

Hydrazoic acid is an unstable compound with a low boiling point, 35.7°C, making it volatile at room temperature, and has the potential to explode. Savannah River Site conducted a study to better evaluate the safety basis for utilizing hydrazine as a holding reductant and the potential generation of hydrazoic acid. The study provided the following results and recommendations [30]:

- The critical explosive concentration for hydrazoic acid is 4.7 M in aqueous solution.
- It is recommended to use a dilute solution of hydrazine in the reductant system to limit the amount of hydrazoic acid generated.

- There is the potential for extraction of hydrazoic acid into the organic phase. This would result in the formation of sodium azide in the solvent wash stages.
- It is recommended that hydrazoic acid should be treated with sodium nitrite prior to disposal.

4.3.1.4. Acetohydroxamic Acid (AHA)

Acetohydroxamic acid (AHA) complexes and reduces plutonium from the organic phase for selective uranium-plutonium partitioning, mainly for UREX-based flowsheets designed to hinder the ability to produce a purified plutonium stream. Although effective at plutonium reduction, AHA/$CH_3CONHOH$ is known to degrade in acidic solution via hydrolysis to form acetic acid (HAc/CH_3COOH) and hydroxylamine (HAN/NH_3OH^+):

$$CH_3CONHOH + H_3O^+ \rightarrow CH_3COOH + NH_3OH^+.$$

With the production of HAN from AHA degradation, similar hazards and recommendations to HAN utilization are still applicable, especially in the presence of nitrous acid and iron [31]. In addition, these hazards can be mitigated by limiting the amount of time between production of AHA and implementing it into the flowsheet and limiting the concentration of AHA used in the process.

4.3.1.5. Uranous Ion, U(IV)

Uranous ion, U(IV), is utilized to reduce Pu(IV) to Pu(III) and is shown in the following reaction [32]:

$$U^{4+} + 2Pu^{4+} + 2H_2O \rightarrow U_2^{2+} + 2Pu^{3+} + 4H^+$$

$$3U^{4+} + 2PuO_2^{2+} + 2H_2O \rightarrow 3U_2^{2+} + 2Pu^{3+} + 4H^+.$$

U(IV) is advantageous as a reductant system as it does not introduce additional volatile or corrosive constituents to the solvent extraction process. Savannah River Site conducted studies on U(IV) as a potential reductant to replace the ferrous sulfamate-hydrazine reductant system. Although U(IV) is effective at reducing plutonium, it is not very stable in its oxidation state. Therefore, additives such as hydrazine are incorporated to complex the nitrous acid and provide stability for U(IV) in solution. Recommendations and hazard mitigations for hydrazine were discussed previously. It is currently being utilized as the reductant for the Rokkasho Mura reprocessing plant in Japan [24].

4.4. Solidification

Solidification involves the conversion of the purified uranyl nitrate solution to a solid oxide form. There are various methods that can be utilized including denitration, precipitation/calcination, and co-precipitation. In addition to various solidification methods, various equipment types can be utilized for these processes. This includes fluidized beds, stirred pot reactors, rotary kilns, calciners, and evaporators. Several, if not all, of these equipment types utilize high temperatures for operations. An HLW calciner is shown in Figure 22 [33]. This report section will cover the various solidification methodologies and operating equipment, where there is significant overlap in operations and potential hazards.

Figure 22. Photograph of an HLW calciner at Orano la Hague vitrification plant.

For evaporation operations, steam is the primary heat source. Steam can be hazardous as it can cause severe burns or scalding to personnel. Equipment malfunctions such as an increase in pressure, aging or unmaintained equipment may result in explosions or steam leaks. Introducing chemicals that should not be heated or may cause unintended reactions are a hazard when operating high-temperature equipment. To date, several evaporator explosions have been caused due to the introduction of chemicals and therefore unintended reactions with TBP and HAN [22]. Toxic vapors and gases may be generated during evaporation operations. These gases may be harmful to personnel or the surrounding environment if released. In addition to being harmful to the environment and surrounding population, these gases may cause equipment corrosion or accumulation, leading to potential equipment malfunctions. Therefore, off-gas treatment processes are implemented to provide a method for the capture or treatment of toxic vapors prior to release.

There are several methodologies to mitigate the potential hazards of solidification equipment operations and chemistry involved [22], as follows:

- Incorporate conservative safety-envelope limits into appropriate safety documents, standards, and procedures recognizing the uncertainties in available data. This includes:
  - Limiting the use of reductants to aid in decreasing the potential for unwanted reactions.
  - Limiting the concentration and accumulation of TBP and nitrates throughout the process with regular cleaning operations.
- Operate heated equipment below threshold temperatures to avoid the generation of potential excursions.
- Proper off-gas and ventilation equipment and operations to limit the buildup of vapors and pressure within the equipment.

4.4.1. Denitration

The main goals of denitration are to remove the excess nitric acid and nitrates from the uranyl nitrate solution to produce a purified uranium oxide product [34]. Denitration methodologies focus on either direct denitration or modified direct denitration.

Direct denitration can be described as a two-step process. First, the dilute uranyl nitrate solution is evaporated to reduce its water and nitric acid content. This produces a uranium nitrate hexahydrate molten salt. The evaporation process is then followed by calcining and decomposing the solution to a solid oxide product. The dehydration and decomposition reaction mechanisms for uranyl nitrate are provided below [35]:

$$UO_2(NO_3)_2 \cdot 6H_2O\ (aq) \xrightarrow{\Delta} UO_2(NO_3)_2\ (l) + 6H_2O(g)$$

$$UO_2(NO_3)_2\ (l) \xrightarrow{\Delta} UO_3\ + NO_2 + NO + O_2.$$

During the denitration processing, off-gas species, such as nitrogen oxides (NO_x), are generated. NO_x has harmful environmental and health effects. Environmental effects include air pollution and interactions with other chemicals in the atmosphere to produce acid rain. NO_x can have respiratory, systemic, and reproductive effects on humans and animals [36]. Therefore, NO_x is treated through off-gas treatment systems such as scrubbers.

The modified direct denitration (MDD) process reacts concentrated uranyl nitrate solution with ammonium nitrate to yield an NH_4:U mole ratio that is between 2.0 and 2.6. This forms a double salt of uranyl nitrate-ammonium nitrate. The double salt solution is then introduced into a rotary kiln for calcination at elevated temperatures. As mentioned above, the calcination process is a well-studied process developed by ORNL in the 1980s that produced a powder form of uranium oxide with good ceramic properties used for fuel [37, 38]. The decomposition behavior within the rotary kiln consists of a five-step process: (1) double salt formation, (2) evaporation of remaining water/nitric acid, (3) dehydration of the double salt, (4) partial denitration, and (5) full denitration/oxide formation [35]. The decomposition of the varying double salts is complex, but the overall reactions taking place are provided below:

$$(NH_4)_2UO_2(NO_3)_4 \cdot 2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_4 + 2H_2O$$

$$(NH_4)_2UO_2(NO_3)_4 \rightarrow NH_4UO_2(NO_3)_3 + N_2O + 2H_2O$$

$$NH_4UO_2(NO_3)_3 \rightarrow UO_3 + N_2O_5 + N_2O + 2H_2O.$$

The above equations show the dehydration of the double salt, which takes place at 50°C. The decomposition of the tetranitrate salt takes place between 170 and 270°C. Lastly, UO_3 is produced with the decomposition of the trinitrate salt taking place between 270 and 300°C. Further heating in excess of 500°C results in crystalline U_3O_8 [37]. This decomposition takes place within a rotary kiln inner tube that is maintained at a furnace temperature setpoint between 650 and 675°C.

The main difference between direct denitration and MDD is the use of ammonium nitrate, which is used in MDD to produce a more free-flowing, high surface area powder for calcination. However, ammonium nitrate can have explosive properties and is a component in explosive mixtures in the mining and construction industry; therefore, additional care for storage and usage of the chemical should be implemented. A study was performed by Baker Risk to assess the detonability of various ammonium nitrate solutions at elevated temperatures [39].

4.4.2. Precipitation/Calcination

For uranium precipitation processes, a precipitant is added to the uranyl nitrate solution such as ammonia, ammonium carbonate, or hydrogen peroxide. These precipitants complex the uranyl nitrate to

produce an intermediate product and generate slurry. The intermediates include ammonium diuranate (ADU), ammonium uranyl carbonate (ACU), or uranyl peroxide (UO_4), respectively. The precipitate slurry is then filtered from the supernate and calcined to a uranium oxide powder, UO_3 or U_3O_8, depending on calcination temperature [40].

For plutonium solidification processes, the plutonium nitrate is initially evaporated to create a concentrated solution. Next, an additive such an oxalic acid is used to precipitate the plutonium oxalate. The precipitate slurry is then filtered from the supernate and calcined to a plutonium oxide powder. [40].

4.4.3. Co-Precipitation

The co-precipitation process involves the solidification of a mixed plutonium/uranium oxide product rather than solidification of individual purified plutonium and uranium oxide products. Feedstock to a co-precipitation process may be produced through careful control of solvent extraction conditions to generate a mixed uranium/plutonium nitrate liquid product directly from solvent extraction, or by separating individual uranyl nitrate and plutonium nitrate streams in solvent extraction followed by liquid blending to the desired U/Pu ratio prior to co-precipitation. Co-precipitation methodologies are mainly focused on mixed oxide (MOX) fuel production and provide a non-proliferation pathway to prevent a purified plutonium stream. The French Alternative Energies and Atomic Energy Commission (CEA) and AREVA SA are implementing the operation of the COEX (co-extraction) processes. Germany has their own co-precipitation process, and the Japanese reprocessing facility, Rokkasho, has implemented co-precipitation technologies.

The co-precipitation methodologies are similar to single species precipitation and calcination operations, especially in terms of precipitation additives and utilized equipment types. The main processes are ammonia co-precipitation, oxalate co-precipitation, and ammonium-uranyl-plutonyl-carbonate (AUPuC). The ammonia co-precipitation process is very similar to the ammonium diuranate precipitation process. The main variance is the use of a lower calcination temperature to ensure good MOX powder homogeneity. The oxalate co-precipitation is very similar to oxalate precipitation processes for plutonium, but it requires an additional front-end step by introducing hydrazine as a “holding reductant” for uranium in the solution. AUPuC co-precipitation initially requires a conversion of plutonium to its hexavalent state from the tetravalent state by heating the solution. Next, the precipitation process utilizes ammonia and carbon dioxide to precipitate the two species from the nitrate solution [41].

4.4.4. Chemical Process Safety Considerations: Red Oil

According to a 2003 technical report from Robinson et al., “Red oil is defined as a substance of varying composition formed when an organic solution, typically tributyl phosphate (TBP) and its diluent (kerosene), comes in contact with concentrated nitric acid at a temperature above 120°C” [42]. At temperatures above 130°C, the decomposition of the red oil generates significant amounts of heat and gases. The heat and gas generation may lead to an autocatalytic reaction and a subsequent runaway reaction.

Explosions or chemical excursions in nuclear fuel reprocessing facilities can result in significant releases of radioactive materials to the environment. The NRC report titled *Review of Spent Fuel Reprocessing and Associated Accident Phenomena* [43] provides a review of requirements for the safe operation of a nuclear fuel reprocessing facility utilizing an aqueous reprocessing approach, such as the PUREX process. From the conclusions presented by these authors, the types of unit operations that have the potential to produce red oil when TBP, nitric acid, and an organic diluent are mixed are process evaporators, acid concentrators, and denitrators. The formation and subsequent catastrophic decomposition of red oil may be mitigated by maintaining process temperatures below 130°C, ensuring sufficient process venting to prevent pressurization of process equipment, minimizing the concentration of organics present in feed to unit operations where heating occurs, and maintaining nitric acid concentration below 10 M.

Several reviews of red oil explosions or other chemical excursions in nuclear fuel processing facilities have appeared in the literature [44, 45, 46, 47, 48, 49]. Liu et al. [50] conducted an analysis of eighteen explosions that have occurred in nuclear fuel reprocessing facilities worldwide since the early 1950s. The authors grouped these incidents into red oil explosions, detonation of nitrogenous substances, hydrogen explosions, and hydroxylamine nitrate explosions. A common theme is the inadvertent introduction of an organic compound (TBP and kerosene diluent) into evaporators used for nitric acid concentration or uranium denitration.

TBP ($OP(OC_4H_9)_3$) and nitric acid (HNO_3) can react in different ways to form phosphoric acid (H_3PO_4), nitrogen gas (N_2), nitrogen oxide gases (NO_x), carbon dioxide gas (CO_2), and steam (H_2O) [51].

The following reaction shows the complete oxidation of TBP:

$$OP(OC_4H_9)_3 + 14.4\ NHO_3 = H_3PO_4 + 7.2\ N_2(g) + 12\ CO_2(g) + 19.2\ H_2O(g).$$

The following alternative reactions show the partial oxidation of TBP. The reactants are TBP as the *fuel* and nitric acid as the *oxidizer*. Nitrate salts can also serve as *oxidizers*.

Complete oxidation of reaction products

$$OP(OC_4H_9)_3 + 24\ NHO_3 = H_3PO_4 + 24\ NO(g) + 12\ CO_2(g) + 24\ H_2O(g)$$

Partial oxidation of reaction products forming CO(g)

$$OP(OC_4H_9)_3 + 16\ NHO_3 = H_3PO_4 + 16\ NO(g) + 12\ CO(g) + 20\ H_2O(g)$$

Partial oxidation of reaction products forming $N_2O(g)$

$$OP(OC_4H_9)_3 + 18\ NHO_3 = H_3PO_4 + 9\ N_2O(g) + 12\ CO_2(g) + 21\ H_2O(g).$$

These reactions are meant only to be illustrative of "red oil" excursion chemistry. Reality is much more complex, and additional effects must be considered such as the concentration of nitric acid, the presence of TBP radiolysis and hydrolysis products, the presence of nitrate salts, and temperature. Nevertheless, all these reactions are thermodynamically spontaneous, exothermic, and generate gaseous reaction products. Limiting the availability of either of the reactants (*fuel* or *oxidizer*) will limit the extent to which these energetic reactions can occur.

Hyder [51] recommended the following preventative measures, which are captured here:

1. Ventilation of the vessels is the first defense against a damaging runaway reaction. Based on the data obtained by Fauske[25], in vessels containing nitric acid where TBP accumulation is a concern, a vent should be provided that provides a vent area of 0.032 cm^2 per kg of TBP that it is considered possible to accumulate in them. Maintaining continuous airflow through the headspace is also desirable, as it provides cooling and removes accumulating gases. [Note: The system venting sizes required to handle excursions are reported by Paddleford [52].
2. TBP that has degraded as the result of radiation or hydrolysis should be washed and tested before reuse. TBP allowed to stand for several months in the presence of aqueous acids or bases and/or radiation should be regarded as suspect in this regard.
3. Evaporators in which TBP may be present should be controlled to prevent local high temperatures. No portion or surface of the evaporator should exceed 130°C, and operating temperatures substantially lower than this are desirable. If evaporators, calciners, or other heating units must operate at higher temperatures, the procedures for preventing the introduction of TBP into them must be correspondingly rigorous.
4. Evaporated solutions are a particular concern, as they come from the evaporator hot, and are typically allowed to settle while cooling. A variety of measures may be appropriate to guard against runaway reactions of TBP unintentionally introduced into such solutions. Sparging,

mechanical mixing, cooling by cooling coils, operation of the condenser, or provision of a large vent may be appropriate for this purpose, depending on the design of the system and the perceived hazard.

5. Operators of PUREX and similar solvent extraction processes should be aware of the potential for reaction of nitric acid or nitrates with TBP. Perhaps the greatest potential accidents lie in non-standard operations (e.g., startup, shutdown, maintenance, extended shutdown) that must be performed from time to time. The potential for accidents should be taken into account whenever changes are made in process or equipment.

Robinson [42] recommended preventative measures, similar to those of Hyder [51], which are captured here:

- Temperature. Maintaining a temperature of less than 130°C is generally accepted as a means to prevent any red oil explosions.
- Pressure. Sufficient venting serves to prevent an over-pressure from destroying the process vessel while also providing the means for evaporative cooling to keep red oil from reaching the runaway temperature.
- Mass. Mass control utilizes decanters or other liquid-liquid separation equipment to remove TBP from feed streams entering heated process equipment, eliminating one of the necessary components to form red oil. In robust containment (i.e., canyons), mass control can be used to mitigate the consequences of a red oil explosion by limiting vessel size and organic concentration to a maximum available explosive energy the containment can withstand.
- Concentration. Concentration control can be utilized to keep the nitric acid below 10 *M*.

4.5. Off-Gas Systems

Gaseous emissions are relevant to each unit operation of aqueous reprocessing, and Figure 23 provides a schematic of where these emissions may evolve throughout the process [53]. Aqueous reprocessing facilities have robust off-gas stream treatment to prevent the release of semi-volatile elements and other hazardous gaseous vapors to the atmosphere. A more indepth discussion of the various off-gas stream treatment methodologies are provided in the counterpart report, *Aqueous and Pyrochemical Reprocessing Chemical Safety: Technical Descriptions to Aid Regulatory Considerations* [54].

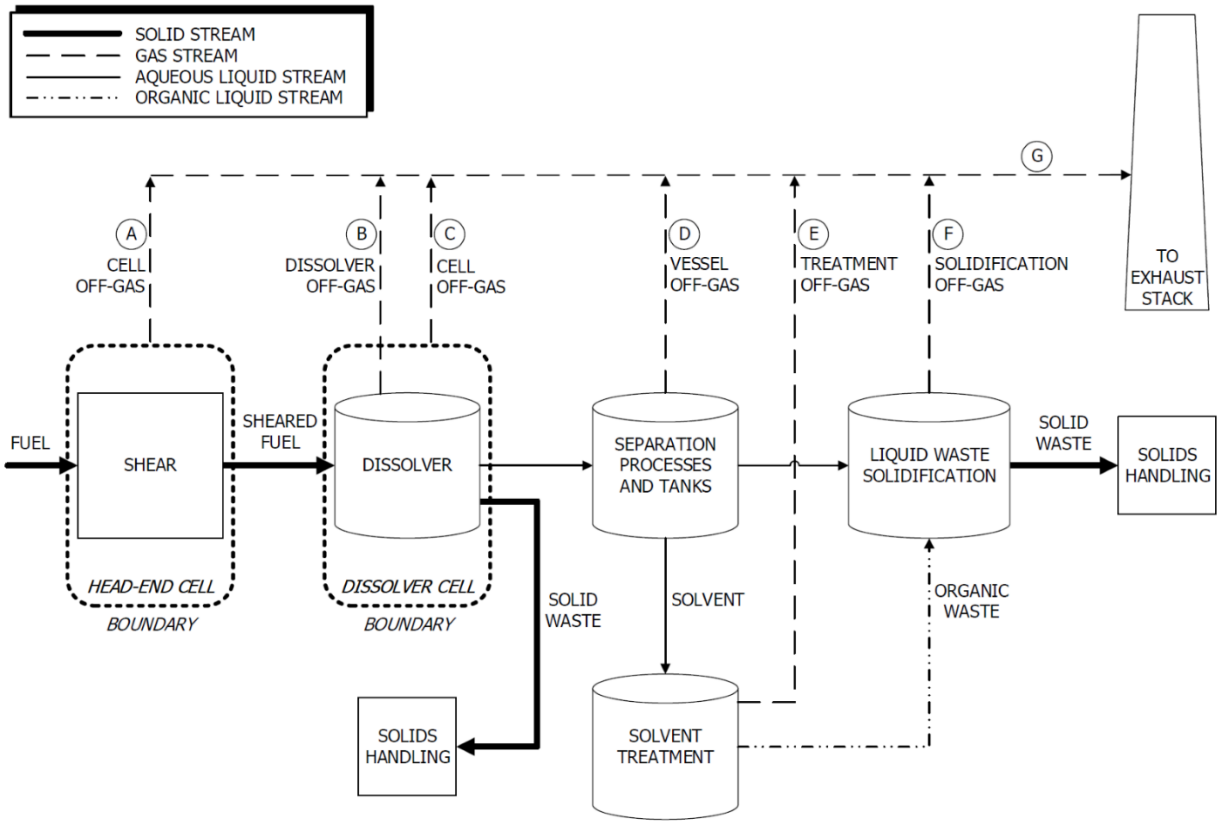

Figure 23. Schematic diagram showing aqueous reprocessing off-gas streams.

The unit operations that produce the most significant chemical hazards, in terms of gaseous release, include dissolution, separation processes, and solidification.

DOG streams are focused on treating the volatile species that are generated during spent fuel dissolution processes. Each species generated during dissolution that is harmful to downstream processes, personnel, and the environment is discussed in this section. During the dissolution of spent nuclear fuel in concentrated nitric acid, generation of nitric oxide (NO) and nitrogen dioxide (NO_2) occurs. The governing chemical reactions for this gas generation are shown below for uranium oxide and uranium metal dissolution:

Uranium oxide dissolution [55]

$$3\ UO_2 + 8\ HNO_3 \rightarrow 3\ UO_2(NO_3)_2 + 2\ NO(g) + 4\ H_2O(g)$$

$$UO_2 + 4\ HNO_3 \rightarrow UO_2(NO_3)_2 + 2\ NO_2(g) + 2\ H_2O(g)$$

Uranium metal dissolution [56]

$$U + 4\ HNO_3 \rightarrow UO_2(NO_3)_2 + 2\ NO(g) + 2\ H_2O(g)$$

$$U + 8\ HNO_3 \rightarrow UO_2(NO_3)_2 + 6\ NO_2(g) + 4\ H_2O(g).$$

Concentrations of NO and NO_2 in the DOG stream may vary depending on the nitric acid concentration and dissolution temperature. There are several reasons for the implementation of NO_x removal technologies into aqueous reprocessing off-gas treatment. NO_x removal is pertinent for downstream equipment lifecycles as it is corrosive. Removal, and therefore collection, provides acid recycle technologies to reduce the HNO_3 makeup [13]. In addition, NO_x has harmful environmental and health effects. Environmental effects include air pollution and interactions with other chemicals in the

atmosphere to produce acid rain. NO_x can have respiratory, systemic, and reproductive effects on humans and animals [36]. Nitric oxide and nitrogen dioxide release from aqueous reprocessing facilities is mitigated using off-gas treatment systems such as scrubbers. Although not all gas release is mitigated, the consensus is that release is below harmful levels and emission regulation levels to protect the environment and population.

In addition to NO_x generation, the release of volatile and semi-volatile radionuclides occurs during the dissolution operation. This includes tritium (^{3}H), carbon-14 (^{14}C), ruthenium (^{106}Ru), krypton (^{85}Kr), and iodine (^{129}I). These species can pose harmful effects on the environment and populations and are as such regulated via the U.S. Environmental Protection Agency (EPA) and the U.S. Nuclear Regulatory Commission (NRC). The applicable EPA and NRC regulations for radionuclide release include 40 CFR 190 and 10 CFR 20, respectively. Both regulations discuss the release limits not only to nuclear facility workers but also to the general environment and populations [57]. Volatile and semi-volatile radionuclide release from aqueous reprocessing facilities is mitigated using focused off-gas treatment technologies for each regulated species. Additional information regarding specific species' treatment technologies is provided in the counterpart report, *Aqueous and Pyrochemical Reprocessing Chemical Safety: Technical Descriptions to Aid Regulatory Considerations* [54].

During dissolution processes, there is the potential for hydrogen generation. Hydrogen gas is flammable and can lead to explosions and therefore unplanned releases of radionuclides [58].

Vessel off-gas is focused on the venting of the vessel processes, mainly for the separation processes. Organics, especially organic iodides, are a large source of gaseous species that are generated in this off-gas stream. Organic iodide specification can be quite complex in the vessel off-gas but includes species such as methyl iodide (CH_3I), butyl iodide (C_4H_9I), and dodecyl iodide ($CH_3(CH_2)_{11}I$). In addition to the complex organic iodide speciation, it is harder to treat. Organic iodides are radiotoxic and therefore, if not properly captured, can be released and are harmful to the environment and the surrounding population [59].

Similar to dissolution, there is the potential for high hydrogen or tritium content to be in the vessel off-gas stream. This could create a potential ignition source and damage to the off-gas system, leading to unintended release, or potential pressurization [60].

Solidification off-gas is focused on the release of volatile radionuclides, steam, and nitrogen oxides that may occur during the evaporation and denitration of the waste streams [61]. The capture technologies for these species are similar to the technologies discussed previously.

5. GOVERNING DOCUMENTS

Protecting the health and safety of workers, the surrounding population, and the environment is of paramount importance.

Chemical processes at NRC regulated facilities may involve occupational safety under the purview of both the NRC and the Occupational Safety and Health Administration (OSHA). In 2013, 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 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 occupational hazards 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.

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.

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 following OSHA regulations may or may not apply to an NRC-licensed facility:

- 29 CFR Part 1910, “Occupational Safety and Health Standards,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-29/subtitle-B/chapter-XVII/part-1910
- 29 CFR Part 1910.120, “Hazardous Waste Operations and Emergency Response,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-29/subtitle-B/chapter-XVII/part-1910/subpart-H/section-1910.120
- 29 CFR Part 1910.1096, “Ionizing Radiation,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-29/subtitle-B/chapter-XVII/part-1910/subpart-Z/section-1910.1096
- 29 CFR Part 1910.1450, “Occupational Exposure to Hazardous Chemical in Laboratories,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-29/subtitle-B/chapter-XVII/part-1910/subpart-Z/section-1910.1450
- 29 CFR Part 1926, “Safety and Health Regulations for Construction,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-29/subtitle-B/chapter-XVII/part-1926?toc=1

Additional regulations and directives pertaining to chemical process safety primarily at DOE facilities are cited below. These references included for information and are not part of the NRCs regulatory framework.

- 10 CFR Part 830, “Nuclear Safety Management,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-10/chapter-III/part-830
- 10 CFR Part 850, “Chronic Beryllium Disease Prevention Program,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-10/chapter-III/part-850?toc=1
- 10 CFR Part 851, “Worker Safety and Health Program,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-10/chapter-III/part-851?toc=1
- 40 CFR Part 355, “Emergency Planning and Notification,” Code of Federal Regulations, National Archives and Records Administration, https://www.ecfr.gov/current/title-40/chapter-I/subchapter-J/part-355
- DOE O 200.1A, “Information Technology Management,” U.S. Department of Energy, https://www.directives.doe.gov/directives-documents/200-series/0200.01-BOrder-a
- DOE O 440.1B, “Worker Protection Program for DOE (Including the National Nuclear Security Administration) Federal Employees,” U.S. Department of Energy, https://www.directives.doe.gov/directives-documents/400-series/0440.1-BOrder-b-chg2-AdmChg
- DOE O 458.1, “Radiation Protection of the Public and the Environment,” U.S. Department of Energy, https://www.directives.doe.gov/directives-documents/400-series/0458.1-BOrder
- “Dose Coefficients for Intakes of Radionuclides by Workers,” Annals of the International Commission on Radiological Protection, Publication 68, Volume 24, Number 4, 1994
- “Age-dependent Doses to Members of the Public from Intake of Radionuclides - Part 5 Compilation of Ingestion and Inhalation Coefficients,” Annals of the International Commission on Radiological Protection, Publication 72, Volume 26, Number 1, 1995.

6. PUREX CHEMICALS LIST

The chemicals approved for use in the FCF transuranic glovebox for aqueous reprocessing research are listed in Table 8. Not all the chemicals in this table are included in the hazardous chemicals analysis and materials-at-risk (MAR) analysis. This is because either the chemicals are not hazardous, or the chemicals are hazardous but are exempt from the hazards analyses because they are only used in diminutive quantities.

Table 8. Chemical list for aqueous reprocessing research glovebox.

Chemical	Purpose	Primary Hazards
Acetohydroxamic acid	UREX Pu complexant	Reproductive toxicity
Ag exchanged zeolite (IONEX Type AG-900)	Iodine off-gas capture	Carcinogen
Aluminum nitrate	Fluoride complexant for HF dissolution	Irritant, acute toxicity, carcinogen
Ammonia	Uranium precipitation	Flammable, corrosive, environmental toxicity
Ammonium hydroxide	Precipitation	Environmental toxicity, corrosive
Ammonium nitrate	Solidification, pH adjustment	Oxidizer, irritant
Dodecane	Solvent extraction (diluent)	Combustible, aspiration toxicity
Dowex 50Wx8 (resin)	Ion exchange purification	Eye damage/irritant
Dowex 50W x12 (resin)	Ion exchange purification	Eye damage/irritant
Exxsol D80	Solvent extraction (diluent)	Combustible, aspiration toxicity
Ferrous sulfamate	Plutonium reductant in solvent extraction	Irritant
Hydrazine	Nitrous acid scavenger for Pu reductants in solvent extraction	Severe acute toxicity, carcinogen, environmental toxicity, corrosive
Hydrofluoric acid	Fuel dissolution	Severe acute toxicity, corrosive
Hydrogen	Uranium oxide reduction, generated in some dissolution processes	Flammable
Hydrogen peroxide	Dissolution, precipitation	Acute toxicity, environmental toxicity
Hydroxylamine nitrate	Plutonium reductant in solvent extraction	Severe acute toxicity, irritant, carcinogen, environmental toxicity
Isopar L (exon mobile)	Solvent extraction (diluent)	Combustible, aspiration toxicity
Kerosene (lamp oil)	Solvent extraction (diluent)	Combustible, aspiration toxicity

Chemical	Purpose	Primary Hazards
Nitric acid	Dissolution, solvent extraction, solvent rinsing, NO_x scrubbing	Oxidizer, severe acute toxicity, corrosive
Nitric oxide	Generated during dissolution processes	Oxidizer, corrosive, severe acute toxicity
Nitrogen	Cover gas, pneumatics	Asphyxiant
Nitrogen dioxide/dinitrogen tetroxide	Generated during dissolution processes, oxidization processes	Oxidizer, corrosive, severe acute toxicity
Nitrous oxide	Generated during solidification	Oxidizer, asphyxiant
Oxalic acid	Plutonium precipitation	Corrosive, environmental toxicity
Oxygen	Fumeless dissolution, voloxidation	Oxidizer
poly-4-vinyl-pyridine resin (Reillex)	Plutonium anion exchange	Non-hazardous
sodium carbonate	Solvent washing, neutralization	Irritant
sodium nitrite	Plutonium oxidation state adjustments	Oxidizer, acute toxicity, irritant
Sulfuric acid	Specialized precipitation processes	Corrosive, irritant
tributyl phosphate	Extractant in solvent extraction	Irritant, carcinogen, acute toxicity
zirconyl nitrate	Fluoride complexant for HF dissolution	Oxidizer, corrosive

7. SUMMARY

NRC has regulatory responsibility for chemical hazards associated with nuclear material processing when the chemical hazard is associated with, or derived from, licensed material (e.g., UF_6), when the chemical hazard is intimately mixed with the licensed material (e.g., a solution of uranium nitrate in nitric acid), and when a chemical hazard could impact the ability of plant personnel to control license material operations (e.g., toxic chemical release into a control room).

Aqueous and pyrochemical reprocessing both aim to recover fissile and fertile material from spent nuclear fuels but use very different chemical processing media and separation concepts. Aqueous reprocessing generally uses a solvent extraction system that can selectively recover uranium and plutonium from a nitric acid solution. Pyrochemical reprocessing generally relies on electrochemical differences to recover uranium from a molten salt media. However, each technology route presents its own set of chemical safety considerations. For example, aqueous reprocessing utilizes aqueous and organic solutions to affect separations, while pyrochemical reprocessing utilizes high-temperature molten salts.

This report introduces the general concepts of aqueous and pyrochemical reprocessing, presents examples of common steps in the two general forms of reprocessing, and presents examples of potential chemical hazards (toxic and energetic reactions) for the various process steps. This information can help the staff as they conduct application-specific chemical safety reviews.

While the focus of this document is chemical safety, it is pointed out that chemical safety can be impacted by or can impact chemical/physical phenomena in other safety areas and so safety reviews should be coordinated. For example, chemical reactions can produce combustible material and therefore impact fire safety. Also, chemical reactions can result in the precipitation of fissile material and therefore impact criticality safety.

Other safety areas that can be impacted by or can impact chemical physical/phenomena are as follows.

Criticality Safety: Fissile materials must be handled accordingly to prevent conditions that can lead to a criticality event. Staff responsible for handling fissile materials are subject to rigorous training and supervision protocols.

Materials Control and Accountancy: Though this topic pertains to safeguards and security considerations, materials control and accountancy practices are essential for knowing the type, form, quantity, and location of all fissile and radioactive materials will help inform all facility safety analyses will be predicated on accurate knowledge of the process inventories of all materials.

Materials Containment: Engineered systems are used to prevent the spread of radionuclides and chemicals, within regulatory limits, that are dangerous to people and the environment.

Decay Heat Management: The radioactive decay of certain fission products can result in significant heat generation, particularly in younger spent fuels. These radioisotopes can accumulate in process equipment and must be managed accordingly.

Chemical Safety: Chemical toxicity and radiological toxicity effects must be considered for all process chemicals. For certain isotopes, it is possible that chemical toxicity outweighs radiological toxicity, and vis versa. The process chemicals required will be dependent on the reprocessing technologies selected, and the acceptable quantities may be limited by consideration of the consequences of plausible accident scenarios.

Robust Waste Forms: Certain process wastes will contain radioactive fission products and other hazardous chemicals. These wastes must be long-lasting under their intended storage environment to prevent the release and spread of these constituents into the environment.

Administrative and Engineering Controls: All aspects of chemical safety will rely on administrative controls that proceduralize and standardize the many tasks performed by operations staff, and engineering controls that ensure the process equipment is safely operated well within the design specifications.

Safety Culture: A strong safety culture relies on training, experience, and human reliability. Training establishes both foundational knowledge and expectations. Experience leads to process improvements. Human reliability decreases human errors.

Finally, it should be noted that considerations of chemical safety are not merely restricted to the reagent chemicals supplied to the processes but must also consider the constituents of the spent fuels being processed. At some point in any process, the constituents of the spent fuels and those of the process chemicals become indistinguishable from each other. This occurs in aqueous reprocessing as the fuels are dissolved into nitric acid solutions, and in pyrochemical reprocessing as the fuels are electrochemically treated in molten salts.

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