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Technology Development Roadmap for Volatile Radionuclide Capture and Immobilization

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Technology Development Roadmap for Volatile Radionuclide Capture and Immobilization

Nuclear Fuel Cycle and Supply Chain

Prepared for
U.S. Department of Energy
Material Recovery and Waste Form Development Campaign

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SUMMARY

An "Off-Gas and Waste Forms Strategy Workshop" was held in Washington, D.C. on January 31, and February 1, 2023, to review the current state of the art (baseline) technologies for capturing and immobilizing these volatile radionuclides in waste forms (WFs). The discussions in that workshop were used to develop a roadmap for future research and development to mature technologies that are presently not ready for use in a commercial reprocessing facility and develop and demonstrate technologies that provide more safety, more simplicity, or lower costs compared to the current baseline.

Relatively mature capture technologies are available for ^{3}H and ^{14}C, and cryogenic distillation has been successfully used to capture Kr and Xe. Capture technologies for ^{3}H in the form of tritiated water include conventional condensation, wet scrubbing, and solid regenerable sorbent, followed by grouting the captured water and placement, if needed, in a high-integrity container. Capturing ^{14}C in the form of $^{14}CO_2$ can be accomplished with wet scrubbing. The captured ^{14}C can be converted into relatively insoluble $Ca^{14}CO_3$ or similar low-solubility solids, and grouted. The Kr and Xe can be captured and separated from each other in cryogenic distillation, after which the Kr can be stored in compressed gas cylinders. Even these most mature technologies require integrated, high-fidelity, pilot-scale demonstration to reduce the cost, schedule, and technical risk for a future aqueous reprocessing facility**.**

Solid sorbents have been studied as potentially simpler, lower cost and lower risk alternatives to cryogenic Kr/Xe separations. Solid sorbents studied to date include hydrogen and silver mordenites in polyacrylonitrile matrix (HZ-PAN and AgZ-PAN) and metal organic frameworks (MOFs). Further research and development (R&D) is needed to develop and demonstrate solid sorbent performance and capabilities for capturing and separating Kr and Xe under prototypic off-gas compositions.

Silver nitrate coated ceramic supports have been used in the past to chemisorb iodine from the off-gas streams in reprocessing facilities; but these materials did not reliably meet the current more-stringent removal requirements in the U.S. Silver mordenite is currently considered a baseline technology for iodine capture in the U.S. because it has been shown to achieve the needed iodine removal efficiency. Iodine capture and WF technologies still require R&D, including high-fidelity pilot-scale testing, to reduce cost, schedule, and technical risk for a future aqueous reprocessing facility. Various iodine WFs have been studied, with the primary focus on WFs that are durable, leach-resistant, and can be produced at lower temperatures or higher pressures to retain, rather than revolatilize, the chemisorbed iodine.

Voloxidation of used nuclear fuel prior to aqueous processing may simplify the design and lower the cost of a reprocessing facility. Voloxidation variants are being studied to volatilize a significant fraction of one or more of the volatile radionuclides into a single gas stream rather than multiple gas streams, which would simplify volatile radionuclide control. Voloxidation is also being studied to oxidize the used fuel and may enable the oxidized fuel to be directly dissolved into an organic solvent rather than first into aqueous HNO_3 solution. If successful, this would eliminate the first solvent extraction step. Further R&D is needed to address performance, system design, and operating conditions. In the near term, research is needed to determine the applicability of voloxidation to fuel recycling and, if viable, lay out a development plan.

Research and development of real-time, highly sensitive ^{129}I analysis should accompany future ^{129}I capture R&D. If ^{129}I analysis technology with higher sensitivity can be developed in parallel with iodine control technologies, the performance of the iodine control technologies can be better evaluated for use in a reprocessing plant.

New potential sorbents have been identified for ^{85}Kr and ^{129}I. Some show promise under theoretical or idealized conditions but have not yet been developed to the degree that cryogenic Kr and Xe capture and separation and AgZ chemisorption of iodine have. In general, these new sorbents are in the early stages of development, and their technology readiness level (TRL) is generally low. While researching new technologies may provide alternatives to more mature technologies, future R&D should focus on advancing and filling in data gaps on the existing and most mature technologies, including the

demonstration of viable WFs and advancing the TRL through large-scale demonstrations and testing under high-fidelity conditions.

Long term R&D (out to 25–100 years) should continue on less mature or even currently unknown technologies to lower the costs and risks of UNF reprocessing. Some workshop participants suggested multiradionuclide sorbents and WFs. These are currently not technically possible considering the differences in the chemical, physical, and radiological properties of the four volatile radionuclides.

CONTENTS

FIGURES

TABLES

ACRONYMS

AgZ	silver mordenite (zeolite)
ALARA	As Low As Reasonably Achievable
ANL	Argonne National Laboratory
BAT	Best Available Technology
CD	Conceptual Design
DF	decontamination factor
DOE	Department of Energy
DOG	dissolver off-gas
LWR	light-water reactor
HIC	high-integrity container
HZ	hydrogen mordenite (zeolite)
ICRP	International Commission on Radiological Protection
INL	Idaho National Laboratory
MOF	metal organic framework
NEUP	Nuclear Energy University Program
NE	Office of Nuclear Energy
ORNL	Oak Ridge National Laboratory
PAN	polyacrylonitrile
PNNL	Pacific Northwest National Laboratory
R&D	research and development
SRL	System Readiness Level
TRL	Technology Readiness Level
UNF	used nuclear fuel
WF	waste form

TECHNOLOGY DEVELOPMENT ROADMAP FOR VOLATILE RADIONUCLIDE CAPTURE AND IMMOBILIZATION

1. INTRODUCTION

Reprocessing used nuclear fuel (UNF) is an option for recovering the valuable materials contained in UNF. During used fuel reprocessing, some of the radionuclides generated during irradiation in a nuclear reactor are volatile and must be removed from the off-gas streams (Jubin and Strachan 2015; Jubin et al. 2016) in order to meet United States (U.S.) radionuclide emissions regulations. The four volatile radionuclides of primary concern are ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I. Methods and materials to remove these radionuclides from aqueous reprocessing facility off-gas streams have been studied and reported on for many years (e.g., Spencer et al. 2008; Spencer et al. 2017; Jubin and Spencer 2017; Spencer et al. 2018; Banerjee et al. 2015; Thallapally et al. 2013; Garino et al. 2011; Chapman et al. 2010; Patton et al. 2014; Riley et al. 2016; and Soelberg et al. 2013).

This report is a summary of the results of an “Off-Gas and Waste Forms Strategy Workshop” held in Washington, DC January 31–February 1, 2023. Workshop attendees included researchers in volatile radionuclide capture and WFs from several national laboratories, including Argonne National Laboratory (ANL), Idaho National Laboratory (INL), Oak Ridge National Laboratory (ORNL), and Pacific Northwest National Laboratory (PNNL), with Department of Energy (DOE) Office of Nuclear Energy (NE) managers for the Material Recovery and Waste Form Development Campaign, the DOE office through which this research is authorized. More information about this workshop is provided in **APPENDIX A–F**, including lists of in-person and online attendees and presentations made during the workshop. Attendees reviewed the current state of the art (baseline) technologies for capturing and disposing of these volatile radionuclides and developed a roadmap for future research and development (R&D) to mature technologies that have been recently studied, increase efficiency, simplify, or reduce costs compared to the current baseline technologies, and identify opportunities for future new technologies. This report documents the roadmap developed as a workshop output.

This roadmap provides near, medium, and long-term objectives to enable simpler and less costly means to meet the volatile radionuclide capture and disposal requirements for future and advanced aqueous reprocessing plants. This roadmap outlines a logical sequence of R&D activities needed to achieve this vision of a simpler and less costly reprocessing system. It includes developing technologies for removing compounds bearing any of the four volatile radionuclides from reprocessing facility gas streams before the facility stack and for disposing them as appropriate waste forms (WFs).

The overarching vision of this roadmap is to develop and demonstrate volatile radionuclide capture technologies and associated WFs for the next-generation reprocessing plants that potentially reduce the facility size and associated capital and operating costs. Rethinking the entire headend portion of the facility may be required. The following objectives or results are herein proposed:

- Capture the volatilized radionuclides with sufficient efficiency to achieve the decontamination factor (DF) needed to meet existing regulatory requirements
- Develop WFs for each of the four volatile radionuclides that meet repository acceptance criteria with minimal processing
- Develop online sensors that provide real-time measurements of the volatile radionuclides to demonstrate designed performance objectives and DFs
- Simplify reprocessing plant headend to minimize solids handling and control fine particulate

- Release all volatile radionuclides that require abatement into a single off-gas stream sufficiently to eliminate the need to treat any other off-gas stream in the reprocessing plant.

1.1 Limitations and Assumptions of This Roadmap

The scope of the workshop focused on producing a useable product within two days, and so was limited to addressing the current and future inventory of commercial light water reactor used fuel in the U.S.:

- Aqueous reprocessing.
- Uranium oxide (UO_x) fuel from light water reactors (LWRs).
- Processing of 5-y cooled, 60 gigawatt-day per tonne (GWd/t) fuel used to determine radionuclide content.
- Durable and leach-resistant WFs for longer-lived ^{14}C and ^{129}I, which require geologic disposal based on current regulations.
- Shorter-lived ^{3}H and ^{85}Kr require isolation consistent with their shorter half-lives.

Most of the DOE-sponsored off-gas technology research over the past two decades has used these or similar assumptions. **Figure 1-1** shows how the four volatile radionuclides tend to partition during aqueous used fuel reprocessing into different off-gas streams. Most of the iodine evolves into the dissolver off-gas (DOG); but the expected DFs needed for ^{129}I are high enough that iodine capture may be required in practically every off-gas stream. Tritium disperses through all aqueous streams and into any gas streams that evolve from the aqueous streams. Noble gases (Kr and Xe) and ^{14}C evolve mainly into the DOG.

If this roadmap can be used to advance the maturity of current technologies, then when a mission need for an aqueous reprocessing facility is determined (Critical Decision 0 according to DOE Order 413.3B [DOE 2023]), these technologies would be available for a technology demonstration of the integrated processes.

A goal of a development program for volatile radionuclide capture and WFs is to achieve a level of development to support an assignment of Technology Readiness Level (TRL) of 6 as described in **APPENDIX E** and DOE G 413.3-4A (DOE 2015):

> *Engineering-scale models or prototypes are tested in a relevant environment. This represents a major step up in a technology's demonstrated readiness. Examples include testing an engineering scale prototypical system with a range of simulant.*[a] *Supporting information includes results from the engineering scale testing and analysis of the differences between the engineering scale, prototypical system/environment, and analysis of what the experimental results mean for the eventual operating system/environment. TRL 6 begins true engineering development of the technology as an operational system. The major difference between TRL 5 and 6 is the step up from laboratory scale to engineering scale and the determination of scaling factors that will enable design of the operating system. The prototype should be capable of performing all the functions that will be required of the operational system. The operating environment for the testing should closely represent the actual operating environment.*

This roadmap for off-gas control for aqueous UNF reprocessing of used LWR UO_x fuel can be a template or example for roadmapping off-gas control R&D for other used fuels, reactor types, and fuel

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[a] Simulants should match relevant chemical and physical properties.

cycles that may be implemented in addition to, or instead of, aqueous reprocessing of used UO_x fuel from LWRs.

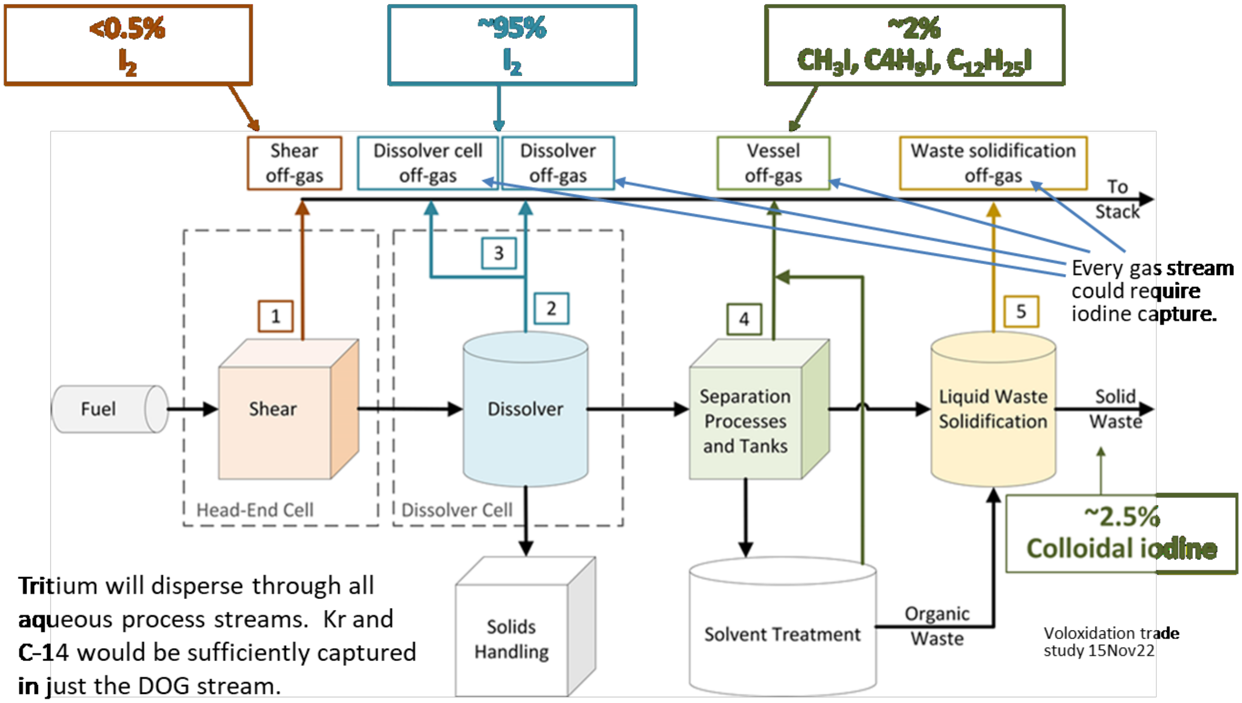

Figure 1-1. Dispersion of volatile radionuclides into aqueous used fuel reprocessing facility off-gas streams.

Volatile radionuclide capture and WF technologies are at various levels of development. Some volatile radionuclide capture technologies are mature and available for inclusion in UNF reprocessing facility designs with little added R&D. However, an integrated, high-fidelity, pilot-scale demonstration of these more mature technologies is needed to prove and optimize performance and provide final design and economic data for a specific future reprocessing facility design. Such testing would provide data for the facility design to achieve the needed DFs, selectivity (that can affect WF performance and disposability), sorbent capacities, and tolerance of the technologies to deleterious effects, such as chemical, physical, or radiological degradation.

The R&D for volatile radionuclide capture and WFs can progress in a tiered fashion as needed. Some technologies are ready for integrated, high-fidelity, pilot-scale demonstration and inclusion in a current-generation aqueous UNF reprocessing facility, while potentially lower cost or lower risk technologies can be further investigated for a next-generation reprocessing facility.

This roadmap is based on currently known technologies. Advances in technology continue that may change the trajectory of this roadmap. This roadmap is a living document that must be revised periodically to incorporate those advances when they occur.

1.2 Decontamination Factor Targets

The DF refers to the control efficiency of a gaseous radionuclide control technology. For example, a DF of 100 is achieved if the control technology removes 99% of that gaseous radionuclide from the off-gas stream, DF = 100/(100-control efficiency).

The target performance of a control technology is to achieve the DF needed to meet regulatory compliance, ensure safety, and gain stakeholder acceptance of the reprocessing facility. Over the past two decades, the authors of several studies have estimated the DFs needed to meet current regulatory requirements (Soelberg et al. 2008; Jubin et al. 2012b; Jubin et al. 2012c).[b] Results from these studies are summarized in **APPENDIX C** and in **Table 1-1**.

Table 1-1. Summarized volatile radionuclide DF targets.

Radionuclide	Order-of-Magnitude DF Range[1]	Regulatory Drivers
^{3}H	10–1000	Dose to the public (maximum exposed individual or MEI)—Code of Federal Regulations (CFR), Title 40, Part 190, Subpart B, Section 190.10(a). This limits the annual dose equivalent to a member of the public to ≤25 millirems to the whole body, 75 millirems to the thyroid, and 25 millirems to any other organ.
^{14}C	1–30	
^{85}Kr	10–100	Dose to the public and entire uranium fuel cycle limits—CFR, Title 40, Part 190, Subpart B, Sections 190.10(a) and (b). 40 CFR 190.10(b) limits the total quantity emitted per gigawatt-year of electrical energy produced to <50 000 Ci of ^{85}Kr, 5 mCi ^{129}I, and 0.5 mCi combined ^{239}Pu and other alpha-emitting transuranic radionuclides with half-lives greater than one year.
^{129}I	1 000–10 000	
1. These values are for the reprocessing of commercial used UO_x fuel.		

Each of these DF ranges is necessarily broad because the actual DF requirements needed for a specific future reprocessing facility can depend on various controllable and uncontrollable factors. Uncontrollable factors include the applicable emissions regulations and stakeholder requirements. Controllable factors include the degree of conservatism in the off-gas system design and the engineering safety factors used to ensure that emissions are well, not just marginally, below the regulatory limits.

Some controllable factors can change DF requirements by a factor of two or more by affecting the total dose to the maximum exposed individual (MEI). These include UNF burnup and cooling, the UNF reprocessing rate, the reprocessing facility fence-line location (how close a member of the public can live to the emission point and in what direction), the local meteorology, food sources for the surrounding area, reprocessing plant stack design, and stack parameters such as stack gas velocity and temperature.

For these reasons it is impossible to assign a single DF value or a narrower DF range for these volatile radionuclides. It could be argued for the short half-lived ^{85}Kr and ^{3}H isotopes that, if the UNF is cooled for sufficient time prior to reprocessing, DFs needed for those isotopes could be reduced to one (no control needed). This strategy would eliminate the need to capture ^{85}Kr and ^{3}H but would require cooling the UNF for many decades prior to reprocessing (Jubin et al. 2012a). For this reason, prolonged storage is not considered for the DF ranges above. A typical cooling time, if that approach were to be taken, is 10–20 half-lives or 120–240 years for ^{3}H and 107–214 years for ^{85}Kr.

If a potential technology cannot meet even the lower value of the DF ranges, other technologies should be sought. Technologies that can meet the lower value in the DF range, but not the higher value in the DF range, should be considered viable, but their use could impose constraints on the reprocessing facility. Control technologies capable of meeting the higher value of DF ranges may reduce or eliminate constraints on the facility, potentially allowing shorter UNF cooling times, faster reprocessing rates, more

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[b] The applicable regulations cover the allowable release(s) and the maximum dose, including to the thyroid. Doses to the maximum exposed individual (MEI) were calculated with the EPA code CAP-88 (Rosnick 1992, 2007). Since 2012, the CAP-88 code has been revised. Several comparisons of the 2007 version and the recent version have been made (Rhoads et al. 2013; Farfan et al. 2013; Jannik et al. 2015; Stagich et al. 2017). Unfortunately, most of the volatile radionuclides of concern in this roadmap are not evaluated in these references cited.

potential locations, and more flexible facility design.

1.3 International Radionuclide Air Emission Regulations

Radionuclide emission regulations in the U.S. differ in some respects from those in other countries. First, other countries do not have the same regulation as in the U.S. Code of Federal Regulations (CFR), Title 40, Part 190, Subpart B, Sections 190.10(b), in which the emissions of ^{85}Kr and ^{129}I are based on the amount of electricity generated in the fuel cycle. Regulating ^{85}Kr based on dose alone, and not on the amount of electricity generated, can reduce the needed DF to 1–10 (Jubin et al. 2012c). This is why, in other countries such as in the United Kingdom (UK) and France, the DF needed for ^{85}Kr can be reduced to one (no capture required). Thus, in other countries the uncontrolled release of ^{85}Kr from a reprocessing facility is within current dose limits.

According to the International Atomic Energy Agency (IAEA 2010) most other countries with, and even some countries without, nuclear facilities generally follow the dose limits to the public recommended by the International Commission on Radiological Protection (ICRP) shown in **Table 1-2**. Some countries follow the ICRP recommended dose limit of 100 mrem/y, which is 4× higher than the U.S. dose limit in 40 CFR 190.10(a), at 25 mrem/yr for NRC-licensed commercial facilities. Some countries have lower limits, such as the Czech Republic (25 mrem/y) that are the same as the U.S. limit in 40 CFR 190.10(a).

Table 1-2. International Commission on Radiological Protection recommended dose limits (from Smith 1991).

Application	Dose Limit, mrem/y	
	Occupational	Public
Effective dose	2000 averaged over 5 y (not to exceed 5000 in any year; additional restrictions apply for pregnant women)	100
Annual dose equivalent in:		
Lens of the eye	15 000	1500
Skin	50 000 (This limit is protective of stochastic effects; an added limit is needed for localized exposures to prevent against deterministic effects)	5000
Hands and feet	50 000	—

Some countries, such as the United Kingdom, have “dose constraints” that are lower than the recommended international dose to the public limit of 100 mrem/yr, to reduce doses to As Low As Reasonably Achievable (ALARA), and use Best Available Technology (BAT). Yet other countries, including China and Slovenia, follow the recommended annual dose limit of 100 mrem/y, but allow a 1-year exceedance of that limit, if the average dose over 5 years is within 100 mrem/y.

France, which operates the La Hague used fuel reprocessing facilities, uses compliance approaches including BAT and extensive monitoring around the La Hague facility (IAEA 2010; European Commission Directorate-General for Energy 2018).

Second, different U.S. regulations limit the dose to the MEI to either 10 mrem/y (10 CFR 20, just for DOE facilities), 25 mrem/y (40 CFR 190, to the whole body, and also 75 mrem/y to the thyroid and 25 mrem/y to any other organ), or 100 mrem/y (40 CFR 61, with a compliance limit of 50 mrem/y). The dose-based DF ranges in the previous section are based on the 40 CFR 190 limits for commercial, NRC-licensed facilities, which a future U.S. reprocessing facility is presumed to be.

The dose from ^{14}C, when considered alone, is low enough that it does not need emissions control in most countries, except in the UK, where a ^{14}C DF of 100 is required, because that value is considered ALARA with BAT. The DFs needed for ^{3}H and ^{129}I can be lower than those estimated for the U.S. For example, no ^{3}H capture is required in the UK, because of the expected high cost of ^{3}H capture and disposal, until such a technology as voloxidation can significantly reduce that cost. The "reduction factors" for airborne emissions at the La Hague reprocessing facility are one for "gases" other than ^{3}H, 15 for ^{3}H, and nine for halogens + aerosols (Table 8 in IAEA 2010). Chronic public total dose measurements around the La Hague facility range between 0.8 and 23 mrem/y, even without specifically capturing ^{85}Kr and ^{14}C and with currently used ^{3}H and ^{129}I control technologies (Rommens et al. 2000).

Third, reprocessing facilities outside of the U.S. have used wet scrubbing and disposed of scrubbed iodine in nearby oceans or rivers. In France, at the La Hague facility, the iodine is first captured when the process gas stream is passed through an aqueous soda scrubber and further captured with silver mordenite (AgZ) with a total DF that is unreported. The wet scrubbed iodine is disposed of in the sea (Yiou et al. 1994, Yiou et al. 1995, Zhou et al. 1993).

Typically, the DF values for the iodine removal are in the range of 50 to 150 (Gombert et al 2007; IAEA 1987; Kawaguchi et al. 1983; Fukushima et al. 1983). At the Tokai Reprocessing facility in Japan, a DF value of "about 100" was found for the removal of iodine on silver-exchanged zeolite (Kawaguchi et al. 1983; Fukushima et al. 1983).

The iodine DF at the Rokkasho reprocessing plant in Japan (Satoh et al. 2019) is 250, achieved with Ag-alumina iodine filters. The "Enforcement Order of the Law Concerning the Final Disposal of Specific Radioactive Waste" (Cabinet 2000) defines metals used for adsorption of iodine and its compounds contained in the air discharged from reprocessing facilities during spent fuel reprocessing as a target for geological disposal. The captured iodine is intended for geological disposal as specified in the "Order for Enforcement of the Law Concerning the Final Disposal of Specific Radioactive Waste" (Cabinet 2000). Studies on an iodine WF for geological disposal have been performed (Inagaki et al. 2007; Inagaki et al. 2008) and Kawaguchi et al. (1983) show the AgX filter material going to the waste disposal facility, where it is stored until it can be sent to geological disposal.

Japanese regulations stipulate that the effective dose outside the perimeter monitoring area should be less than 1 mSv/year (100 mrem/y) (Prime Minister's Office 1971; Nuclear Regulation Authority 2015). In addition, under the ALARA concept, the target is set at an effective dose of 50 μSv/year (5 mrem/y) (Nuclear Regulation Authority 2013). At the Rokkasho Reprocessing Plant, radiation doses to the general public are minimized by the diffusion of the off-gas after exiting the 150-meter-high stack (JNFL 2020). Iodine remaining in waste solution is released into the sea through an ocean discharge pipe (JNFL 2020). Carbon-14 as CO_2(g) dissolved in solution is also disposed to the sea (Fukumatsu et al. 1999).

At the Wiederaufarbeitungsanlage Karlsruhe facility in Germany, DF values approaching 500 were observed for $AgNO_3$-based materials (Herrmann et al. 1993; Herrmann et al. 1997a; Herrmann et al. 1997b). These references indicate that iodine DF requirements were generally lower than current U.S. requirements and ocean disposal was used for iodine-containing scrubber solutions.

In the case of Russia, the supposition was that high levels of dissolved concentrations of ^{129}I in the Ob River were from disposal, at least in part, of waste from the Mayak reprocessing facility into the Tobal River (Cochran et al. 2000).

With lower iodine DF requirements, and with the availability of ocean and river disposal, wet scrubbing for iodine capture is a viable technology in foreign countries. The U.S. has both higher estimated DF requirements and no assumed river or sea disposal availability, which drives the need for high-performance sorbents for iodine capture.

2. CURRENT STATUS OF VOLATILE RADIONUCLIDE CAPTURE AND IMMOBILIZATION TECHNOLOGIES

Different volatile radionuclide capture and immobilization technologies are at various levels of maturity for use in used fuel aqueous reprocessing. A complete discussion is outside the scope of this report; many cited references provide more detail. This status discussion is for the aqueous reprocessing of used UO_x fuels. Off-gas radionuclide capture technologies for other reprocessing technologies and other used fuels are generally not as mature.

2.1 Tritium Capture and Immobilization

Tritium is generated during fuel irradiation from tertiary fission and the neutron activation of contaminants, such as H, B, and Li (IAEA 2004). While a large fraction of the ^3H is retained in Zircaloy cladding, enough is released during reprocessing to require control (Jubin et al. 2016). It is readily converted to tritiated water, ^3H_2O (T_2O) and ^3HHO (THO). Tritiated water can be condensed, scrubbed, and sorbed on molecular sieve sorbents, as described by Law et al. (2015) and Vienna et al. (2015). These water capture technologies are mature and used in many industries (nuclear and nonnuclear) worldwide. However, a system that incorporates these water capture technologies has not yet been demonstrated beyond System Readiness Level (SRL) 5, specifically for tritiated water capture during UNF reprocessing, considering potential cosorption or interferences from other gas species in dissolver and other off-gas streams, such as iodine, other halides, NO_x, and organic species. These cosorbing or interfering species may also affect potential tritium WFs.

2.2 Carbon-14 Capture and Immobilization

Carbon-14 is generated primarily though the neutron activation of the ^{14}N present in trace levels in both the fuel and cladding and the ^{17}O in trace amounts in the oxide fuel (IAEA 2004). The primary gaseous form of ^{14}C is assumed to be $CO_2(g)$ to which the ^{14}C is converted (if not already in that form) upon the oxidation and dissolution of the fuel. The primary method for removing $CO_2(g)$ is caustic scrubbing, as described by Law et al. (2015) and Vienna et al. (2015). The primary immobilization material is $CaCO_3$ or $(Ba,Ca)CO_3$ (Haag 1982). Wet scrubbing is a mature technology but has not yet been demonstrated specifically for ^{14}C capture beyond TRL 5, considering the need account for cosorbing or interfering species, such as NO_x, and the need to produce a durable $(Ba,Ca)CO_3$-bearing WF.

2.3 Krypton-85 Capture and Immobilization

Krypton-85 is generated as a fission product. As a noble gas, Kr is inert and does not readily react chemically. It tends to partition to the DOG stream unless it is evolved earlier during reprocessing. While the cryogenic capture and separation of both Kr and Xe has been done during aqueous reprocessing (Brown et al. 1978), that process is expensive and complicated. Cryogenic Kr and Xe capture and separation in the DOG stream would require the near-quantitative removal of gas species such as NO_x, CO_2, H_2O, and O_2, that would condense and interfere with cryogenic Kr and Xe capture and separation. Nitrogen oxides, CO_2, and H_2O, if not removed, would freeze and plug the process equipment. Oxygen and ozone, formed by the radiolysis of oxygen in the presence of a high-radiation field at low temperatures, pose an explosion hazard for the cryogenic distillation process. These considerations add off-gas process steps that are unnecessary for noncryogenic Kr and Xe capture and separation processes.

The baseline Kr WF for both cryogenic or solid sorbent Kr and Xe capture and separation is storing the captured Kr as a compressed gas in metal cylinders long enough for the ^{85}Kr to decay to inactive ^{85}Rb. Rubidium with a melting point of 38.9°C is potentially a liquid at storage temperatures and corrosive to the Kr-containing canister material. However, Asmussen and Neeway (2020) determined that, while some corrosion might occur, it is limited to the Rb in contact with the inside of the container.

2.4 Iodine-129 Capture and Immobilization

Effective removal of ^{129}I from off-gas waste streams requires high DFs (Jubin et al. 2013; Jubin et al. 2011, 2012a; Jubin et al. 2012c). Iodine chemisorption on AgZ is the current iodine capture baseline, although silver functionalized aerogel (Ag aerogel) can also capture iodine. Other chemisorbing sorbents, such as zeolites and metal organic frameworks (MOFs) that use other metals (Nenoff et al. 2012; Sava et al. 2012) are also being studied as alternatives to reduce sorbent cost and eliminate silver (a hazardous characteristic waste when disposed [EPA 2023]).

Wet scrubbing has also been used but is insufficient without downstream "polishing" with chemisorption (Burger and Scheele 2004; Soelberg et al. 2013; Jubin and Spencer 2017). A sorbent bed system containing silver mordenite cartridges has been installed for iodine capture in the Hanford Waste Treatment and Immobilization high-level waste vitrification facility (Burger and Scheele 2004; Scheele and Wend 2015). This facility has not yet been operated for actual high-level waste treatment.

Limited data are available on the use of silver-bearing sorbents in NO_2 voloxidation off-gas streams (Greaney et al. 2022a). The use of AgZ and $AgNO_3$-impregnated alumina in NO_2-rich off-gas streams is currently being evaluated. Early results suggest that the NO_2 will decompose when in contact with AgZ and $AgNO_3$ alumina, forming a nonlabile nitrate species. The decomposition may also compromise the capture of iodine on the sorbent, but additional research is needed to understand how these sorbents will perform in highly oxidizing environments.

Various iodine WF studies for iodine-laden, silver-bearing sorbents have been conducted over the past decade (Matyáš et al. 2013, Bruffey and Jubin 2015, Matyáš and Walters 2015, Matyáš et al. 2016, Ebert et al. 2016, Ebert et al. 2017, Asmussen et al. 2019, Asmussen and Ebert 2020, Ebert et al. 2021, and Stariha et al. 2022). These studies included both experimental and modeling efforts. Various WF production techniques have been studied, focusing on relatively low-temperature or high-pressure techniques intended to retain the chemisorbed iodine as AgI during the WF production process.

Iodine capture on Ag aerogel has been successful. Converting the iodine-loaded Ag aerogel to a durable WF has shown promise (Asmussen et al. 2019). Other Ag-containing sorbents have been explored, including $AgNO_3$-containing materials (e.g., AC-6120), that also show promise (Wilhelm and Schuttelkopf 1972). Many other technologies have been evaluated for capturing iodine including non-Ag materials containing other chemisorbing metals, like Bi, Sn, and Cu (Reda et al. 2021; Chong et al. 2022; Zhou et al. 2022; Zhou et al. 2022); other sorbents utilizing non-chemisorbing approaches (i.e., physisorption) include activated carbon (Chebbi et al. 2022).

3. FUTURE TECHNOLOGICAL DEVELOPMENTS AND NEEDS

A workshop goal was to develop an outline for near term (up to 5 years) to longer term (25 years and longer) research needs. In this report, those ideas are collated in a technology development roadmap over those time periods. This is by no means comprehensive; future technological developments will certainly alter this roadmap, but the major ideas discussed in the workshop are summarized. Detours are inevitable, but the roadmap is intended to arrive at the same end point—a reprocessing facility that meets the needs of the nuclear community while protecting human health and the environment.

One technology, voloxidation,[c] is under development that, if successful, could lead to a major revision of the current plans for technological development. Voloxidation with NO_2 (called in this report "advanced voloxidation," "NO_2 voloxidation," or "voloxidation" unless indicated otherwise [Del Cul et al. 2013; Greaney et al. 2022a; Greaney et al. 2023b; Soelberg et al 2023]) as the oxidant (see Section 3.5) could lead to a change in the front end of a reprocessing facility, resulting in the consolidation of several unit operations into a single unit operation. Voloxidation with NO_2 gas is being studied to oxidize

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[c] "Voloxidation" refers to the use of a gaseous oxidant (air, O_2, or NO_2) to oxidize the used fuel, volatilize the most volatile elements, and chemically "pulverize" the used fuel, making it easier to dissolve.

the fuel, converting it to a fine, more easily dissolved powder, and volatilize enough of the volatile radionuclides to enable removing these radionuclides from a single gas stream, making treatment of other gas streams unnecessary.

3.1 Tritium Capture and Waste Forms

A roadmap for tritium capture and WFs is shown in **Figure 3-1**. The shaded blocks in the roadmap figures indicate which items are considered completed or partially completed at the time of writing.

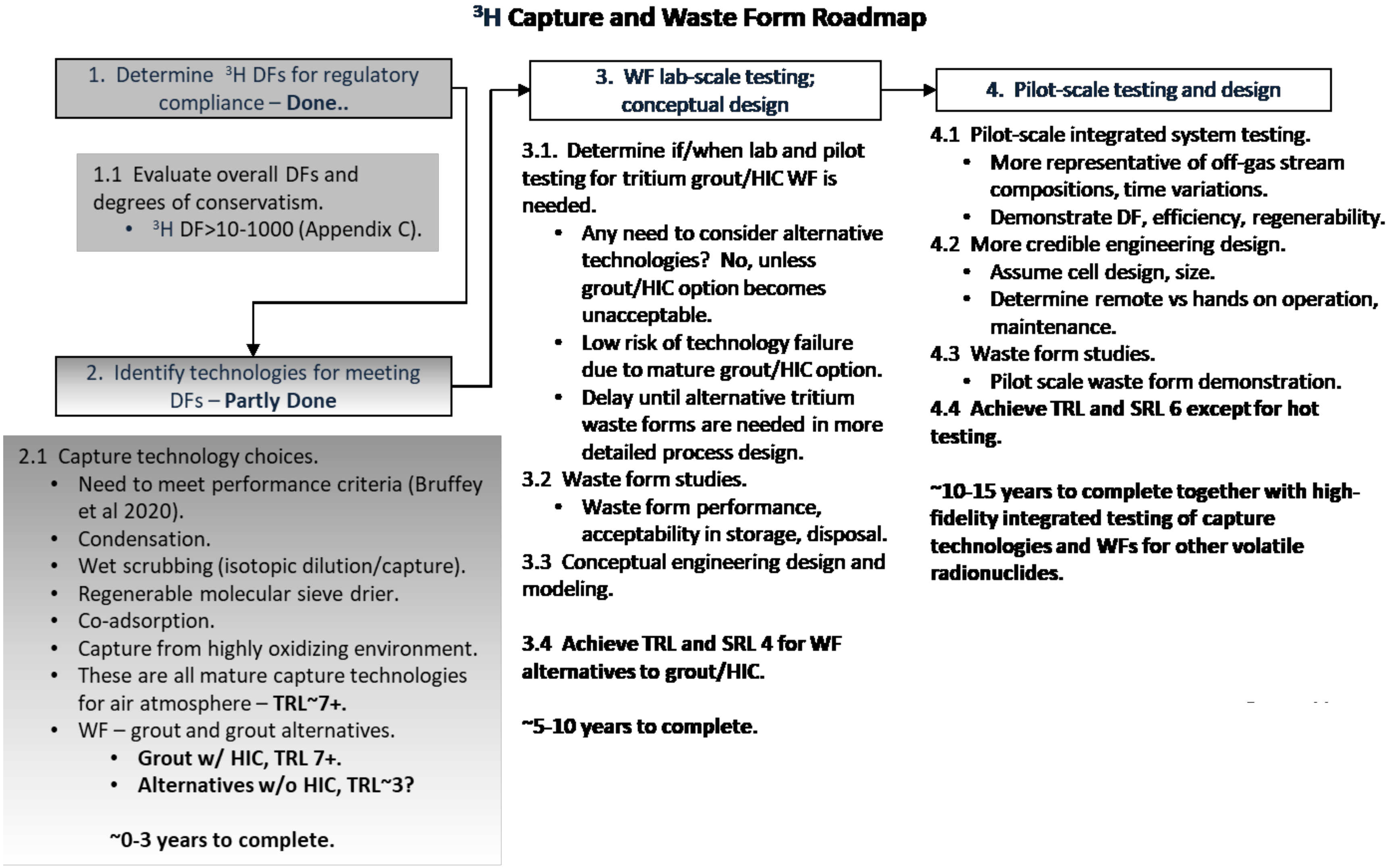
Several assumptions have been made. First, because of the oxidizing aqueous reprocessing environment, it has been assumed that the form of ^{3}H in off-gas streams from aqueous UNF reprocessing is tritiated water (^3H_2O and H^3HO), rather than diatomic $^3H_2$ or H^3H. Tritiated water capture is complicated by the abundance of process water starting in the dissolver. This makes capturing the tritiated water expensive because it requires either isotopic separation of the tritiated water from the H_2O or an orders-of-magnitude increase in the amount of the tritium WF, which would contain mainly H_2O with only small amounts of tritiated water. This was a key driver in the initial development of the voloxidation process (Goode 1973; Goode 1978; Jubin et al. 2009) to volatilize and capture the tritium before tritiated water can contaminate downstream processes.

Second, it has been assumed that technologies for the capture of tritiated water are mature technologies—capture with water condensation, wet scrubbing, and water sorption on regenerable molecular sieve sorbents. Once captured, the water would be mixed with grout or cement to make a solid, monolithic WF. The high mobility of tritiated water in grout limits the performance of this WF. Depending on the classification and disposition for tritiated water, storing liquid tritiated water in containers designed to isolate the tritiated water for sufficient time (perhaps 10–20 half-lives or about 123–240 years) for the tritium to decay in storage to levels below regulatory concern has been proposed.

Because tritiated water capture and WF technologies are considered relatively mature, no specific tritium capture and WF R&D has been recently undertaken by DOE. However, advanced technologies for tritium capture are being investigated for several applications other than UNF processing. These lower TRL capture technologies are being investigated for a variety of applications from fusion to the operation of heavy-water and molten-salt reactors (Forsberg et al. 2017; Kim et al. 2020).

Some uncertainties remain, depending on the off-gas stream and other gas constituents. Wet scrubbing and sorbents are known (and often used) for capturing not just water but other gas constituents that are scrubbable with aqueous solutions or compatible with sorbents for water capture. Cocondensation, coscrubbing, and cosorbing of other off-gas constituents could affect the performance of the scrubber or regenerable sorbent systems and could contaminate the grouted water WF with other radionuclides (e.g., ^{129}I) or contaminants that could affect the WF disposition. For example, the cosorption of iodine on molecular sieve Type 3A has been studied for use in drying voloxidizer off-gas (Holland et al. 1981); and sparging of dissolved fuel solutions to remove iodine has also been studied (Morgan and Holland 1980). Specific uncertainties, depending on the off-gas stream and other gas constituents, include:

- What other off-gas impurities could cocondense or be wet scrubbed along with tritiated water?
- What impurities cosorb or interfere with water sorption on sorbents such as molecular sieves?
- Will interference from other off-gas components affect water sorbent performance or sorbent regenerability?



^{3}H Capture and Waste Form Roadmap

1. Determine ^{3}H DFs for regulatory compliance – **Done..**

1.1 Evaluate overall DFs and degrees of conservatism.
- ^{3}H DF>10-1000 (Appendix C).

2. Identify technologies for meeting DFs – **Partly Done**

2.1 Capture technology choices.
- Need to meet performance criteria (Bruffey et al 2020).
- Condensation.
- Wet scrubbing (isotopic dilution/capture).
- Regenerable molecular sieve drier.
- Co-adsorption.
- Capture from highly oxidizing environment.
- These are all mature capture technologies for air atmosphere – **TRL~7+.**
- WF – grout and grout alternatives.
  - **Grout w/ HIC, TRL 7+.**
  - **Alternatives w/o HIC, TRL~3?**

~0-3 years to complete.

3. WF lab-scale testing; conceptual design

3.1. Determine if/when lab and pilot testing for tritium grout/HIC WF is needed.
- **Any need to consider alternative technologies? No, unless grout/HIC option becomes unacceptable.**
- **Low risk of technology failure due to mature grout/HIC option.**
- **Delay until alternative tritium waste forms are needed in more detailed process design.**

3.2 Waste form studies.
- **Waste form performance, acceptability in storage, disposal.**

3.3 Conceptual engineering design and modeling.

3.4 Achieve TRL and SRL 4 for WF alternatives to grout/HIC.

~5-10 years to complete.

4. Pilot-scale testing and design

4.1 Pilot-scale integrated system testing.
- **More representative of off-gas stream compositions, time variations.**
- **Demonstrate DF, efficiency, regenerability.**

4.2 More credible engineering design.
- **Assume cell design, size.**
- **Determine remote vs hands on operation, maintenance.**

4.3 Waste form studies.
- **Pilot scale waste form demonstration.**

4.4 Achieve TRL and SRL 6 except for hot testing.

~10-15 years to complete together with high-fidelity integrated testing of capture technologies and WFs for other volatile radionuclides.

Figure 3-1. Tritium capture and waste form roadmap.

- Will cocaptured off-gas components affect the ability to produce a suitable tritium WF, and could cocaptured radionuclides, such as ^{129}I, affect the handling, waste classification, storability, and disposability of the tritium WF?
- Should capture and recovery for economic use be considered for tritium and its decay product ^{3}He? If so, would that change how tritium is captured and managed?

These uncertainties will need to be resolved for tritium capture and WFs in designs for aqueous UNF reprocessing facilities. An optimal time to address these uncertainties is prior to or during high-fidelity, integrated pilot-scale testing for the other volatile radionuclides and WFs. Until then, capture and WF technologies for iodine and noble gases need further development so that they are also ready for integrated, representative pilot-scale testing. This may be a higher priority than expending resources on tritium capture and WFs.

3.2 Carbon-14 Capture and Waste Forms

A roadmap for carbon capture and WFs is shown in **Figure 3-2**. Several assumptions have been made regarding carbon capture in the past decade. First, it has been assumed that ^{14}C in aqueous reprocessing facility off-gas streams could require capture based on conservative DF calculations, with a DF up to 30. Depending on such conditions as ^{14}C levels in the UNF, parameters that affect dose to the public from radionuclide emissions, and the amount of the total dose to the public that can be attributed to ^{14}C, ^{14}C capture may be unnecessary to meet radionuclide air emission regulations in the U.S. Carbon capture was included in such studies as the Case Study (Law et al. 2015) for completeness, because under some conditions, ^{14}C capture and disposal may be required.

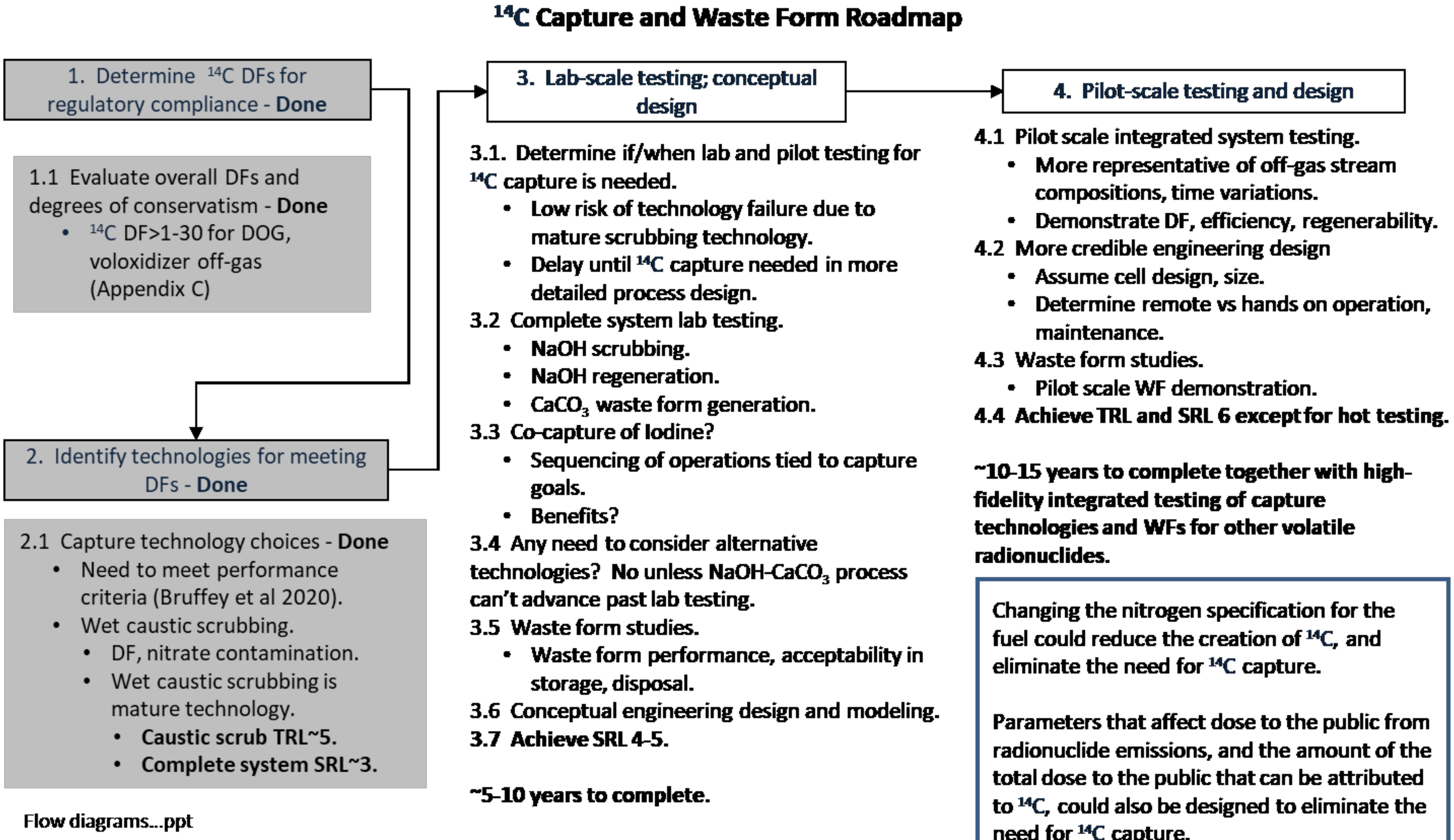
Second, it has been assumed that ^{14}C evolved from the UNF would be in the form of $^{14}CO_2$, because of the oxidizing conditions during UNF dissolution.

Third, it has been assumed that technologies for the capture of CO_2, and CO_2 WFs, are generally mature—capture via wet scrubbing in a moderately alkaline scrub solution, followed by reacting with $Ca(OH)_2$ to form precipitated $CaCO_3$ (which also restores the solution alkalinity), and then grouting the $CaCO_3$ into an acceptable WF (Vienna et al. 2015). The very low solubility of $CaCO_3$ or $(Ba,Ca)CO_3$ contributes to the effectiveness of a grouted WF in retaining ^{14}C.

Because wet caustic scrubbing and grouting WF technologies have been considered relatively mature, no specific ^{14}C capture and WF R&D has recently been undertaken in the U.S. However, some uncertainties remain, including:

- What scrubber conditions ensure ^{14}C capture with the needed DF?
- How could other off-gas components, such as $NO_x(g)$, interfere with or coscrub with the CO_2, for instance by changing the pH of the scrubber solution?
- Will cocaptured off-gas components affect the ability to produce a suitable WF, and could cocaptured radionuclides affect the handling, classification, storability, and disposability of the WF?
- Could solid sorbents be used to capture $^{14}CO_2$ in addition to, or instead of, wet scrubbing, and could the spent sorbents be converted into an acceptable WF?

These uncertainties need to be resolved for the inclusion of ^{14}C capture and WFs in designs for aqueous UNF reprocessing facilities. An optimal time to address these uncertainties is prior to or during high-fidelity, integrated pilot-scale testing for the other volatile radionuclides and WFs. Maturing capture and WF technologies for iodine and noble gases, so they are ready for integrated, representative pilot-scale testing, may be a higher priority than expending resources for ^{14}C capture and WFs prior to that point.



^{14}C Capture and Waste Form Roadmap

1. Determine ^{14}C DFs for regulatory compliance - **Done**

1.1 Evaluate overall DFs and degrees of conservatism - **Done**
- ^{14}C DF>1-30 for DOG, voloxidizer off-gas (Appendix C)

2. Identify technologies for meeting DFs - **Done**

2.1 Capture technology choices - **Done**
- Need to meet performance criteria (Bruffey et al 2020).
- Wet caustic scrubbing.
  - DF, nitrate contamination.
  - Wet caustic scrubbing is mature technology.
    - **Caustic scrub TRL~5.**
    - **Complete system SRL~3.**

Flow diagrams….ppt

3. Lab-scale testing; conceptual design

3.1. Determine if/when lab and pilot testing for ^{14}C capture is needed.
- **Low risk of technology failure due to mature scrubbing technology.**
- **Delay until ^{14}C capture needed in more detailed process design.**

3.2 Complete system lab testing.
- **NaOH scrubbing.**
- **NaOH regeneration.**
- **CaCO$_3$ waste form generation.**

3.3 Co-capture of Iodine?
- **Sequencing of operations tied to capture goals.**
- **Benefits?**

3.4 Any need to consider alternative technologies? No unless NaOH-CaCO$_3$ process can't advance past lab testing.

3.5 Waste form studies.
- **Waste form performance, acceptability in storage, disposal.**

3.6 Conceptual engineering design and modeling.

3.7 Achieve SRL 4-5.

~5-10 years to complete.

4. Pilot-scale testing and design

4.1 Pilot scale integrated system testing.
- **More representative of off-gas stream compositions, time variations.**
- **Demonstrate DF, efficiency, regenerability.**

4.2 More credible engineering design
- **Assume cell design, size.**
- **Determine remote vs hands on operation, maintenance.**

4.3 Waste form studies.
- **Pilot scale WF demonstration.**

4.4 Achieve TRL and SRL 6 except for hot testing.

~10-15 years to complete together with high-fidelity integrated testing of capture technologies and WFs for other volatile radionuclides.

Changing the nitrogen specification for the fuel could reduce the creation of ^{14}C, and eliminate the need for ^{14}C capture.

Parameters that affect dose to the public from radionuclide emissions, and the amount of the total dose to the public that can be attributed to ^{14}C, could also be designed to eliminate the need for ^{14}C capture.

Figure 3-2. Carbon-14 capture and waste form roadmap.

3.3 Krypton-85 Capture, Noble Gas Separation, and Waste Form

A roadmap for ^{85}Kr capture and separation with solid sorbents and a ^{85}Kr WF, is shown in **Figure 3-3**. Two advanced technologies are available for Kr capture—HZ-PAN with AgZ-PAN and MOFs. It may be easier to capture both Kr and Xe together, but the UNF contains about 10× more Xe[d] than Kr. If the Kr can be separated from the Xe (and from other gas constituents that could also cosorb with Kr and Xe), the Kr WF volume can be reduced, hence the reason for separating Kr from Xe.

If solid sorbents can be used to capture and separate Xe and Kr at higher-than-cryogenic temperatures, solid sorption may be able to replace cryogenic Xe and Kr capture and separation. Two sorbent processes are currently being investigated as alternatives to cryogenic capture and separation. At INL), sodium mordenite [$(Na_2,K_2,Ca)Al_2Si_{10}O_{24}\cdot 7H_2O$], is treated with acid to dissolve some of the Al and tune the size of the zeolite cage into a hydrogen form. It is then bound with polyacrylonitrile (PAN) to make an engineered bead form (HZ-PAN), for the Kr sorbent. The sodium mordenite can also be converted to a silver form (AgZ) by treatment with an $AgNO_3$ solution and bound in the PAN to form engineered beads of AgZ-PAN. The AgZ-PAN sorbent is used at ambient temperatures to adsorb Xe while leaving Kr, thus separating the two. The HZ-PAN sorbent is used at about 200 K to adsorb the Kr from the resulting Xe-free off-gas stream. This separation has been accomplished with temperature-swing operating conditions.

The use of HZ-PAN followed by Ag-PAN for Xe and Kr capture and separation is being investigated as an alternative to cryogenic capture and separation to reduce complexity, cost, and risk (Nguyen et al. 2009; Garn and Greenhalgh 2013; Garn et al. 2014; Coopersmith et al. 2023; Torcivia et al. 2023; Ladshaw et al. 2019; Welty et al. 2018).

In the second solid sorbent capture and separation process, another class of compounds is being investigated at Pacific Northwest National Laboratory (PNNL) for capturing ^{85}Kr are MOFs (Liu et al. 2014; Elsaidi et al. 2020; Gantzler et al. 2022; Thallapally et al. 2021). These materials are organic compounds containing selected metals. These form lattices containing cages that can be tuned to accommodate atoms of various sizes utilizing a molecular sieve approach similar to zeolites. Several MOFs have been developed with a specificity for either Xe or Kr, but the overwhelming majority have a higher Xe selectivity than for Kr when both are present in the gas stream. Like the HZ-PAN materials, MOFs can be used to capture and separate the noble gases (Xe and Kr) from the off-gas stream at higher-than-cryogenic temperatures. Among the many MOFs tested to date, two have been the best for capturing and separating Xe and Kr. A calcium-based MOF [SDB = 4,4'-sulfonyldibenzoate, known as CaSDB] was selective to Xe in the presence of other competing gases. Similarly, a partially fluorinated MOF with copper as the metal nodes (FMOFCu) had Kr selectivity at -40 °C. By controlling the temperature, PNNL demonstrated the ability to switch the Xe/Kr selectivity of FMOFCu.

These solid sorbent technologies are intended for use in capturing and separating noble gases at higher-than-cryogenic temperatures, to eliminate the need to purify the gas stream of interfering species. The sorbents are intended to be regenerable by pressure- or temperature-swing volatilization of the captured Xe and Kr, so the same sorbent can be used in repeated sorption cycles. These technologies are in the early stages of development with TRLs ranging from 1–3, depending upon the sorbent.

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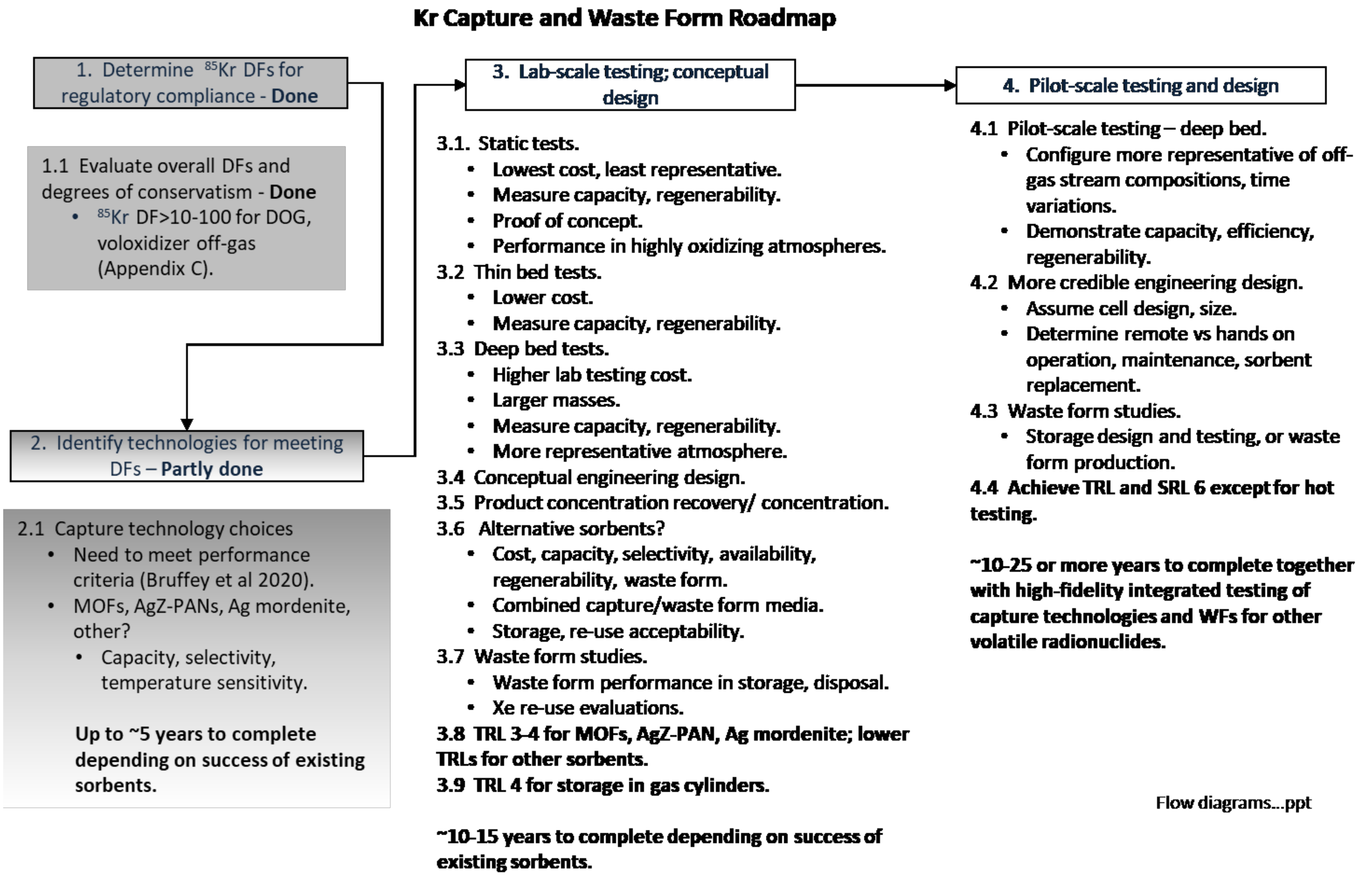
[d] The radioactive Xe isotope with the longest half-life of 36.4 days is ^{127}Xe. Ambient air contains about 100× less Xe than Kr by volume (about 7× less by mass).



Kr Capture and Waste Form Roadmap

1. Determine ^{85}Kr DFs for regulatory compliance - **Done**

1.1 Evaluate overall DFs and degrees of conservatism - **Done**
- ^{85}Kr DF>10-100 for DOG, voloxidizer off-gas (Appendix C).

2. Identify technologies for meeting DFs – **Partly done**

2.1 Capture technology choices
- Need to meet performance criteria (Bruffey et al 2020).
- MOFs, AgZ-PANs, Ag mordenite, other?
  - Capacity, selectivity, temperature sensitivity.

Up to ~5 years to complete depending on success of existing sorbents.

3. Lab-scale testing; conceptual design

3.1. Static tests.
- **Lowest cost, least representative.**
- **Measure capacity, regenerability.**
- **Proof of concept.**
- **Performance in highly oxidizing atmospheres.**

3.2 Thin bed tests.
- **Lower cost.**
- **Measure capacity, regenerability.**

3.3 Deep bed tests.
- **Higher lab testing cost.**
- **Larger masses.**
- **Measure capacity, regenerability.**
- **More representative atmosphere.**

3.4 Conceptual engineering design.

3.5 Product concentration recovery/ concentration.

3.6 Alternative sorbents?
- **Cost, capacity, selectivity, availability, regenerability, waste form.**
- **Combined capture/waste form media.**
- **Storage, re-use acceptability.**

3.7 Waste form studies.
- **Waste form performance in storage, disposal.**
- **Xe re-use evaluations.**

3.8 TRL 3-4 for MOFs, AgZ-PAN, Ag mordenite; lower TRLs for other sorbents.

3.9 TRL 4 for storage in gas cylinders.

~10-15 years to complete depending on success of existing sorbents.

4. Pilot-scale testing and design

4.1 Pilot-scale testing – deep bed.
- **Configure more representative of off-gas stream compositions, time variations.**
- **Demonstrate capacity, efficiency, regenerability.**

4.2 More credible engineering design.
- **Assume cell design, size.**
- **Determine remote vs hands on operation, maintenance, sorbent replacement.**

4.3 Waste form studies.
- **Storage design and testing, or waste form production.**

4.4 Achieve TRL and SRL 6 except for hot testing.

~10-25 or more years to complete together with high-fidelity integrated testing of capture technologies and WFs for other volatile radionuclides.

Flow diagrams....ppt

Figure 3-3. Krypton-85 capture and waste form roadmap.

- For both the mordenite PAN and MOF materials, significant development is needed before a decision can be made to select, scale-up, and deploy either of these technologies. Future work is needed to understand the sorbent selectivity and capacity when exposed to off-gas compositions typical of those expected in a reprocessing facility
- Improve the capacity, selectivity, and kinetics near room temperature
- Improve Kr selectivity
- Improve mechanical stability (new sorbents)
- Evaluate desorption conditions
- Determine how many sorption and desorption cycles are possible before the sorbent capacity degrades to less than optimum for use in an operating facility
- Improve the radiation and mechanical stability with minimal loss of capacity
- Determine what WF options are possible
- Determine what other off-gas impurities could cosorb or interfere with Xe and Kr sorption, sorbent regenerability, or WF properties
- Evaluate multiradionuclide sorbent systems.

The base case ^{85}Kr WF is storage in compressed gas cylinders. An alternative WF is a MOF- or zeolite-filled gas cylinder. A canister filled with sorbent may allow more Kr to be stored at the same total pressure. Scaling production of HZ-PAN and MOF to the scale needed for use in industrial facilities is a challenge yet to be addressed.

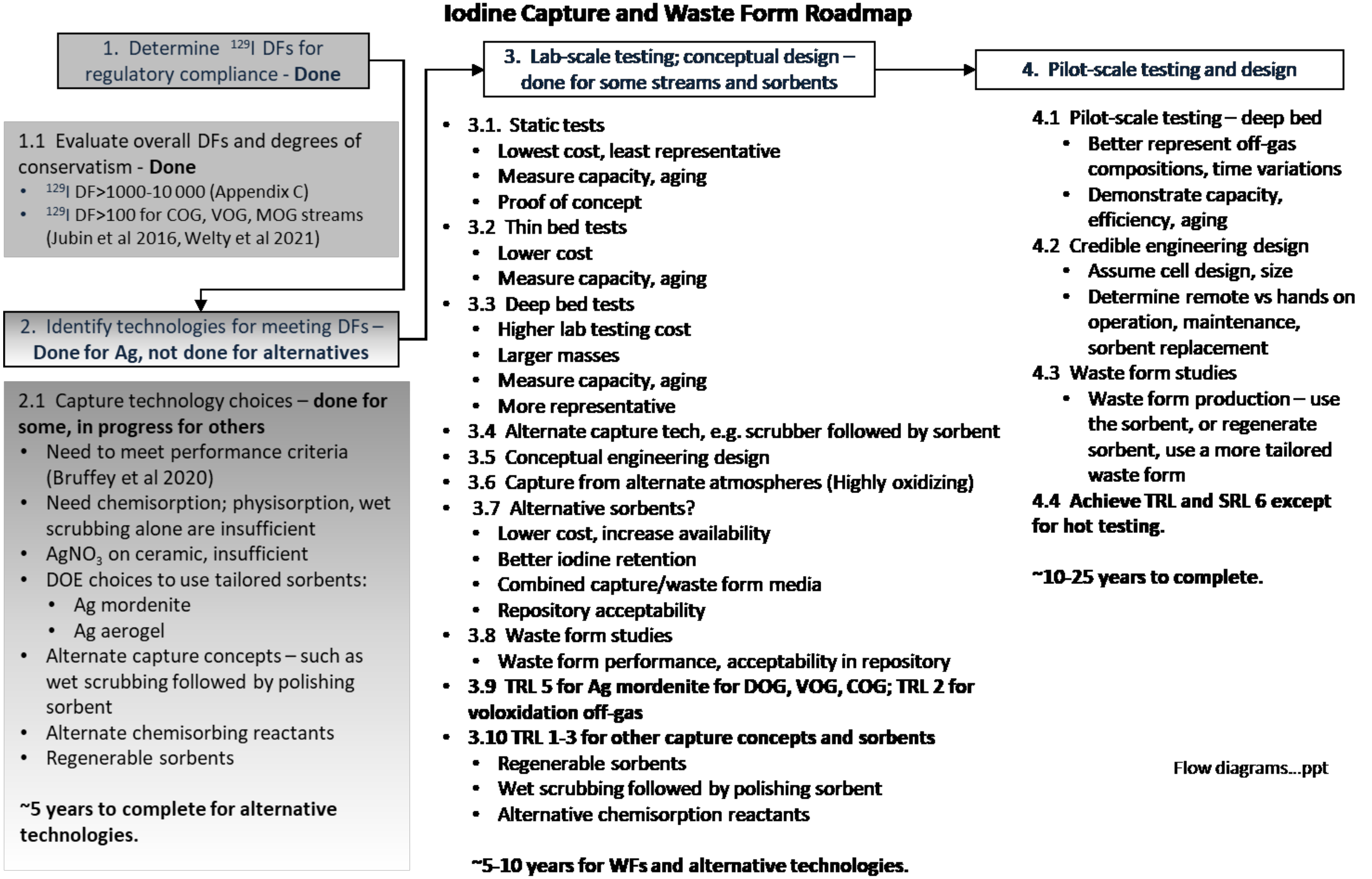
Another alternative for immobilizing ^{85}Kr is ion implantation in ceramic matrices, like SiC, where loadings of up to 9.3 mass% were demonstrated (Tingey et al. 1979a; Tingey et al. 1979b; Tingey et al. 1980; Tingey et al. 1982a; Tingey et al. 1982b; Strachan et al. 2011).

3.4 Iodine-129 Capture and Waste Forms

A roadmap for iodine capture and WFs is shown in **Figure 3-4**. Iodine capture research has been conducted for the past half-century. During the last decade, efforts have been focused on sorbents that contain Ag to chemisorb iodine, thereby improving both iodine capacity and DFs. Two sorbents have been developed to bench scale, AgZ and Ag aerogel, for use in DOG and vessel off-gas (VOG) streams.

Other iodine capture concepts, such as wet scrubbing and $AgNO_3$-coated ceramic supports, are reportedly insufficient to reliably meet expected ^{129}I DF requirements (Burger 1991). While the target ^{129}I DF range in the U.S. is 1000–10 000, Savannah River National Laboratory (SRNL) and Hanford silver nitrate iodine reactors and wet scrubbing achieved DFs ranging between about 100–1000 ((Burger 1991, Burger and Scheele 2004). At the Wiederaufarbeitungsanlage Karlsruhe facility in Germany, DF values approaching 500 were observed for $AgNO_3$-based materials (Herrmann et al. 1993; Herrmann et al. 1997a; Herrmann et al. 1997b).

The differences in performance between $AgNO_3$-based sorbents and AgZ and Ag aerogel sorbents may be due to the different chemical form of silver. Differences in the sorbent configurations, with different sorbent and $AgNO_3$ substrate physical configurations and surface areas, can cause differences in gas-solid contacting and gas-solid mass transfer.



Iodine Capture and Waste Form Roadmap

1. Determine ^{129}I DFs for regulatory compliance - **Done**

1.1 Evaluate overall DFs and degrees of conservatism - **Done**

- ^{129}I DF>1000-10 000 (Appendix C)
- ^{129}I DF>100 for COG, VOG, MOG streams (Jubin et al 2016, Welty et al 2021)

2. Identify technologies for meeting DFs – **Done for Ag, not done for alternatives**

2.1 Capture technology choices – **done for some, in progress for others**

- Need to meet performance criteria (Bruffey et al 2020)
- Need chemisorption; physisorption, wet scrubbing alone are insufficient
- AgNO$_3$ on ceramic, insufficient
- DOE choices to use tailored sorbents:
  - Ag mordenite
  - Ag aerogel
- Alternate capture concepts – such as wet scrubbing followed by polishing sorbent
- Alternate chemisorbing reactants
- Regenerable sorbents

~5 years to complete for alternative technologies.

3. Lab-scale testing; conceptual design – done for some streams and sorbents

- 3.1. Static tests
  - Lowest cost, least representative
  - Measure capacity, aging
  - Proof of concept
- 3.2 Thin bed tests
  - Lower cost
  - Measure capacity, aging
- 3.3 Deep bed tests
  - Higher lab testing cost
  - Larger masses
  - Measure capacity, aging
  - More representative
- 3.4 Alternate capture tech, e.g. scrubber followed by sorbent
- 3.5 Conceptual engineering design
- 3.6 Capture from alternate atmospheres (Highly oxidizing)
- 3.7 Alternative sorbents?
  - Lower cost, increase availability
  - Better iodine retention
  - Combined capture/waste form media
  - Repository acceptability
- 3.8 Waste form studies
  - Waste form performance, acceptability in repository
- **3.9 TRL 5 for Ag mordenite for DOG, VOG, COG; TRL 2 for voloxidation off-gas**
- **3.10 TRL 1-3 for other capture concepts and sorbents**
  - Regenerable sorbents
  - Wet scrubbing followed by polishing sorbent
  - Alternative chemisorption reactants

~5-10 years for WFs and alternative technologies.

4. Pilot-scale testing and design

4.1 Pilot-scale testing – deep bed
- Better represent off-gas compositions, time variations
- Demonstrate capacity, efficiency, aging

4.2 Credible engineering design
- Assume cell design, size
- Determine remote vs hands on operation, maintenance, sorbent replacement

4.3 Waste form studies
- Waste form production – use the sorbent, or regenerate sorbent, use a more tailored waste form

4.4 Achieve TRL and SRL 6 except for hot testing.

~10-25 years to complete.

Flow diagrams...ppt

Figure 3-4. Iodine-129 capture and waste form roadmap.

Alternative capture concepts continue to be proposed and studied, including (a) concepts such as wet scrubbing followed by a polishing sorbent, (b) sorbents containing metals other than Ag (to lower cost and improve disposability), and (c) sorbents that are potentially regenerable. Development programs for these concepts are ongoing, either directly funded through DOE, or funded in collaborations with universities through the Nuclear Energy University Program (NEUP) and Small Business Innovation Research projects. These alternative sorbent technologies are less mature than AgZ and Ag aerogel for iodine capture.

Potential WFs for spent iodine-laden sorbents can be made by processes such as hot isostatic pressing or hot uniaxial pressing to form a consolidated, dense material in which the iodine has been retained. Characterization of mordenite-based and aerogel-based WFs has shown micrometer-sized AgI particles form during processing that are micro-encapsulated in a matrix of various silicate phases. The sparingly soluble AgI particles and silicate matrix provide a durable WF. If iodine is still mobile in grouted WFs, they may be limited to disposal in a salt repository or may require containment in a high-integrity container (HIC). Even though no U.S. nuclear waste repository is available currently, an iodine WF is needed so that it does not become a hindrance to the construction and licensing of the reprocessing facility.

Further research on iodine sorbents and WFs is needed to provide data on sorption performance under various conditions and to evaluate WF options and to eventually select the most promising iodine sorbent and WF combinations for further development.

Several types of low-temperature WFs could be further developed for the immobilization of iodine. Iodine-loaded sorbents can be encapsulated into physically and chemically robust cementitious WF or polymer matrices, which allow incorporation through processes such as polymerization, melt blending, or chemical crosslinking. Polymer-based WFs offer versatility in terms of tailoring properties and can accommodate a wide range of materials. Both can provide good chemical durability and long-term stability. The selection of a specific low-temperature WF depends on factors such as the type and composition of the iodine-loaded sorbent, regulatory requirements, long-term stability considerations, and the desired disposal method. Each WF has its advantages and limitations, and extensive research and testing should be conducted to ensure the suitability and safety of the chosen waste immobilization approach.

Integrated pilot-scale testing with more representative surrogate or real gas streams, integrated into a more complete off-gas system, is needed to demonstrate and optimize the iodine capture and WF process performance, develop a more credible engineering design, and confirm the potential costs associated with the incorporation of iodine capture and WFs into a reprocessing facility (Greaney et al. 2022c).

3.5 Voloxidation

Several studies have described the NO_2 voloxidation process and reviewed the advantages of this advanced voloxidation compared with other processing methods (Del Cul et al. 2013; Greaney et al. 2022a; Greaney et al. 2022b; Soelberg et al 2023). Some of these studies have tested NO_2 voloxidation in shielded facilities with SNF (Johnson et al. 2013; Johnson et al. 2017). However, questions remain as to the effectiveness of advanced voloxidation, especially for the evolution of volatile and semivolatile fission products (Greaney et al. 2022b).

The quantitative release of tritium during conventional voloxidation (O_2-based, ~600 °C) and advanced voloxidation (NO_2/O_2-based, ~350 °C) has been well documented. Conventional voloxidation has been shown to release >99.9% of the tritium in the fuel but may not release tritium trapped as zirconium hydride deep within the cladding (Uchiyama et al. 1992). Quantitative tritium volatilization and its capture on silica gel was demonstrated with tritiated water in the advanced voloxidation process (Jubin et al. 2019).

The release of ^{85}Kr from the UNF was studied during conventional voloxidation with O_2 at Oak Ridge National Laboratory in the Coupled End to End campaign (Jubin et al. 2008; Jubin et al. 2009). In this program, two pieces of UNF rods were oxidized in an O_2 atmosphere at 500 °C. In the first experiment, 43% of the ^{85}Kr inventory was released; in the second experiment, 24% of the ^{85}Kr inventory was released. In each experiment, Kr release began as soon as the fuel was chopped at 100 °C.

In volatilization, the behavior of iodine is less understood. Iodine is likely present in the fuel as CsI that thermally decomposes at 670 °C (Kulikov and Malyshev 1983)—a higher temperature than the operating temperature of the voloxidation processes. Some iodine is volatilized in an as-yet unknown gaseous species. Preliminary studies suggest that only 1% of the iodine may be released during conventional oxidation (Goode et al. 1973) while more recent work suggests that >99.9% of iodine may be removed during NO_2 voloxidation per the following reaction (Johnson et al. 2013):

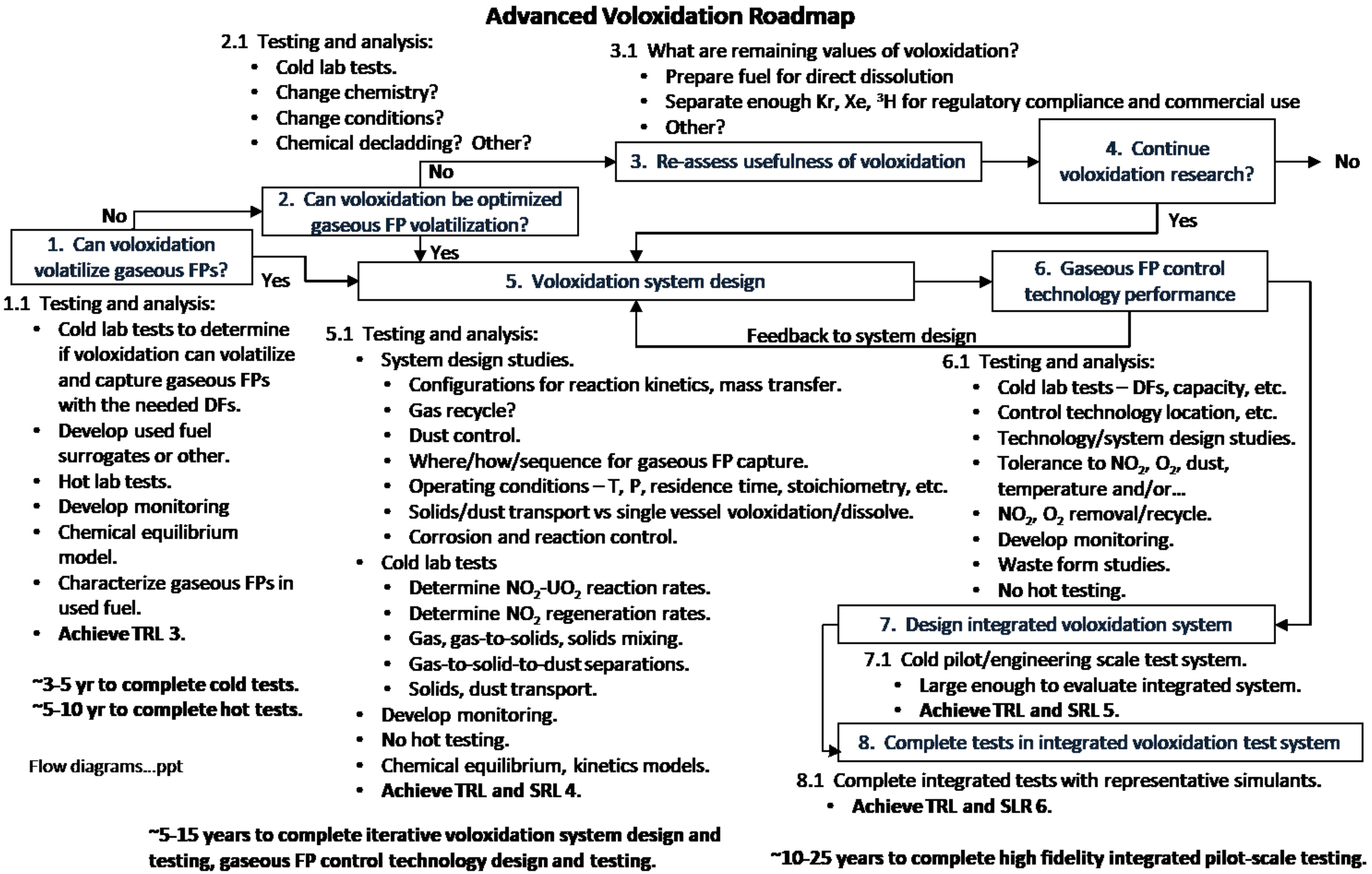
$$2CsI(s) + 2NO_2(g) + O_2(g) \rightarrow 2CsNO_3(s) + I_2(g)$$

The fraction released may depend on the distribution of iodine through the fuel and access of the oxidizing reagent to the iodine species. Further work is needed to quantify the efficiency of iodine release during advanced voloxidation and the effects of NO_2 on volatile fission products.

A decision about the feasibility of NO_2 voloxidation and volatile radionuclide release and abatement will require further testing with SNF (Greaney 2022a). This testing should include determining the partitioning of fission products between the remaining voloxidized fuel, the remaining cladding, and the voloxidizer gas stream. The products trapped in off-gas components also need to be quantified.

A roadmap for advanced voloxidation is shown in **Figure 3-5**. Advanced voloxidation can simplify the plant design if it can evolve the volatile radionuclides to be captured in a single gas stream rather than multiple gas streams and enable direct dissolution of the recyclable actinides into the organic solvent rather than first into aqueous HNO_3 solution (Goode and Stacy 1978; Bresee et al. 2012; Del Cul et al. 2013; Rudisill et al. 2019; Gogolski et al. 2022; Greaney et al. 2022b; Hall et al. 2022; Moyer and Lumetta 2023; Soelberg et al. 2023). Trade-offs and current unknowns with this process include:

- Sufficient volatilization of the four radionuclides of concern has not yet been demonstrated. Recent R&D indicates that voloxidation may not adequately volatilize all four volatile radionuclides (especially ^{129}I) with the needed efficiencies to prevent contamination of downstream process and gas streams. However, sufficient volatilization of ^{3}H alone (plus enabling direct dissolution) could make voloxidation worth using because this process would limit the dilution of the tritium with H_2O and limit tritium contamination in downstream processes.
- In the voloxidation process, the UO_2 fuel is oxidized and reduced to a very fine powder, a few micrometers in diameter. Handling fine powders is difficult in hot cells and can lead to unexpected down time for the process(es) taking place in that hot cell. A design for interfacing UNF chopping, the voloxidizer, the dissolver, and cladding hull management has not yet been developed.
- Dissolution of fine UO_3 powders in an organic extractant has only been demonstrated at small lab scale. A number of reaction parameters at large scale may cause incomplete dissolution of the UO_3 powder. Further, some fission products in the UNF are insoluble in organic solvent, which may be a benefit in achieving early separation from the soluble actinides, but undissolved solids may present new filtration challenges, especially if the undissolved material consists of even finer powder.
- Other elements may become volatile. For example, Ru in air at elevated temperatures forms volatile RuO_4 and must be removed before it condenses in or on system components and results in thermal and radioactive hot spots in an off-gas system. The volatility of other elements during voloxidation is also not well known.



Advanced Voloxidation Roadmap

1. Can voloxidation volatilize gaseous FPs?

1.1 Testing and analysis:
- Cold lab tests to determine if voloxidation can volatilize and capture gaseous FPs with the needed DFs.
- Develop used fuel surrogates or other.
- Hot lab tests.
- Develop monitoring
- Chemical equilibrium model.
- Characterize gaseous FPs in used fuel.
- **Achieve TRL 3.**

~3-5 yr to complete cold tests.
~5-10 yr to complete hot tests.

Flow diagrams…ppt

2. Can voloxidation be optimized gaseous FP volatilization?

2.1 Testing and analysis:
- Cold lab tests.
- Change chemistry?
- Change conditions?
- Chemical decladding? Other?

3. Re-assess usefulness of voloxidation

3.1 What are remaining values of voloxidation?
- Prepare fuel for direct dissolution
- Separate enough Kr, Xe, ^{3}H for regulatory compliance and commercial use
- Other?

4. Continue voloxidation research?

5. Voloxidation system design

5.1 Testing and analysis:
- System design studies.
  - Configurations for reaction kinetics, mass transfer.
  - Gas recycle?
  - Dust control.
  - Where/how/sequence for gaseous FP capture.
  - Operating conditions – T, P, residence time, stoichiometry, etc.
  - Solids/dust transport vs single vessel voloxidation/dissolve.
  - Corrosion and reaction control.
- Cold lab tests
  - Determine NO_2-UO_2 reaction rates.
  - Determine NO_2 regeneration rates.
  - Gas, gas-to-solids, solids mixing.
  - Gas-to-solid-to-dust separations.
  - Solids, dust transport.
- Develop monitoring.
- No hot testing.
- Chemical equilibrium, kinetics models.
- **Achieve TRL and SRL 4.**

Feedback to system design

6. Gaseous FP control technology performance

6.1 Testing and analysis:
- Cold lab tests – DFs, capacity, etc.
- Control technology location, etc.
- Technology/system design studies.
- Tolerance to NO_2, O_2, dust, temperature and/or…
- NO_2, O_2 removal/recycle.
- Develop monitoring.
- Waste form studies.
- No hot testing.

7. Design integrated voloxidation system

7.1 Cold pilot/engineering scale test system.
- Large enough to evaluate integrated system.
- **Achieve TRL and SRL 5.**

8. Complete tests in integrated voloxidation test system

8.1 Complete integrated tests with representative simulants.
- **Achieve TRL and SLR 6.**

~5-15 years to complete iterative voloxidation system design and testing, gaseous FP control technology design and testing.

~10-25 years to complete high fidelity integrated pilot-scale testing.

Figure 3-5. Advanced voloxidation roadmap.

In the near term, research is needed to determine the viability of voloxidation and plan its development. This research is needed to address the above-listed items and obtain the data needed to design the voloxidation system.

Several options may be considered for designing the voloxidation system and integrating it into the UNF reprocessing facility. **Figure 3-6** shows one possibility for integrating the voloxidation system into an aqueous headend process. Chopped fuel is transported batchwise from shearing into the voloxidizer vessel, where batch voloxidation occurs. The cladding and voloxidized fuel are then transported batchwise into the direct dissolver vessel. Direct dissolution into the organic solvent replaces the hot HNO_3 dissolution that is currently used. This eliminates the need for the traditional first solvent extraction step in which recyclable actinides are extracted from the nitric acid.

Another possibility is shown in **Figure 3-7** where direct dissolution might be done in the same reactor vessel as the voloxidation. This eliminates the transfer of fines that would result if the fine fuel powder were to be transferred from the voloxidizer to the dissolver vessel, as in **Figure 3-6**. This case has not been tested at the laboratory scale; many process controls are yet to be determined and investigated. Among the uncertainties yet to be investigated are the voloxidizer and dissolver vessel design, construction materials that can tolerate both voloxidizer and dissolver operating conditions, transitioning from gaseous high-temperature voloxidation to lower temperature solid and liquid dissolution in the same reactor vessel, and managing (discarding or retaining) the voloxidizer gas.

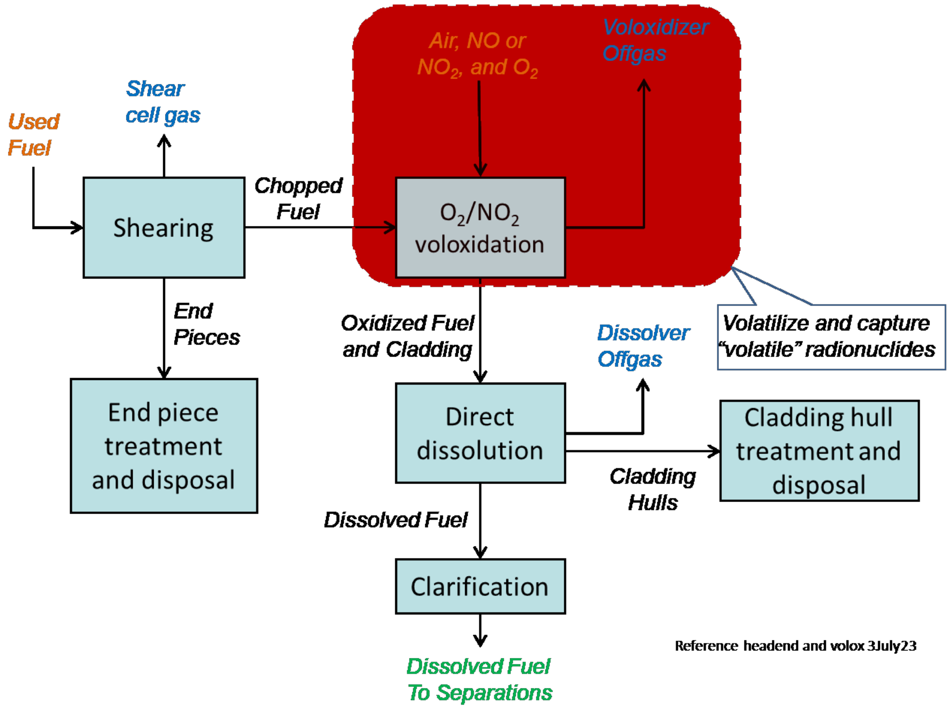


Figure 3-6. Voloxidation in aqueous reprocessing headend.

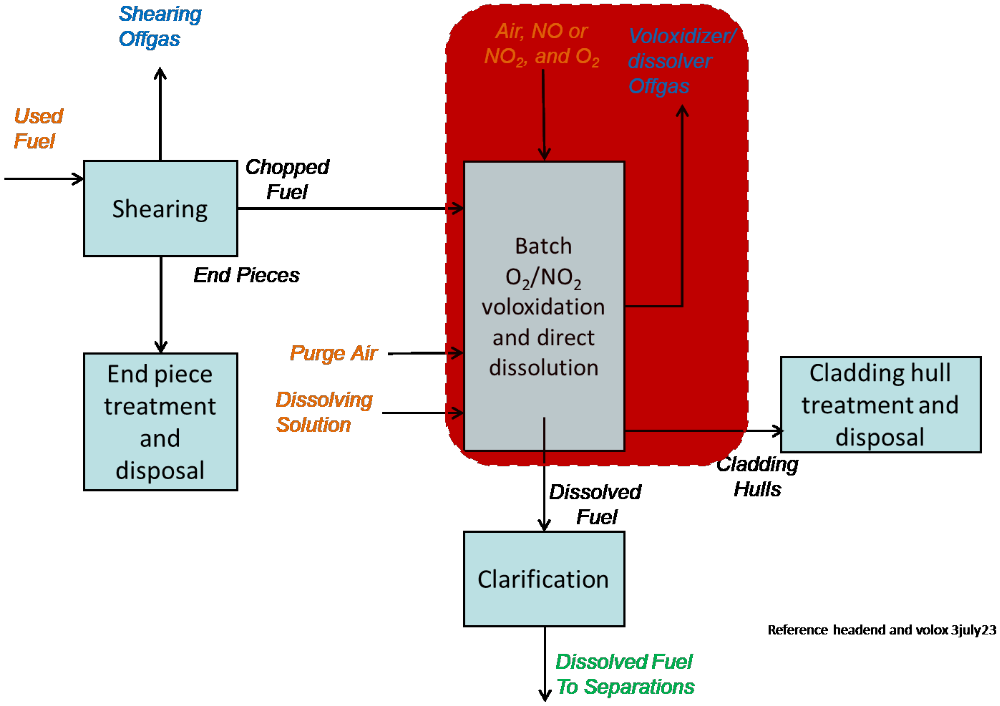


Figure 3-7. Combined sequential batch voloxidation and direct dissolution in same vessel.

Potential options for voloxidation gas management in a gas recycling system are shown in **Figure 3-8** and **Figure 3-9**. In this case, separate vessels are used for voloxidation and NO_2 regeneration, so each of these operations can be performed at their separate, optimal temperature, residence time, stoichiometry, and mixing conditions. The oxidized fuel and cladding are discharged batchwise to the direct dissolver as in the first case (**Figure 3-8)** or remain in the voloxidizer for sequential dissolution (**Figure 3-9)**. The NO_2-depleted voloxidizer gas is recycled through the NO_2 regeneration reactor where O_2 is added to react with the NO to regenerate the NO_2. While NO_2 is the reactant in the voloxidation process that most efficiently oxidizes the fuel, it is regenerated in the process, and O_2 is the reagent that is consumed in the voloxidation reactions.

Capture of volatilized radionuclides may occur in the recycle loop (**Figure 3-8**) or in the voloxidizer off-gas system (**Figure 3-9**). The viability of capturing volatilized radionuclides in the recycle loop depends on the compatibility of the control technologies (for tritiated water, ^{14}C, ^{129}I, Kr/Xe, and ^{106}Ru) with the high NO_x and O_2 voloxidizer gas. Additionally, if sorbents are used in the recycle loop, they should not interfere with the voloxidation process by consuming the gaseous reagent (NO_2).

If any capture technologies for volatilized radionuclides cannot tolerate the voloxidizer gas stream, the high NO_x and O_2 levels will need to be reduced. If NO_x and O_2 removal is done in the recycle loop, it reduces the value of having the recycle loop, because NO_x and O_2 would be destroyed or scrubbed from the recycle gas, instead of regenerated and recycled. This may drive the need to capture volatilized radionuclides in a vented slipstream or batch process as shown in **Figure 3-9**.

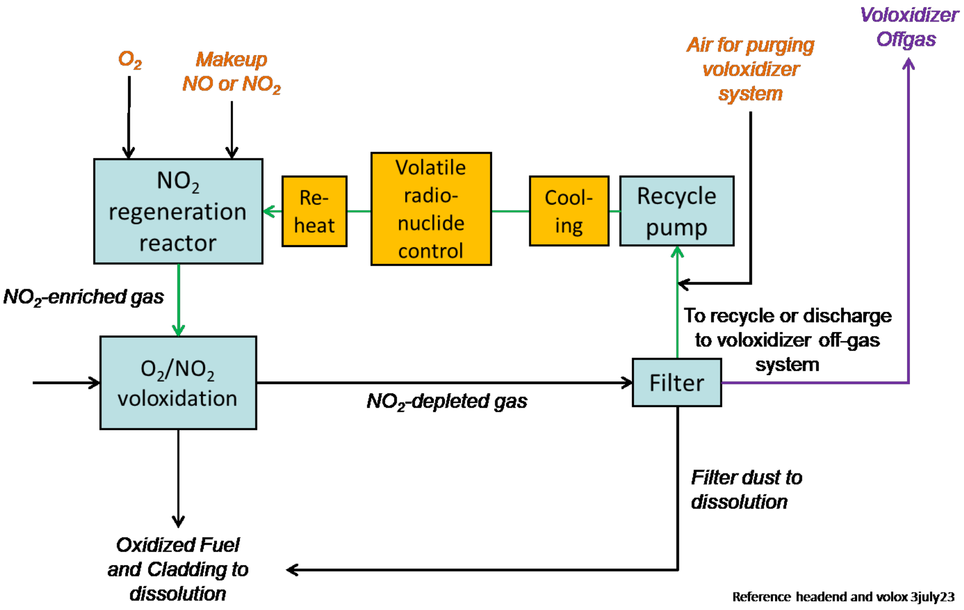


Figure 3-8. Volatile radionuclide control in the voloxidizer gas recycle loop.

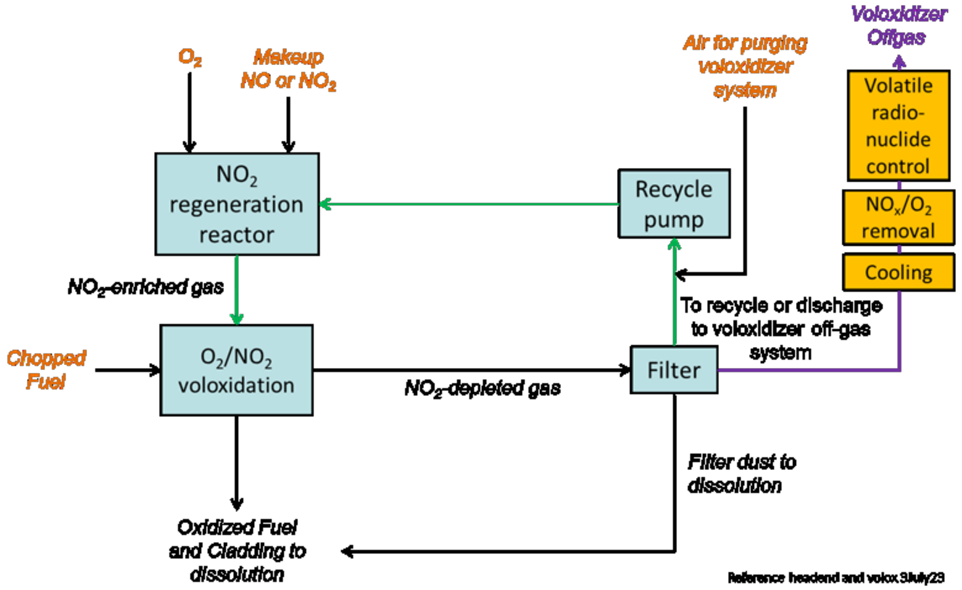


Figure 3-9. Volatile radionuclide control in the voloxidizer off-gas system.

If the NO_2 regeneration kinetics are fast, and if NO_2 regeneration conditions do not interfere with voloxidation conditions and vice versa, then a separate NO_2 regeneration vessel may not be needed, and the voloxidation system may schematically look like that in **Figure 3-10**. In this case, both voloxidation and NO_2 regeneration occur simultaneously in the same vessel thereby eliminating the gas recycle. Volatilized radionuclides would accumulate in the vessel resulting in the need for some or all of the voloxidizer gas to be vented or purged through the voloxidizer off-gas system, where the needed off-gas control would be performed. Options for the voloxidation gas discharge to the off-gas system may be periodic, at the end of a voloxidation cycle, or as a continuous slipstream.

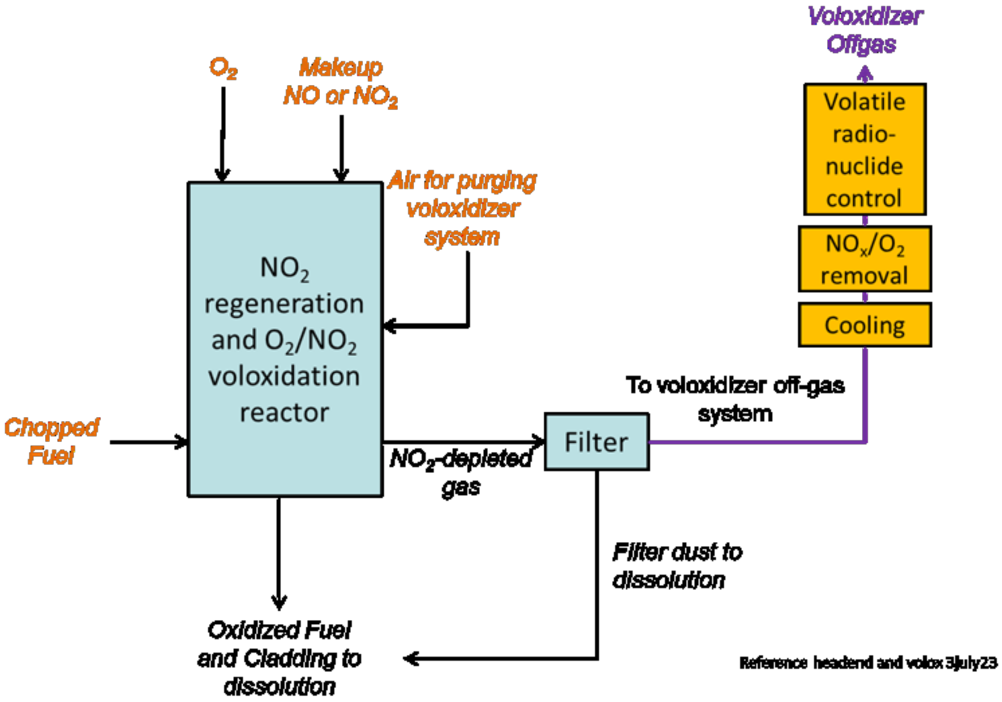


Figure 3-10. NO_2 regeneration and UNF voloxidation in single vessel without voloxidizer gas recycle.

3.6 Analytical Needs

Real-time monitoring is needed to track the performance of the volatile radionuclide capture systems and determine the compliance of the reprocessing facility to applicable air emissions regulations. Current online gas-phase analyses for ^{14}C, Kr, Xe, and ^{3}H have insufficient sensitivity to assure compliance in real time to the projected DF requirements for a new reprocessing facility. Thus, research on analytical instrumentation and techniques is needed to achieve the quantitation limits needed to show the real-time compliance of anticipated regulatory requirements. This is especially true for ^{129}I (not total iodine, just the ^{129}I), because of the high DFs that are anticipated to meet these regulations. These high DFs result in very low ^{129}I concentrations. Development of online, real time, iodine measurement technologies with sufficiently low quantitation limits would assure the public and the regulator that iodine control technologies are sufficient and operating correctly. Being able to qualitatively identify the speciation of the analytes would also be ideal.

Some iodine sorbent testing has been done by artificially spiking higher iodine levels just so the needed DF can be demonstrated. This "spiking" approach is commonly done and is required in other regulatory compliance projects, such as in Comprehensive Performance Tests for regulatory compliance to Hazardous Waste Combustor Maximum Achievable Control Technology standards (CFR, Title 40, Part 63, Subpart EEE, Section 63.1203) for the same reason—insufficiently low quantitation limits for the available analysis technologies. However, spiking iodine to levels higher than expected in the actual gas streams can bias the performance of the iodine control technology. Sorbent R&D could be improved if sensitive, real-time monitoring can be used to measure sorbent performance.

Without sufficiently sensitive measurements, other methods to demonstrate reprocessing facility regulatory compliance would be required, including:

- Collecting, often over one week to several months, a composite iodine sample that can be concentrated enough to be quantified in a subsequent laboratory analysis. This does not provide real-time compliance information, but it demonstrates facility compliance during that sampling period. This method is currently used in radioactive facilities for various radionuclides.

- Mass balances of input and output streams are used to demonstrate, by difference, the amount of iodine released over time to the atmosphere. This is the most unreliable method of determining regulatory compliance because of the inhomogeneity and inconsistency in the fuel entering the facility. Currently, the location and chemical form of the iodine in the fuel is uncertain at best. Therefore, this strategy is less likely to be acceptable to regulators and stakeholders.

It is envisioned that, in the future, iodine sorbents can also be utilized as sensors for detecting and monitoring iodine in reprocessing off-gas streams. Sorbents can be functionalized or designed in such a way that they undergo an observable change when they interact with iodine, allowing for sensitive and selective detection. These observable changes could include color changes or fluorescence, detectable by fluorescence spectroscopy. Fluorescent sensors offer high sensitivity and can be used for real-time monitoring or automated systems.

The selection of the appropriate iodine sorbent and sensor platform depends on factors such as the target application, sensitivity requirements, and desired detection method (e.g., visual, spectroscopic). Additionally, careful consideration should be given to the stability, selectivity, and regeneration capabilities of the sorbent for reliable and continuous sensing.

4. NEAR-, INTERMEDIATE-, AND LONG-TERM RESEARCH PRIORITIZATION, SEQUENCE, AND GOALS

The sequence, prioritization, and near-, intermediate-, and long-term goals for off-gas and WF research were discussed in the workshop. Potential goals for each of these timeframes were introduced in a brainstorming group discussion. These goals were documented and organized by topic and timeframe.

Conceptually, these goals define a “vision” that future UNF reprocessing in the U.S. must differ from previous reprocessing experience in the U.S. and worldwide. The design and function of a future reprocessing facility used as a basis in this report may change depending on the target fuel cycle, UNF storage concepts, and development of a permanent repository for spent fuel and separated waste streams from reprocessing UNF. The vision for future R&D that could simplify and lower cost and risk for reprocessing facility off-gas control is shown in **Table 4-1**.

Somewhat arbitrary timeframes were proposed in the workshop to assess technology development, as illustrated starting in Fiscal Year 2023.[e] These timeframes were used to identify what R&D should be pursued in general terms of soon (near term) and later (intermediate term) and to recognize the potential for future (long term) breakthroughs in UNF reprocessing technologies.

The amount of research that can be conducted and achieved in these timeframes depends on the availability of funding and other resources. Table 4-1 and subsections 4.1–4.3 imply that, given sufficient funding profiles, the off-gas control and WF technology development can be achieved to start the design and construction of an aqueous reprocessing facility with current off-gas control technologies in 10–20 years. If R&D for NO_2 voloxidation and solid sorbent capture and separation of Kr and Xe are successful, complexity and costs could be reduced in the design and construction of a more advanced reprocessing facility in about 20–25 years. In the long term, new technology breakthroughs beyond currently known technologies for reprocessing and off-gas capture (e.g., multiradionuclide sorbents) may enable further simplifications or cost reductions in the 25–100 year timeframe.

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[e] The year of the workshop and this roadmap document.

Table 4-1. Future vision and potential timing for UNF aqueous reprocessing.

Vision Statements	Time Range	R&D Year Range	R&D Support to Reach CD-1 For a Future Reprocessing Plant:		
			With Current Baseline or “Case Study” Technologies in 10–25 yr (Section 4.1)	With Voloxidation and Solid Sorbent Kr/Xe Capture and Separation in 20–50 yr (Section 4.2)	With Future Technology Innovations to Further Reduce Cost in 25–100 yr (Section 4.3)
1. Demonstrate that capture technologies are efficient enough to meet regulatory requirements and selective enough such that subsequent separation steps are unnecessary. 2. Develop and demonstrate WFs for captured radionuclides that can meet expected storage and disposal requirements.	Near term	0–3	X	X	X
		3–5	X	X	X
1. Develop and demonstrate volatile radionuclide capture technologies and associated WFs for the next-generation reprocessing plant that reduce the size and associated capital and operating costs to those portions of the facility. 2. Develop voloxidation or similar processes to release all volatile radionuclides that require abatement into a single off-gas stream to a sufficient degree that treatment of any other off-gas stream within the reprocessing plant to recover them is unnecessary. 3. Simplify reprocessing plant headend operations to minimize solids handling and control of fine particulates. 4. Develop WFs for volatile radionuclides that require no additional processing of the capture media. Ideally, the radionuclide-loaded sorbents can be effectively processed with cost-effective and easily employed methods without the need for high heat, reducing energy consumption and potential environmental impacts, and preventing the loss of captured radionuclides. Develop online sensors that can be used in real time to measure the performance of off-gas control technologies and to demonstrate that in-plant off-gas control technologies are performing correctly and achieving the required DFs.	Inter-mediate term	5–10	X	X	X
		10–25		X	X
1. Develop and demonstrate volatile radionuclide capture processes that effectively capture two or more of the species of interest to reduce the number of unit operations. 2. Develop and demonstrate multiradionuclide WFs that can simplify and reduce costs for storage and disposal.	Long term	25–50			X
		50–100			X

Achievement of any of this vision would help lower costs and risks for UNF reprocessing and help enable reprocessing in the U.S. Some of these vision elements, especially multiradionuclide capture in a single capture process or multiradionuclide WFs, may not be achievable in the near term, or ever, without future technological breakthroughs.

4.1 Baseline (Case Study) Off-Gas Control and Waste Form Research and Development

A roadmap is provided in **Table 4-2** to illustrate the R&D needed for a baseline or "Case Study" UNF reprocessing facility based on existing reprocessing technologies. This table is based on a baseline or Case Study aqueous reprocessing facility that uses the most mature technologies currently available for every operation (Law et al. 2015, Vienna 2015):

- Condensation, wet scrubbing, and sorption for tritiated water; grouted WFs (in a HIC if necessary)
- Wet scrubbing for ^{14}C in the form of $^{14}CO_2$; cemented $CaCO_3$ WF
- Cryogenic capture and separation of Kr and Xe; Kr compressed gas decay storage in metal cylinders
- AgZ chemisorption for ^{129}I; conversion of the spent AgZ into a durable WF.

New potential sorbents have been identified for capturing radionuclides such as ^{85}Kr and ^{129}I. Some show promise under theoretical or idealized conditions but have not yet been developed to the degree that cryogenic Kr and Xe capture and separation and AgZ chemisorption of iodine have. In general, these new sorbents are in the early stages of development and their TRLs are generally low. While researching new technologies may provide alternatives to more mature technologies, future R&D should focus on advancing and filling in data gaps on the existing and most mature technologies, including the demonstration of viable WF and advancing the TRLs through large-scale demonstrations and testing under high-fidelity conditions.

In this roadmap, the more detailed information from Section 3 for individual volatile radionuclide capture and WF technologies is summarized and integrated in a few lines. This roadmap includes the need to complete R&D for the volatile radionuclide WF and to perform high-fidelity pilot-scale testing to mature the above-listed technologies to at least TRL 6. The roadmap distinguishes the time periods between now and when the mission need for a reprocessing facility is approved (CD-0) and between CD-0 and "Alternative Selection and Cost Range Approval" (CD-1) (DOE 2021). Technologies should be matured to at least TRL 4–5 before CD-0 and to at least TRL 6 before CD-1. Advancing technologies beyond TRL 4–5 prior to CD-0 reduces technical, schedule, and cost risks. Advancing beyond TRL 4–5 requires radioactive lab-scale testing and nonradioactive pilot-scale testing for capture and WF technologies.

The time duration between now (2023), CD-0, and CD-1 for a reprocessing facility, even with the baseline (Case Study) technologies, remains unknown and depends on funding and national commitment to proceed with UNF reprocessing. Thus, this time duration may include several of the near- and intermediate-term timeframes. Assuming that the required funding can be available starting now, these activities could be completed in about 7–15 years. This is sufficient to perform the needed off-gas control and WF R&D needed by the time of CD-0 and CD-1 for a baseline or "Case Study" reprocessing facility.

Table 4-2. Off-gas control and waste form technology R&D for a baseline or Case Study reprocessing facility.

Activity	Time sequence, estimated relative duration of the activity, and ending TRL (not to scale)															
	Near-term R&D					Intermediate-term R&D										
	0-3 yrs			3-5 yrs		5-10 yrs				10-25 yrs						
						Notional timing for a reprocessing facility			CD-0			CD-1				
1. Non-rad lab-scale WF R&D for ^{129}I and ^{14}C (AgZ and CaCO$_3$).	▨	▨	▨	▨	▨	▨	▨	▨	TRL 4-5							
a. Bench-scale R&D and down-select WF conversion processes for I-laden AgZ; and ^{14}C.	▨	▨	▨	▨	▨	▨										
b. Perform and complete WF performance models.	▨	▨	▨	▨	▨	▨	▨									
c. Assess acceptability of the resultant WF(s) for storage and disposal.						▨	▨	▨								
2. Rad lab-scale WF testing for ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I.						▨	▨	▨	TRL 4-5							
a. Assess production and performance of WF for each isotope.						▨	▨	▨								
3. High-fidelity, non-rad integrated pilot-scale capture testing for ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I		▨	▨	▨	▨	▨	▨	▨	▨ TRL 4-5	▨	▨	TRL 6				
a. Perform engineering design for integrated pilot-scale system that can achieve more representative gas compositions and operating conditions.			▨													
b. Construct and install pilot-scale test system.				▨												
c. Evaluate system interactions.					▨	▨	▨									
d. Evaluate co-sorption and other interferences.						▨	▨	▨								
e. Produce material for pilot-scale WF testing.							▨	▨	▨							
f. Update conceptual full-scale engineering design.								▨	▨	▨						
g. Perform detailed full-scale design.											▨					
4. Non-rad pilot-scale WF testing for ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I						▨	▨	▨	▨ TRL 4-5	▨	▨	TRL 6				
a. Design and construct pilot-scale WF test system.						▨	▨									
b. Assess production and performance of WF for each isotope.								▨	▨							
c. Demonstrate results of lab-scale testing.								▨	▨	▨						
d. Validate WF performance models.									▨	▨						
e. Perform detailed full-scale design.											▨					

off-gas research roadmap....xlsx

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Tritiated water capture and WF technologies are considered relatively mature, and no specific tritium capture and WF R&D has been recently undertaken by DOE. However, some uncertainties remain, including potential for off-gas impurities to affect the wet scrubbing and WF for tritiated water, and should capture and recovery for economic use be considered for tritium and its decay product ^{3}He.

Wet caustic scrubbing of $^{14}CO_2$ and grouting of the precipitated $CaCO_3$ technologies have been considered relatively mature, so no specific ^{14}C capture and WF R&D has recently been undertaken by DOE. However, some uncertainties remain, including scrubber conditions to achieve the needed DF, how off-gas impurities might interfere with or coscrub with the CO_2, and how coscrubbed off-gas impurities might affect the WF performance, handling, classification, storability, and disposability.

These uncertainties need to be resolved to include ^{3}H and ^{14}C capture and WFs in designs for aqueous UNF reprocessing facilities. An optimal time to address these uncertainties is prior to or during integrated, representative pilot-scale testing for the other volatile radionuclides and WFs. Developing and maturing the capture and WF technologies for iodine and noble gases, so they are ready for integrated, representative pilot-scale testing, may be a higher priority than expending time and funding for ^{14}C capture and WFs prior to that point.

4.2 Near-Term Target Off-Gas Control and Waste Form Research and Development

A roadmap is provided in **Table 4-3** to illustrate the R&D needed to enable UNF reprocessing with "Near-Term Target" technologies, as described in Law et al. 2015. Some technologies are the same as in the Case Study—tritiated water and $^{14}CO_2$ capture, and WF for the captured tritiated water, $^{14}CO_2$, and Kr. Near-Term Target technologies that show promise for reducing the size, complexity, and cost of off-gas control for an aqueous reprocessing facility, including:

- NO_2 voloxidation (or, if NO_2 voloxidation is determined to not be feasible, at least air oxidation that volatilizes the ^{3}H)
- Capture of volatilized radionuclides in the voloxidizer gas stream
- Alternative ^{129}I sorbents not based on Ag
- Solid sorbent capture and separation of Kr and Xe (instead of cryogenic capture and separation)
- Alternative ^{129}I WFs
- Online, real-time monitoring of radionuclides, especially ^{129}I, in the off-gas streams, sensitive enough to enable determination of capture technology DFs and regulatory compliance.

Voloxidation, Ag aerogel, non-Ag iodine sorbents, and solid sorbent Kr and Xe capture technologies are not as mature as the baseline technologies. These require lab-scale testing followed by high-fidelity, integrated pilot-scale or larger testing. The TRLs for these technologies are three or lower. Maturing a selection of these technologies to TRLs of six or higher could improve safety and reduce risk, complexity, and costs for a "Near-Term Target" reprocessing facility (Law et al. 2015) that could be built in the 20–50 year timeframe (depending on R&D funding).

As in the baseline (Case Study), the WF technologies all require nonradioactive lab-scale testing to optimize the WF chemical and physical properties, lab-scale testing with radioactive isotopes to evaluate and determine how to control the impacts of radioactive isotopes in the WF, and provision and evaluation of possible WF optimizations or alternatives. The selected and optimized WF require a pilot-scale demonstration in conjunction with integrated pilot-scale capture technology testing to evaluate large-scale WF production and the impacts, if any, of cosorbed species (such as iodine or NO_x captured with tritiated water or ^{14}C).

Table 4-3. Off-gas control and waste form technology R&D for a Near-Term Target aqueous reprocessing facility.

Activity	Time sequence, estimated relative duration of the activity, and ending TRL (not to scale)				
	Near-term R&D		Intermediate-term R&D		
	0-3 yrs	3-5 yrs	5-10 yrs	10-25 yrs	
				Future reprocessing facility CD-0 ↓	CD-1 ↓
1. **Non-rad lab scale WF R&D** for iodine (Ag mordenite, Ag Aerogel, non-Ag based sorbents, and $CaCO_3$).	▨	▨	▨	▨ TRL 4-5	
a. Bench-scale R&D and downselect WF conversion processes for I-laden AgZ and other sorbents; and ^{14}C.	▨	▨	▨	▨	
b. Continue and complete iodine WF performance model.	▨	▨	▨	▨	
d. Evaluate waste forms for regenerable sorbents.	▨	▨	▨	▨	
c. Assess acceptability of the resultant WF(s) for storage and disposal.			▨	▨	
2. **Rad lab-scale WF testing** for ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I			▨	▨ TRL 4-5	
a. Assess production and performance of WF for each isotope.			▨	▨	
3. **Non-rad lab-scale NO_2 voloxidation testing.**	▨	▨	▨	▨ TRL 4-5	
a. Can voloxidation volatilize all volatile FPs? Or only ^{3}H as in air voloxidation?	▨				
b. If not, re-assess voloxidation usefulness; continue volox research?		▨			
c. Evaluate and test voloxidation system design.		▨			
d. Evaluate and test volatilized radionuclide capture technology.		▨	▨		
e. Evaluate and test integrated voloxidation system design that includes both voloxidation and capture of volatilized radionuclides.			▨	▨	
4. **Rad lab-scale NO_2 voloxidation testing.**			▨	▨ TRL 4-5	
a. Determine extent of volatilization and fines control using real used fuel.			▨	▨	
5. **Non-rad lab-scale capture testing** for Kr/Xe solid sorbents.	▨	▨	▨	▨ TRL 4-5	
a. Evaluate sorbent performance, capacity, regenerability, etc. in static and thin bed tests; multiple sorbent options.	▨	▨			
b. Evaluate sorbent bed performance - mass transfer zone, regeneration system design, etc. in deep bed and more complex gas streams; multiple sorbents.	▨	▨	▨	▨	
c. Perform sorbent downselection and system design.			▨	▨	

Activity	Time sequence, estimated relative duration of the activity, and ending TRL (not to scale)															
	Near-term R&D									Intermediate-term R&D						
	0-3 yrs			3-5 yrs		5-10 yrs				10-25 yrs						
										Potential reprocessing facility						
											CD-0 ↓					CD-1 ↓
6. Non-rad lab-scale capture testing for ^{129}I sorbents – non-Ag and regenerable.	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	**TRL 4-5**					
a. Evaluate sorbent performance, capacity, regenerability, etc. in static and thin bed tests; multiple sorbent options.	▨	▨	▨	▨	▨											
b. Evaluate sorbent bed performance – mass transfer zone, regeneration system design, etc. in deep bed and more complex gas streams; multiple sorbents.			▨	▨	▨	▨	▨	▨	▨	▨						
c. Perform sorbent downselection and system design.						▨	▨	▨	▨	▨						
7. High-fidelity, non-rad integrated pilot-scale capture testing for ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I Near Term Target technologies.		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨ TRL 4-5	▨	▨	▨	▨	**TRL 6**
a. Perform engineering design for integrated pilot-scale system that can achieve more representative gas compositions and operating conditions.		▨	▨													
b. Construct and install pilot-scale test system.				▨												
c. Evaluate system interactions.					▨	▨	▨									
d. Evaluate co-sorption and other interferences.						▨	▨	▨								
e. Produce material for pilot-scale WF testing.							▨	▨	▨							
f. Update conceptual full-scale engineering design.								▨	▨	▨						
g. Perform detailed full-scale design.											▨	▨	▨	▨	▨	
8. Non-rad pilot-scale WF testing for ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I.						▨	▨	▨	▨	▨	▨ TRL 4-5	▨	▨	▨	▨	**TRL 6**
a. Design and construct pilot-scale WF test system.						▨	▨									
b. Assess production and performance of WF for each isotope.								▨	▨	▨						
c. Demonstrate results of lab-scale testing.									▨	▨	▨					
d. Validate WF performance models.											▨	▨	▨			
e. Perform detailed full-scale design.														▨	▨	
9. On-line, real-time, sensitive analytical techniques (especially for ^{129}I).	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	**TRL 6**
a. Evaluate technology options.		▨				▨				▨						
b. Downselect technologies with capabilities of achieving needed quantitation limits.			▨				▨				▨					
c. Evaluate analyzer performance in real-time operation during bench-scale testing.								▨	▨	▨						
d. Evaluate analyzer performance in real-time operation during pilot-scale testing.									▨	▨	▨	▨				
e. Perform detailed full-scale design.													▨	▨	▨	

This roadmap in **Table 4-3** summarizes and integrates in a few lines the more detailed roadmaps shown in Section 3 for individual volatile radionuclide capture and WF technologies. Advancing technologies beyond TRL 4–5 prior to CD-0 reduces technical, schedule, and cost risks. Advancing beyond TRL 4–5 requires radioactive lab-scale testing and nonradioactive pilot-scale testing for capture and WF technologies either prior to, or after the approval of, the mission need (CD-0) for a reprocessing facility.

The time duration between now (2023), CD-0, and CD-1 for a Near-Term Target reprocessing facility remains unknown and depends on funding and national determination to proceed with used fuel reprocessing. Thus, this time duration may include several of the near- and intermediate-term timeframes. Assuming that the required funding can be available starting now, these activities could be completed in about 10–25 years.

R&D of real-time, sensitive analysis techniques, especially for ^{129}I in waste streams, is included in this roadmap. Successful development of real-time, sensitive ^{129}I analysis techniques can improve the ability to demonstrate the performance of iodine capture technologies and could also be available for demonstrating air emissions compliance for a reprocessing facility in real time.

4.3 Long-Term Off-Gas Control and Waste Form Research and Development

The vision for long-term off-gas control R&D is to allow for the discovery and development of currently unknown technologies to improve safety and reduce risk, complexity, and cost of UNF reprocessing. As in the advancements in such areas as air travel, computer hardware and software, space travel, and agriculture, advancements in nuclear fuels, reactors, and nuclear fuel cycles not yet conceived today will facilitate changes in nuclear power generation and fuel cycle policies.

Workshop participants emphasized the need to evaluate multiradionuclide sorbents, capture technologies, WFs, and sensor technologies. The idea of multiradionuclide sorbents and WFs is presently inconsistent with chemical, physical, and radiological differences between the four volatile radionuclides, hence the need for different sorbents, WFs, and disposal requirements. However, to the extent that these multiradionuclide sorbents and WFs could be viable—perhaps only after new, future technologies become available in the coming decades—they could further reduce the size, complexity, and cost of off-gas control for aqueous UNF reprocessing.

It is impractical to roadmap such future R&D other than emphasizing that current R&D should incorporate a level of effort to advance this long-term vision by funding limited long-term efforts in areas identified in the workshop—multiradionuclide capture and WF technologies, advanced sensor technologies, and other as-yet unknown technologies.

An intriguing and promising option is the development of sorbent materials with a hierarchical structure or architecture at multiple length scales. Typically, a hierarchical sorbent consists of multiple levels of porosity and surface chemistry that allow increased surface area, improved mass transfer, and enhanced selectivity. The hierarchical structure is achieved by installing various functional groups onto porous supports containing different types of pores, such as macro-, meso-, and micropores. The macroscopic pores are relatively large voids that facilitate the flow of gas and prevent excessive pressure drop, while the mesopores and micropores provide a high surface area for adsorption. This combination of pore sizes and chemical functionality could enable hierarchical sorbents to effectively capture target radionuclides from complex off-gas streams.

The design of hierarchical sorbents involves the selection of support and utilizing various techniques to install active chemistry and optimal functional groups. Common materials used for hierarchical sorbents include aerogels, xerogels, zeolites, activated carbons, MOFs, porous polymers, and composite materials. The choice of a functionalization method depends on the specific requirements of the application and the desired properties of the sorbent. Functionalization techniques may include treatment under supercritical fluid conditions, template synthesis, sol-gel methods, chemical vapor deposition, and other methods that allow for the control of the distribution and concentration of functional groups.

Hierarchical sorbents have found applications in a wide range of applications, including gas separation, liquid chromatography, water treatment, and environmental remediation. Their enhanced performance, such as high adsorption capacity, improved selectivity, and fast kinetics, make them promising future candidates for efficient sorption of iodine, for example, from reprocessing off-gas streams.

More research should be focused on the development of low-temperature WFs designed to immobilize and safely contain radioactive contaminants at relatively low temperatures, from room temperature to 500 °C. A simple encapsulation of iodine-loaded sorbents into durable WFs is essential for long-term storage and disposal. The low-temperature requirement ensures that the contaminated sorbents can be effectively processed with cost-effective and easily employed methods without a loss of captured radionuclides.

5. SUMMARY AND CONCLUSIONS

This report is a summary of the results of an “Off-Gas and Waste Forms Strategy Workshop” held in Washington, DC on January 31–February 1, 2023. The workshop was held to review the current state of the art (the baseline) technologies for capturing and disposing the volatile radionuclides and to develop a roadmap for future R&D. Future R&D is needed to mature these technologies that are presently not ready for use in a commercial UNF reprocessing facility. Future R&D is also needed to achieve better efficiency, process simplicity, and lower costs compared to the current UNF reprocessing baseline. Workshop attendees included researchers in volatile radionuclide capture and WFs from several national laboratories, including ANL, INL, ORNL, and PNNL, and DOE-NE managers for the Material Recovery and Waste Form Development Campaign, the DOE office through which this research is authorized.

The scope of the workshop, and this report, is limited to the aqueous reprocessing of used UO_x fuel from LWRs, but the technologies and roadmap may be applicable to other used fuels from other reactors and fuel cycles. The assumed DF requirements are based on reprocessing 5-year-cooled, 60 GWd/t fuel.

The sequence, prioritization, and near-, intermediate-, and long-term goals for off-gas and WF research were discussed in the workshop. These goals are summarized in a series of roadmaps that cover the near term (3–10 years), intermediate term (10–25 years), and long term (25–100 years). Near-term goals include:

- Demonstrate that the integrated performance of the most mature “baseline” capture technologies will meet air emission regulatory requirements for used fuel reprocessing in the U.S. as soon as a mission need for such a facility is determined.
- Develop and demonstrate WFs for captured radionuclides that can meet expected storage and disposal requirements.

Intermediate-term goals include:

- Develop and demonstrate volatile radionuclide capture technologies and associated WFs for the next-generation reprocessing plant that reduce the size and associated capital and operating costs to those portions of the facility, while maintaining or improving the safety of the general public.
- Develop voloxidation or similar processes to release all volatile radionuclides that require abatement into a single off-gas stream so that the treatment of any other off-gas stream within the reprocessing plant to recover them is unnecessary.
- Simplify reprocessing plant headend operations to minimize solids handling and control of fine particulates.

- Develop WFs for volatile radionuclides that require no additional processing of the capture media. Ideally, the radionuclide-loaded sorbents can be effectively processed with cost-effective and easily employed methods without the need for high heat, reducing energy consumption and potential environmental impacts and preventing loss of captured radionuclides.
- Develop online sensors that can be used in real time to measure the performance of off-gas control technologies and to demonstrate that in-plant off-gas control technologies are performing correctly and achieving the required DFs.

In the long term, future UNF reprocessing in the U.S. must differ from current methods in the U.S. and worldwide. In short, advances must be made that result in far-reaching decreases in facility cost and complexity while maintaining the safety of the general public. The vision for long-term off-gas control R&D includes the discovery and development of currently unknown technologies to improve safety and reduce risk, complexity, and cost of UNF reprocessing. Long-term goals may not be achievable without future breakthroughs in R&D, such as:

- Develop and demonstrate volatile radionuclide capture processes that effectively capture two or more of the species of interest to reduce the number of unit operations.
- Develop and demonstrate multiradionuclide WFs that can simplify and reduce costs for storage and disposal.

Achievement of any of these goals would help lower costs and risks for UNF reprocessing and help enable reprocessing in the U.S.

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APPENDIX A

WORKSHOP AGENDA

Off-Gas and Waste Forms Strategy Workshop

31 January 2023

8:20 – 8:30	Check in for participants	
8:30 – 8:40	Welcome, Safety (comms check for virtual option)	Ken M./ Kim G.
8:40 – 8:50	Introductions	All
8:50 – 9:00	Workshop Goals and Desired Outcome(s)	Ken M.
9:00 – 9:15	Description of Streams to be treated	Nick S./Bob J.
9:15 – 9:30	Relevant Emission regulations and impacts	Bob/Nick
9:30– 9:45	Waste Form and processing considerations	Denis S.
9:45 –10:00	Previous flowsheet studies – current baseline thinking, past plant experiences, opportunities, and changes	Nick S./Bob J.
10:00 – 10:15	Where are we today? Review of criteria report findings	Bob J./Nick S.
10:15 – 10:25	BREAK	
10:25 – 11:00	Discussion on revisions to criteria to be used to evaluate status of concepts	All
11:00 – 12:00	Brainstorming on alternative flowsheets and Technologies – What is missing / needed? (~3-minute rapid-fire presentations by each participant describing what they think is needed)	All
12:00 – 13:00	LUNCH	All
13:00 – 15:00	Brainstorming on alternative flowsheets and Technologies – Alternate Technologies – advantages, limitations, – What must the technology do to be impactful?	All
15:00 – 15:20	BREAK	
15:20 – 16:45	Brainstorming on alternative flowsheets and technologies – Putting the pieces together - Impacts of alternate technologies on flowsheets	All
16:45 -16:55	Summary of the day's work and goals for tomorrow	Ken M.
17:00	Adjourn and exit building	

1 February 2023

8:20 – 8:30	Check in for participants	
8:20 – 8:30	Comms check for limited virtual option)	Bob J.
8:30– 8:50	Additional concept ideas	All
8:50 – 9:20	Comparison of identified novel approaches to “baseline”	
	– Identify resulting future state vision	
	– Why is concept/technology important?	
	– How does this change the cost/safety of reprocessing?	All
9:20 – 10:00	Gap evaluation of concepts using Criteria Document Tables	All
10:00 – 10:20	BREAK	
10:20 – 11:30	Identification of key research activities required	All
11:30 – 12:30	Lunch	All
12:30 – 14:30	Identification of key activities for the 3-10 yr roadmap	
	– Drafting of detail/annotated outline of workshop report	All
14:30 – 14:50	BREAK***	
14:50 – 16:45	Identification of key activities for the 3-10 yr roadmap	
	– Drafting of detail/annotated outline of workshop report	All
16:45 -16:55	Workshop Summary and next steps	Ken M.
17:00	Adjourn and exit building – Safe Travels	

Note: *** If unable to stay for the entire day, please make every effort to not depart before the afternoon break

APPENDIX B

WORKSHOP NOTES

31 January – 1 February 2023

In-Person Attendees: Bob Jubin, Denis Strachan, Nick Soelberg, Joanna McFarlane, Allison Greaney, Kimberly Gray, Ming Tang, Stephen Kung, Praveen Thallapally, Pepa (Josef) Matyas.

Virtual Attendees (all day or in part): Amy Welty, Mitch Greenhalgh, Meghan Fujimoto, Brian Riley, John Vienna, Bill Ebert, Sarah Stariha, Jim Willit, Bill Del Cul.

31 January

- Started at ~8:30 am ET with participant introductions, review of agenda, and short presentation reviewing workshop goals.
- Clarified workshop scope.
    - Includes all four volatile isotopes ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I.
    - Aqueous reprocessing of uranium-oxide fuel.
    - Broader scope such as pyrochemistry or tri-structural isotropic (TRISO) fuel could be reviewed in the future.
- Overarching observations:
    - If all volatile fission products (FPs) could be removed up front in one process, aqueous reprocessing plant could be significantly simplified.
    - Need to bear in mind waste handling, simplified processing is key.
    - The permanent disposal repository design matters especially for the iodine waste form (WF). The simplest would be a salt repository but we cannot pre-suppose that. So we still need to support a durable leach resistant WF for iodine.
- Technical maturity for full-scale implementation in aqueous reprocessing:
    - Iodine capture: ^{129}I is the main iodine isotope of concern, ^{131}I is assumed to be sufficiently decayed prior to reprocessing. Details of iodine speciation and evolution during reprocessing are poorly understood. This has driven research to target multiple iodine species, both inorganic and organic. If pre-treatment is not pursued, improved understanding of iodine evolution would be beneficial.
    - Savannah River National Laboratory (SRNL) and Hanford silver nitrate iodine reactors (Burger 1991, Burger and Scheele 2004), and wet scrubbing, achieve decontamination factors (DFs) ranging between about 100- and 1,000. Current U.S. regulations require DFs ranging between ~1,000-10,000 (depending on many factors) for a commercial reprocessing plant. Current iodine capture lab-scale testing shows that Ag mordenite and Ag Aerogel can achieve the needed DF range but tests so far used fairly simple synthetically generated off-gas streams, only sufficient for Technology Readiness Level (TRL) ~4 (lab tests), not yet at TRL ~6 (prototypical engineering-scale) that is needed to advance to full scale.

  - Using voloxidation to evolve and capture iodine before it can contaminate downstream processes is not mature (TRL ~2) and may not be able to achieve the needed DFs.
  - Wet scrubbing of ^{14}C in the form of CO_2 is both efficient enough and technically mature enough for implementation in aqueous reprocessing.
  - Capture of tritium in the form of tritiated water with combinations of wet scrubbing, condensation, and capture in molecular sieve is both efficient enough and technically mature. But evolution and capture in one step (voloxidation) to prevent tritiated water contamination in downstream processes is not mature, with a TRL ~2.
  - Cryogenic ^{85}Kr capture and separation is mature and has been done in commercial gas industry and during aqueous reprocessing at INL, but includes hazards, complexity, and is costly for aqueous reprocessing. Kr-85 capture and separation with alternative technologies (sorbents) is not mature, TRL ~3, and performance including capture efficiency, separation efficiency, loading, and operating conditions is not as optimized as for iodine capture. Kr-85 WF (compressed gas cylinders for decay storage) is a mature technology ready for implementation but some issues, especially corrosion from decay products, and management, commercial use, or eventual atmospheric discharge remain uncertain.
  - Voloxidation for gaseous fission product evolution and iodine control is not mature, TRL ~2-3. Voloxidation demonstration performance requires not only voloxidation testing but also better characterization and speciation of gaseous fission products in used fuel. X-ray diffraction (XRD) is not sufficiently sensitive for crystalline material, and not usable for amorphous material. Other techniques that may be better include scanning electron microscopy/energy dispersive spectroscopy SEM/EDS, SEM/transmissive emission spectroscopy (TEM), and SEM/electron backscatter differential spectroscopy (EBDS), such as at the Pacific Northwest National Laboratory (PNNL) Radiochemical Processing Laboratory (RPL).

- There could be economic benefit to capturing tritium (isolated from other FPs) to capture the decay product ^{3}He which is currently in short supply for commercial uses.
- Iodine chemisorption sorbents can be poisoned by certain species, including SbH_3 (stibene) from the Zirflex process (used for aqueous dissolution of zirconium), and chlorine impurities in nitric acid (AgCl is more stable than AgI). Stibene poisoning is not an issue for current or future aqueous used fuel reprocessing. For nitric acid used in aqueous reprocessing with 100 ppm chlorine, iodine and chlorine are present in the process at roughly equal amounts. This is a driver for specifying halide-free nitric acid as much as practical.
- With krypton capture and storage, once it was stored would there ever be authorization to release? Release would meet regulatory requirements after sufficient time for decay; but stakeholders would need to accept and rely upon science to enable atmospheric release at that time.
- There is commercial value for both stable Kr and stable xenon.
- The vessel off-gas flowrate is nominally 10 times larger than the nominal dissolver off-gas volumetric flowrate.
- Tritiated water is mobile in grout, so permanent disposal is assumed to require containment of grout in HICs with adequate lifetime for tritium decay (this had been demonstrated with tritium-producing burnable absorber rod ([TPBAR] getters and ion exchange [IX] resin). Storage of

grouted tritium until sufficient decay may be possible without using HICs, depending on what the eventual disposal option is. There are methods for isotopically separating tritiated water from water, proposed by Energy Solutions and AREVA (now ORANO), to reduce tritiated water WF volume, but these are not mature (TRL ~1-3), and are expensive and complex.

- Geopolymer materials could be alternatives where cement-based compounds are unacceptable
- Reprocessing only aged fuel would reduce the needed DFs for ^{85}Kr and ^{3}H, but this would permanently constrain the reprocessing facility to only reprocess sufficiently aged fuel if it is not designed to capture these isotopes in the off-gas streams.
- Ion implantation or encapsulation in sputtered metals have been evaluated for noble gases. This process is expensive, technically complex, and results in a WF with low storage density.
- Although it would be desirable to reduce handling and have the capture materials also be disposal materials, the nature of krypton selectivity for separation versus high-capacity storage are likely exclusive.
- Krypton-85 storage is likely a remote process.
- High-capacity sorbents with high surface area may increase the capacity of a given storage cylinder design.
- Iodine handling is likely shielded but worker accessible.
- Advanced voloxidation typically has NO_2 concentrations ~50% (could be 60-70%), dissolver off-gas typically has concentrations of ~1-3% NO_2.
- A complete voloxidation system design including NO_2 regeneration and capture of gaseous fission products has not yet been built or tested. Multiple possible configurations have different potential advantages, disadvantages, and risks. Further design and testing are required. Lab testing to-date at Oak Ridge National Laboratory (ORNL) includes a closed loop system that relies on rapid NO_2 regeneration, without an NO_2 regeneration reactor, so the recycle loop is the NO_2 regeneration reactor at that level of development. A complete voloxidation system design must be based on more complete analyses of reaction rates, conditions, and stoichiometries to achieve the required voloxidation performance, capture of gaseous fission products, and management, control, transport of incoming used fuel and voloxidized product, control of powders and fines, and integration with direct dissolution.
- Remote handling of powders can be problematic. It is desirable to avoid or limit powder generation, especially very fine powders.
- Although not completely understood, it is estimated that most iodine in spent fuel resides as CsI, with some in silver/palladium phases. Methods to elucidate iodine speciation in used fuel may be beneficial, and SEM/TEM coupled with EDS analysis may be an option. Upcoming testing at ORNL with CsI in simfuel.
- It is believed that in advanced voloxidation, the method of iodine removal is formation of Cs nitrate and release of I_2
- Iodine-bearing WFs are likely Greater Than Class C (GTCC) wastes.
- There is a data gap on speciation of iodine and Ru in a NO_2 recycle loop. Ru may form volatile RuO_4 (40 C boiling point) via: $Ru + 2NO_2 + O_2 = 2NO + RuO_4$, which may decompose to or condense as RuO_2 (1,200 C boiling point), which could then plate out throughout the recycle loop

and off-gas system. This would cause process problems as the condensed RuO_2 would result in hot spots within the process equipment. We do not want Ru to get into the iodine capture bed as that might push the iodine capture bed media to remote handling.

- A sensitivity analysis is needed on the metrics for sorbent materials to help inform and guide development and innovation. Identifying critical “no-go” issues might also help clarify direction.
- To fully understand tritium behavior, improved data on the fraction of tritium in fuel matrix versus cladding would be beneficial.
- What are current analytical methods typically employed for these off-gas species and what are the gaps? For species requiring very high DFs (such as iodine), reliable measurement methods in the 10-100 ppb range will be required. These gaps should be addressed and resolved before we get into hot cell testing.
- Lacking high confidence in the iodine inventory for U oxide fuel (both amount and location), suggests that demonstrating the required DF for iodine in an operating reprocessing facility must rely on the ability to detect iodine at very low concentrations and the preponderance of laboratory data to provide confidence that the installed system achieves the required DF.
- A background literature review and summary discussion on the status of off-gas capture science would be particularly useful to inform external scientists.
  - There is sufficient, complicated background that a 1-day background workshop might be helpful to bring externals up to speed.
- Setting up a lab with NO_2 testing capability can be challenging. It may be beneficial for DOE to arrange for external parties to have new sorbents tested in existing DOE or non-DOE laboratories.
  - It may be beneficial to develop a list that could be shared with NEUP (or similar) proposal applicants of existing laboratory testbeds (Brian, Joanna [ORNL], Amy [INL]).
- We need to evaluate the process monitoring needed to control voloxidation, what is state of the art and where are gaps.
- Should consider a modular sorbent cartridge approach that could be tested at multiple sites.
- Possible WFs:
  - For iodine, a low T polymer cement instead of high T processes that can evolve captured iodine (Pepa Matyas).
  - Switchable sorbents to evaluate via NEUP (Praveen Thallapally).

APPENDIX C

WORKSHOP PRESENTATIONS

Used Fuel Aqueous Reprocessing Off-gas Streams (Nick Soelberg)

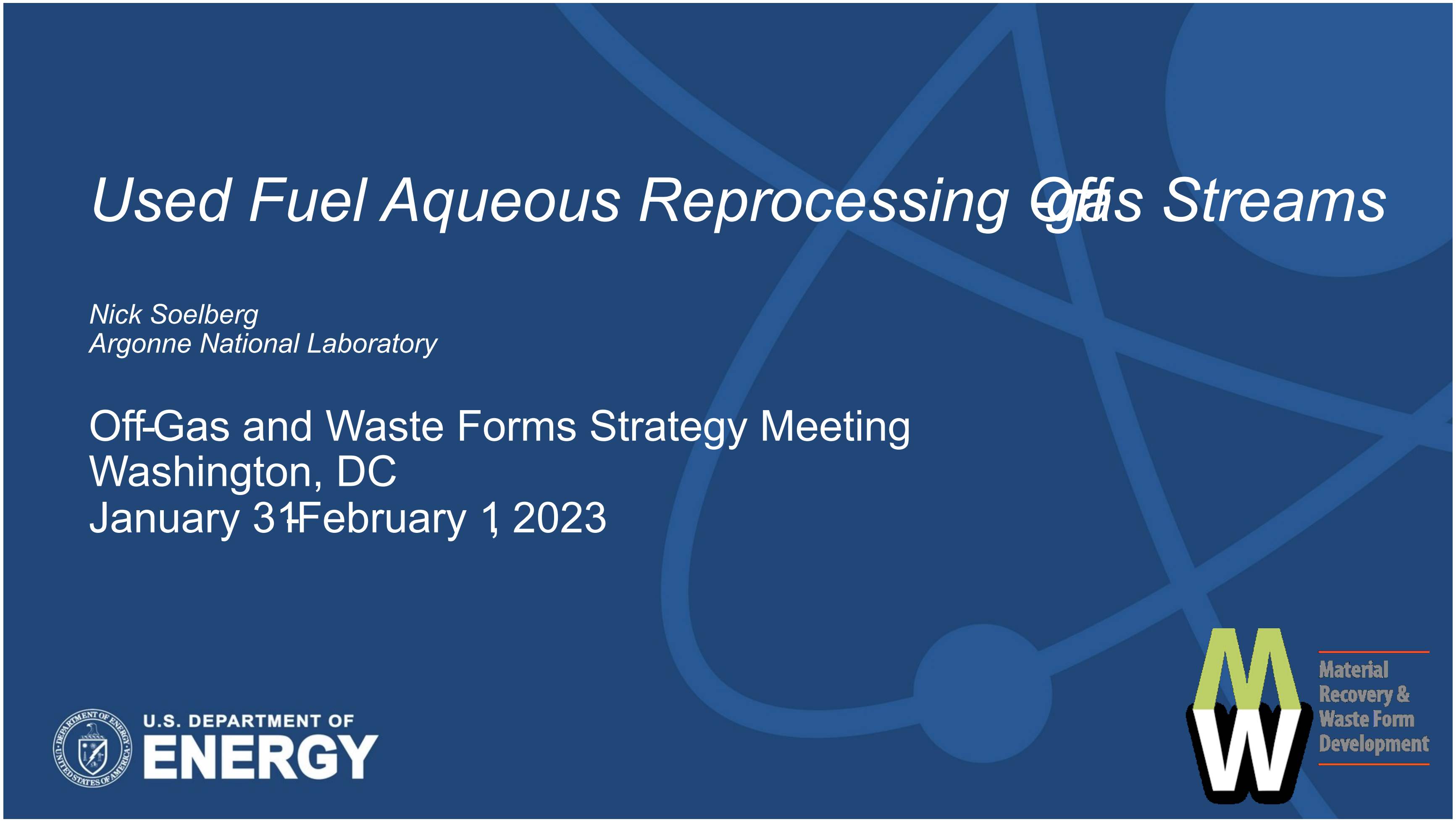
Off-Gas Emission Regulations and DF Requirements (Bob Jubin)

Waste Forms for Volatile and Semivolatile Radionuclides (Denis Strachan)

Previous Flowsheet Studies – Current Baseline, Plant Experiences, Opportunities, Needed Changes (Nick Soelberg)

Off-Gas Treatment in Early Plants (Bob Jubin)

Where Are we Today? Review of Criteria Report and Findings (Bob Jubin)



Used Fuel Aqueous Reprocessing Off-gas Streams

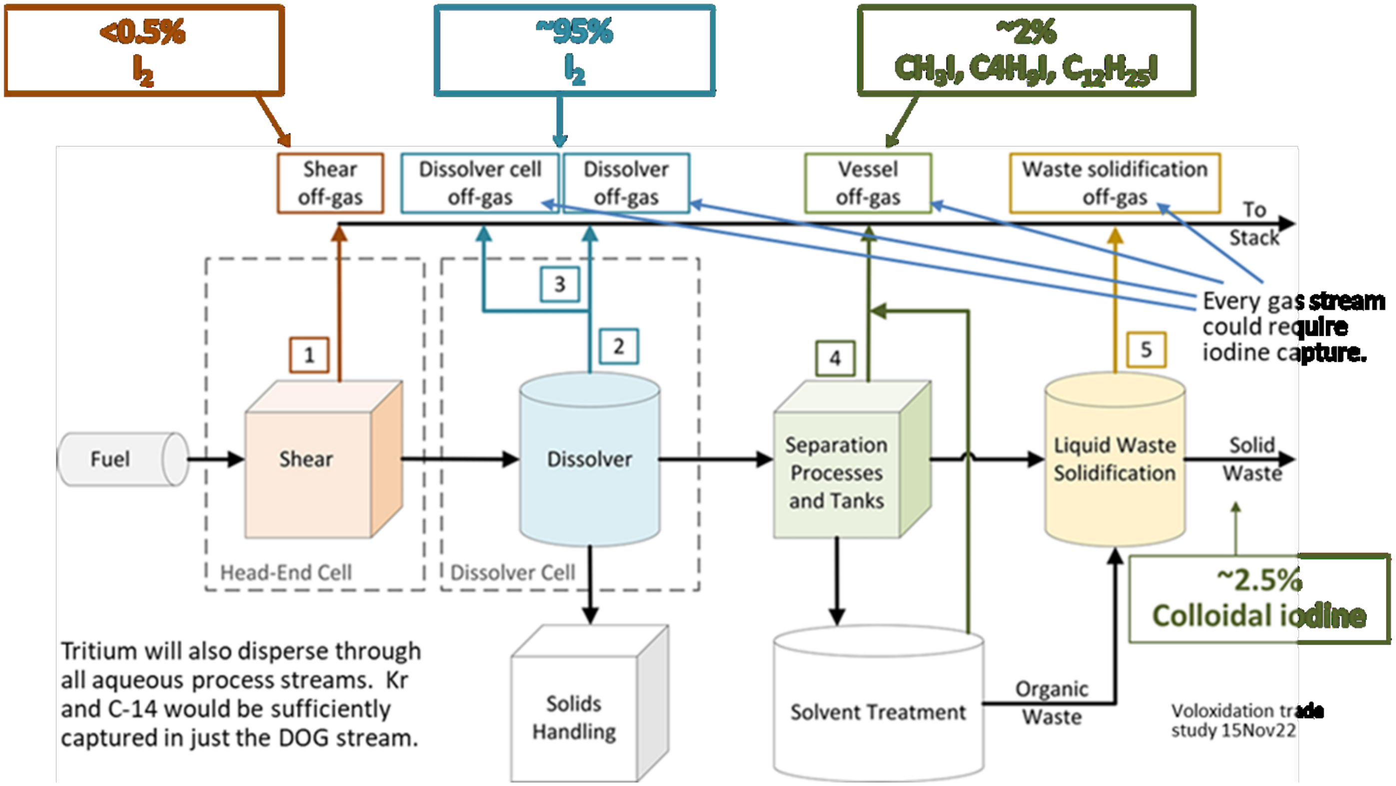
Nick Soelberg
Argonne National Laboratory

Off-Gas and Waste Forms Strategy Meeting
Washington, DC
January 31-February 1, 2023

U.S. DEPARTMENT OF ENERGY

Material Recovery & Waste Form Development

Iodine can evolve into several different aqueous reprocessing facility off-gas streams

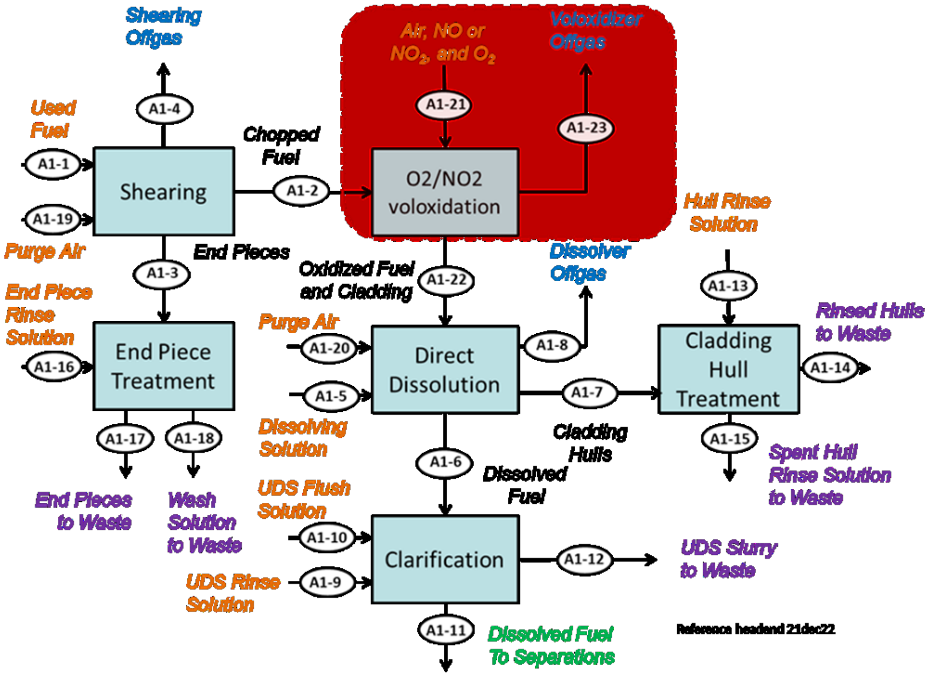


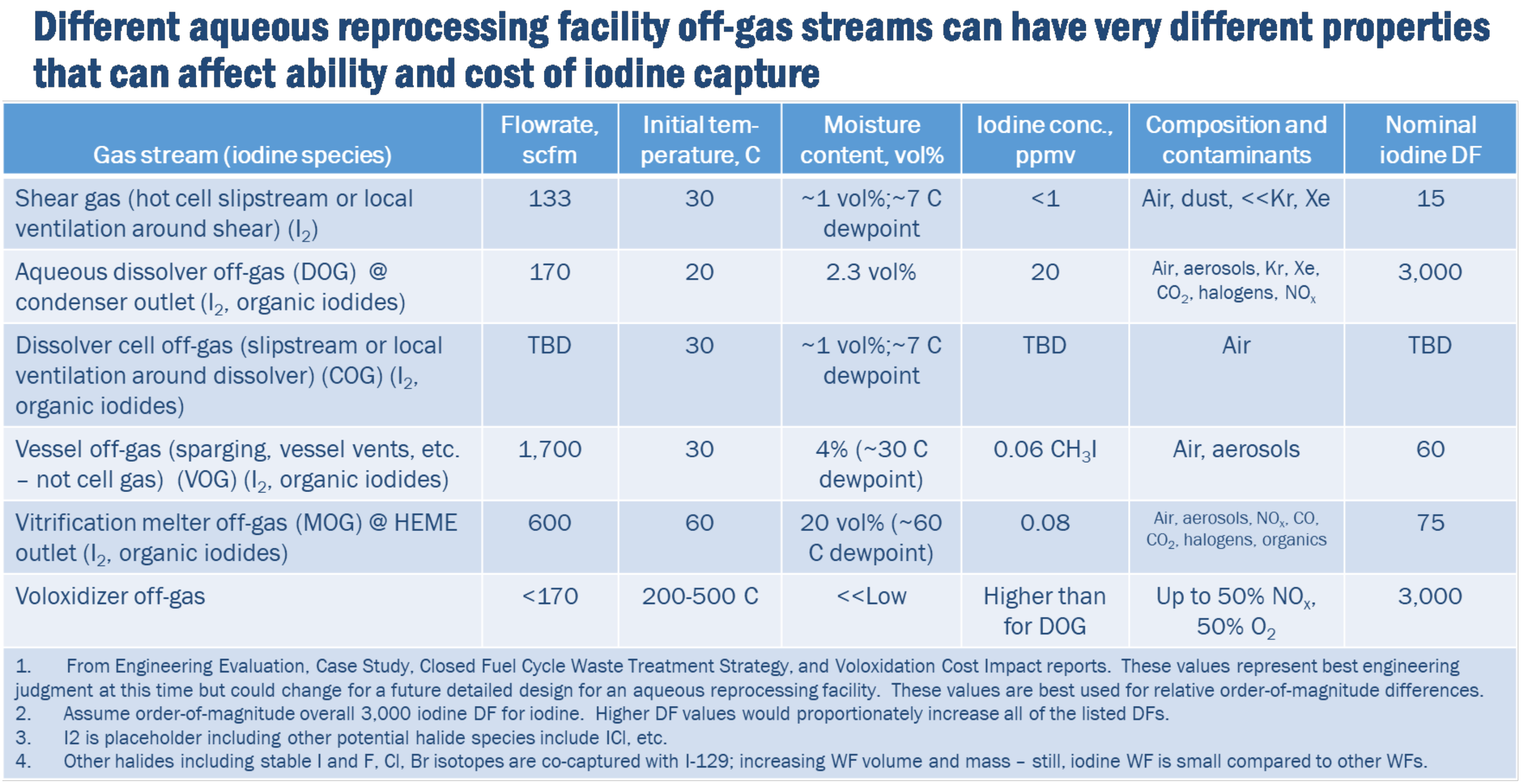
Every gas stream could require iodine capture.

Tritium will also disperse through all aqueous process streams. Kr and C-14 would be sufficiently captured in just the DOG stream.

Voloxidation trade study 15Nov22

If voloxidation can volatilize iodine efficiently enough, then capture in voloxidizer off-gas is required; but capture in downstream off-gas streams would not be needed





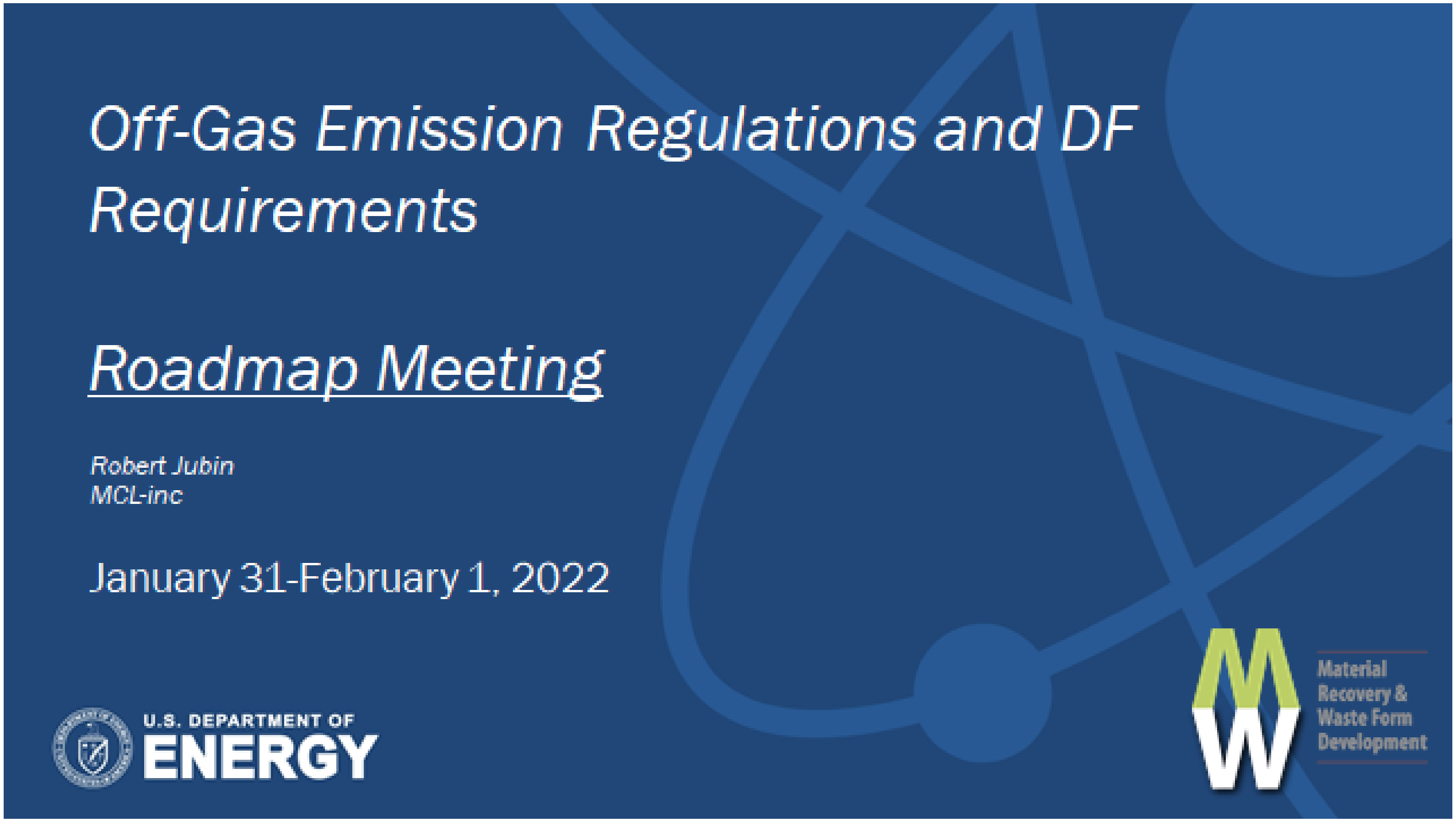
Different aqueous reprocessing facility off-gas streams can have very different properties that can affect ability and cost of iodine capture

Gas stream (iodine species)	Flowrate, scfm	Initial tem-perature, C	Moisture content, vol%	Iodine conc., ppmv	Composition and contaminants	Nominal iodine DF
Shear gas (hot cell slipstream or local ventilation around shear) (I_2)	133	30	~1 vol%;~7 C dewpoint	<1	Air, dust, <<Kr, Xe	15
Aqueous dissolver off-gas (DOG) @ condenser outlet (I_2, organic iodides)	170	20	2.3 vol%	20	Air, aerosols, Kr, Xe, CO_2, halogens, NO_x	3,000
Dissolver cell off-gas (slipstream or local ventilation around dissolver) (COG) (I_2, organic iodides)	TBD	30	~1 vol%;~7 C dewpoint	TBD	Air	TBD
Vessel off-gas (sparging, vessel vents, etc. – not cell gas) (VOG) (I_2, organic iodides)	1,700	30	4% (~30 C dewpoint)	0.06 CH_3I	Air, aerosols	60
Vitrification melter off-gas (MOG) @ HEME outlet (I_2, organic iodides)	600	60	20 vol% (~60 C dewpoint)	0.08	Air, aerosols, NO_x, CO, CO_2, halogens, organics	75
Voloxidizer off-gas	<170	200-500 C	<<Low	Higher than for DOG	Up to 50% NO_x, 50% O_2	3,000

1. From Engineering Evaluation, Case Study, Closed Fuel Cycle Waste Treatment Strategy, and Voloxidation Cost Impact reports. These values represent best engineering judgment at this time but could change for a future detailed design for an aqueous reprocessing facility. These values are best used for relative order-of-magnitude differences.
2. Assume order-of-magnitude overall 3,000 iodine DF for iodine. Higher DF values would proportionately increase all of the listed DFs.
3. I2 is placeholder including other potential halide species include ICl, etc.
4. Other halides including stable I and F, Cl, Br isotopes are co-captured with I-129; increasing WF volume and mass – still, iodine WF is small compared to other WFs.

Summary

- Enough iodine may partition to multiple aqueous reprocessing facility off-gas streams to cause iodine and tritium capture for:*
    - Shear gas (SOG)
    - Dissolver off-gas (DOG)
    - Dissolver cell gas (COG)
    - Vessel off-gas (VOG)
    - Vitrification melter off-gas (MOG)
- *Unless voloxidation can volatilize iodine efficiently enough for iodine capture only in the voloxidizer off-gas stream
- Different aqueous reprocessing streams have different flowrates, iodine concentrations, contaminants that can affect iodine capture (NOx, water, possibly O2, possibly organics), and different iodine capture requirements
    - DOG (or voloxidizer off-gas in a voloxidation case) has highest iodine concentration, highest DF requirement, and high (or highest) interfering contaminants
    - VOG has high (or highest) off-gas flowrate, low (or lowest) iodine concentration, and low DF requirement
    - Shear gas has lowest DF requirement but may still need iodine capture.
    - MOG requires iodine capture but has complicating contaminants and organics (not yet addressed)
- Combine some gas streams for treatment? Shear + DOG, shear + COG?
- Design dissolver to prevent iodine leakage into dissolver cell.
- Advance voloxidation technology for better iodine and tritium control.
- Better quantify iodine evolution during shearing.



Off-Gas Emission Regulations and DF Requirements

Roadmap Meeting

Robert Jubin
MCL-inc

January 31-February 1, 2022

U.S. DEPARTMENT OF
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Material
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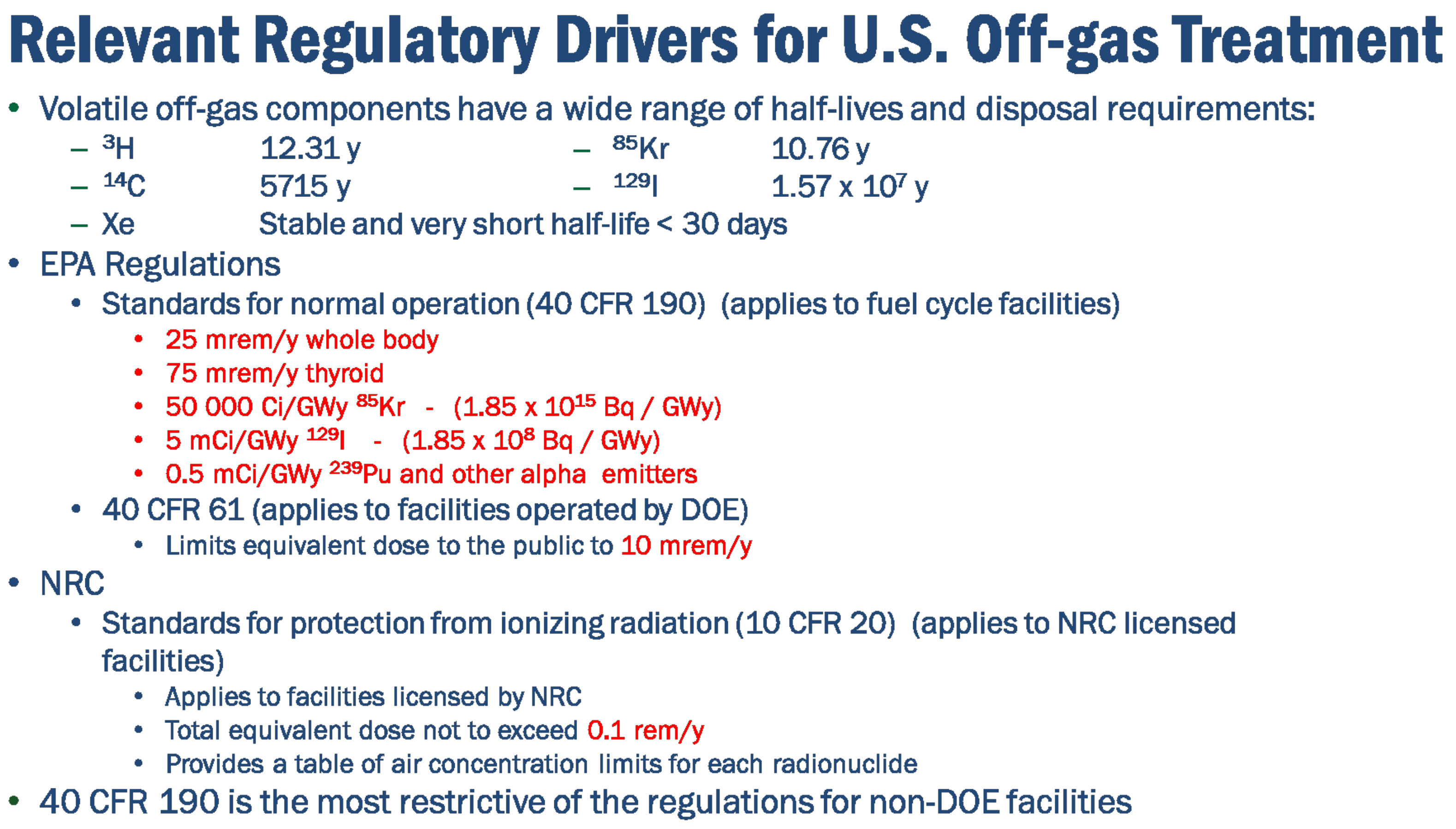


Relevant Regulatory Drivers for U.S. Off-gas Treatment

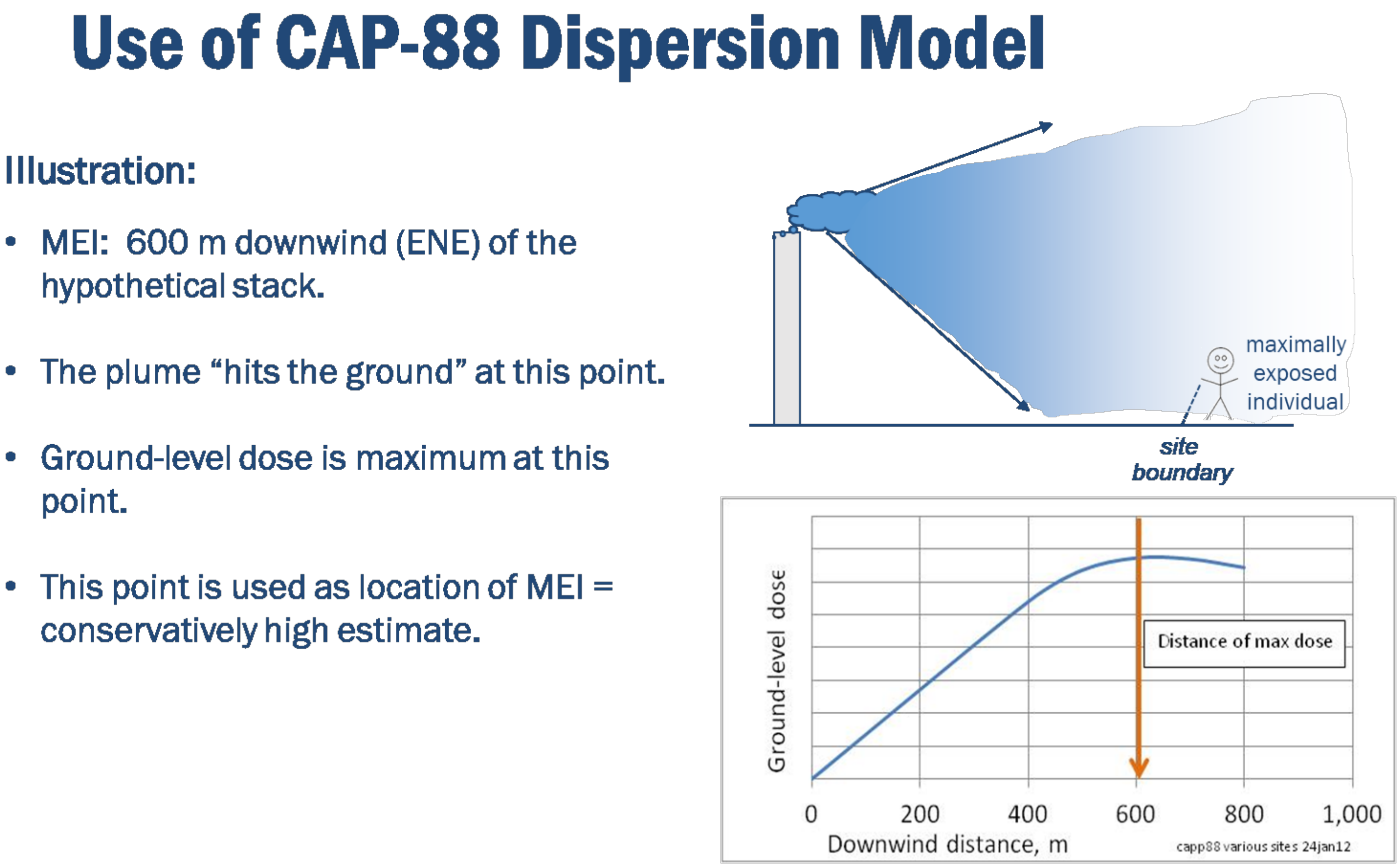
- Volatile off-gas components have a wide range of half-lives and disposal requirements:
  - ^{3}H 12.31 y – ^{85}Kr 10.76 y
  - ^{14}C 5715 y – ^{129}I 1.57×10^{7} y
  - Xe Stable and very short half-life < 30 days
- EPA Regulations
  - Standards for normal operation (40 CFR 190) (applies to fuel cycle facilities)
    - 25 mrem/y whole body
    - 75 mrem/y thyroid
    - 50 000 Ci/GWy ^{85}Kr - (1.85×10^{15} Bq / GWy)
    - 5 mCi/GWy ^{129}I - (1.85×10^{8} Bq / GWy)
    - 0.5 mCi/GWy ^{239}Pu and other alpha emitters
  - 40 CFR 61 (applies to facilities operated by DOE)
    - Limits equivalent dose to the public to 10 mrem/y
- NRC
  - Standards for protection from ionizing radiation (10 CFR 20) (applies to NRC licensed facilities)
    - Applies to facilities licensed by NRC
    - Total equivalent dose not to exceed 0.1 rem/y
    - Provides a table of air concentration limits for each radionuclide
- 40 CFR 190 is the most restrictive of the regulations for non-DOE facilities

Required Removal Efficiencies

- Required decontamination factors
  - What DF is needed to meet the regulations irrespective of what fuel is being processed and how long it has been out of reactor?
  - How does the size of the plant affect these values?
  - How long must the UNF be stored before the short half-life isotopes (^{3}H and ^{85}Kr) no longer need to be removed?

Assumptions for DF Requirement Analysis

- Recycle facility will be licensed by NRC.
    - 40 CFR 61 is not applicable.
    - 40 CFR 190 and 10 CFR 20 apply.
- Dose limits will be derived from 40 CFR 190 based on lower limit.
- Allowable contribution to total dose to maximally exposed individual (MEI) will be 10% of allowable dose.
    - Same factor will apply to thyroid dose.
- No engineering margins will be applied.
- Site boundary will be at max plume concentrations as determined by CAP88
- Fuel age: 2, 5, 10, 20, 30, 50, 70, 100 y of cooling.
- Fuel type: LWR (UOX), MOX.
- Burn-up: 20, 30, 60, 100 GWd/tIHM.
- Size of plant: 1000 t.



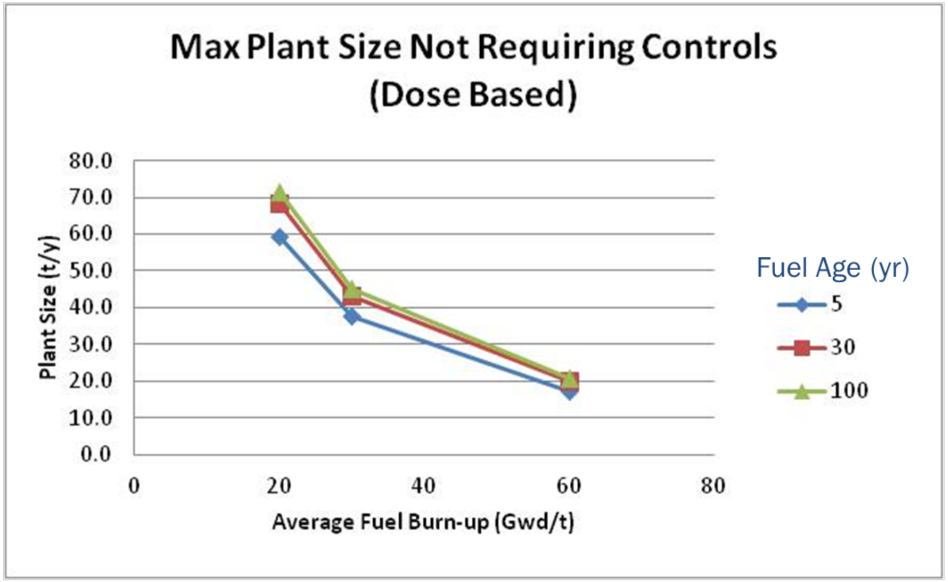
Use of CAP-88 Dispersion Model

Illustration:

- MEI: 600 m downwind (ENE) of the hypothetical stack.
- The plume "hits the ground" at this point.
- Ground-level dose is maximum at this point.
- This point is used as location of MEI = conservatively high estimate.

Max Plant Size with No Volatile Emission Controls

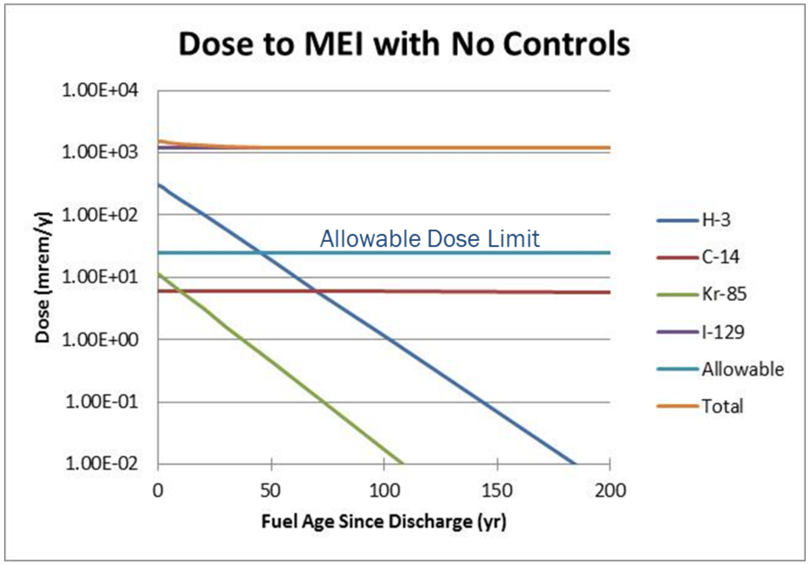
- Total dose to MEI limited to 25 mrem/y
- Dose to MEI attributed to only volatile radionuclides
- Ignores the power based requirements in 40 CFR 190



Illustrative case:

- *36-m stack;*
- *18 m/s stack gas velocity; conservative rural agriculture*

Uncontrolled Dose to MEI



Illustrative case:

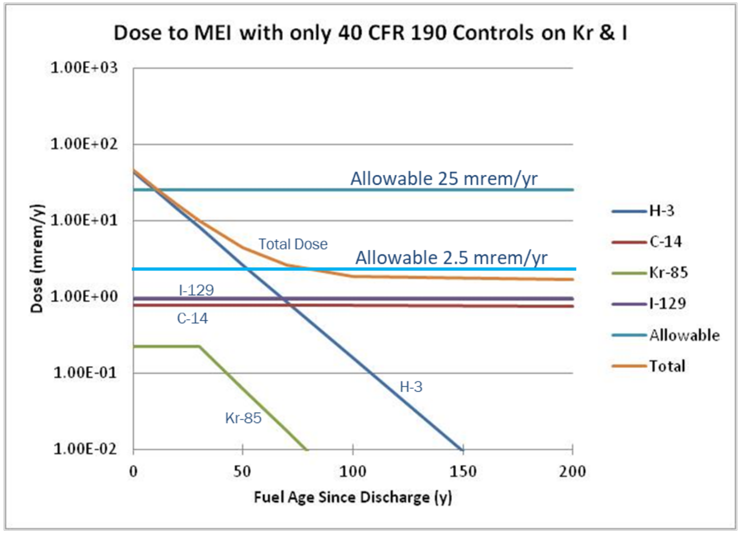
- *60 GWd/t PWR used fuel; 1000 t/y; 36-m stack;*
- *18 m/s stack gas velocity; conservative rural agriculture*

- Total dose exceeds limit of 25 mrem/y at all cooling times.
- Iodine and tritium major dose contributors

Capture Efficiency Required for ^{85}Kr and ^{129}I Based on 40 CFR 190 Fuel Cycle Limits

- Calculate inventories (Ci) of ^{85}Kr (or 129I) per GWe:
  - In used fuel / fuel burnup / reactor thermal efficiency:
  - Per tonne x (tonne/GWth) x (GWth/GWe)
- Needed decontamination factor = Ci/GWe divided by the regulatory limit
- For 60 GWd/tonne used PWR fuel, composition estimated with the SCALE model:
  - ^{129}I: 291 g/t; need DF ~190 to meet fuel cycle limit
  - ^{85}Kr: 48 g/t decreasing with age; need DF ~7 decreasing to 1 (no control needed) at fuel age ~30 years to meet curie release limit
  - ^{3}H: 0.18 g/t decreasing as the fuel ages
  - ^{14}C: 0.38 g/t

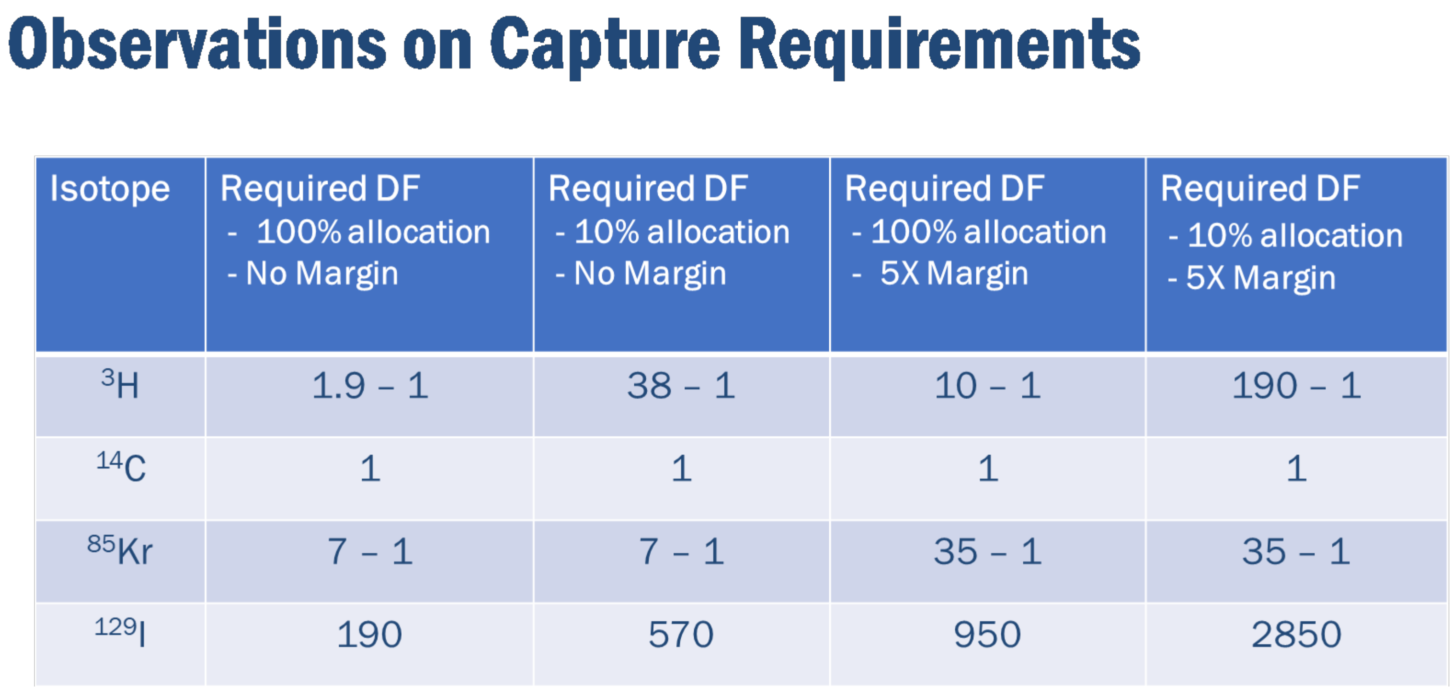
Controlling ^{85}Kr and ^{129}I to Meet 40CFR190 Fuel Cycle Limits Is Not Sufficient to Meet Dose Limits



Illustrative case:

- *60 GWd/t PWR used fuel; 1000 t/y; 36-m stack;*
- *18 m/s stack gas velocity; conservative rural agriculture*
- *Iodine DF of 190; krypton DF of 7 decreasing to 1*

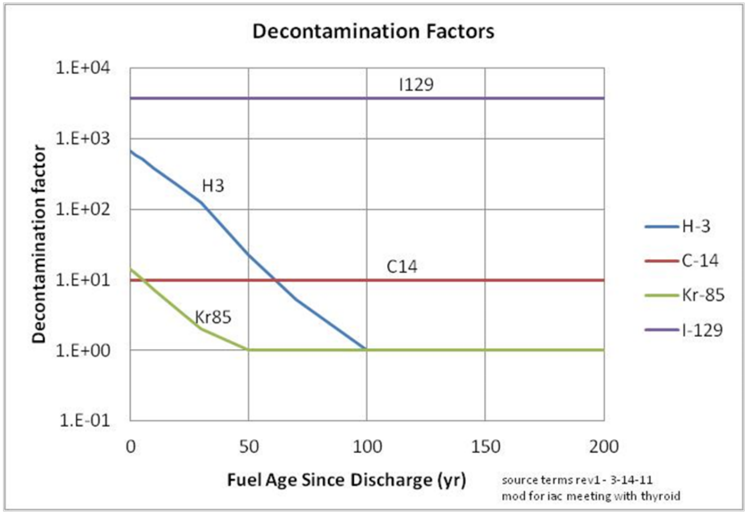
- Total dose exceeds limit of 25 mrem/y until fuel cooled ~10 y, so additional control is needed for ^{3}H (DF of 2)
- If dose contribution for volatile radionuclides is limited to 10% of allowable controls needed for ^{129}I, ^{14}C, ^{85}Kr



Observations on Capture Requirements

Isotope	Required DF - 100% allocation - No Margin	Required DF - 10% allocation - No Margin	Required DF - 100% allocation - 5X Margin	Required DF - 10% allocation - 5X Margin
^{3}H	1.9 – 1	38 – 1	10 – 1	190 – 1
^{14}C	1	1	1	1
^{85}Kr	7 – 1	7 – 1	35 – 1	35 – 1
^{129}I	190	570	950	2850

Emissions Control (DFs) Needed to Meet Fuel Cycle and Dose Limits Varies



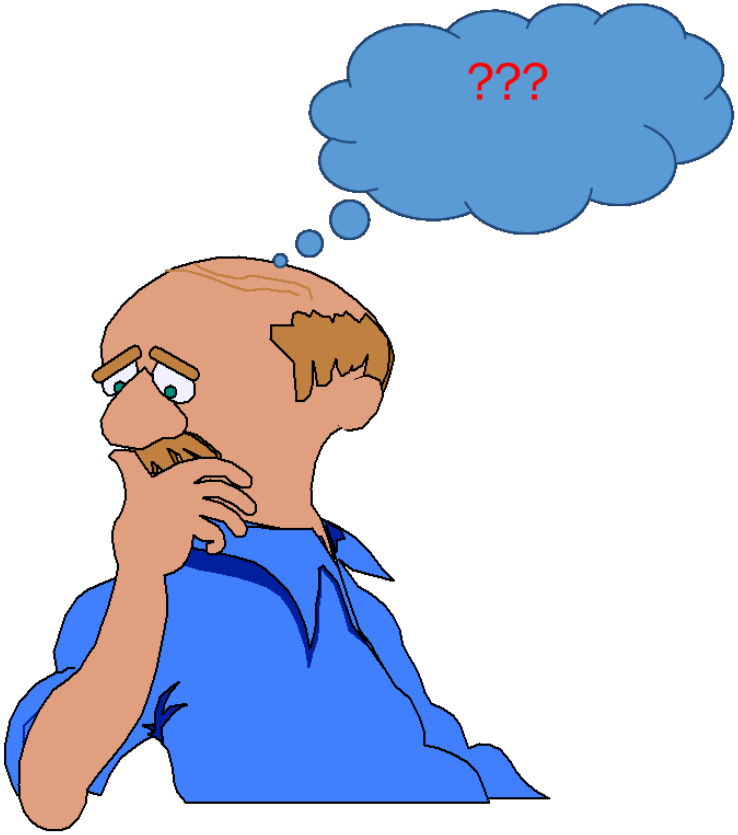
source terms rev1 - 3-14-11
mod for iac meeting with thyroid

- 60 GWd/t PWR used fuel;
  1000 t/y;
  36-m stack;
  18 m/s stack velocity;
  conservative rural agriculture
- Thyroid dose from volatile radionuclides controlled to ≤7.5 mrem/yr.
- No conservatism assumed for safety factors (~3 to >10x) that should be considered to assure regulatory compliance

Isotope	DF	
^{129}I	~3800	For fuel cycle limit and thyroid dose limit
^{3}H	~700 – 1	For dose limit; no control after ~100 y
^{85}Kr	~14 – 1	For fuel cycle and dose limit; no control after ~50 y
^{14}C	~10	For dose limit

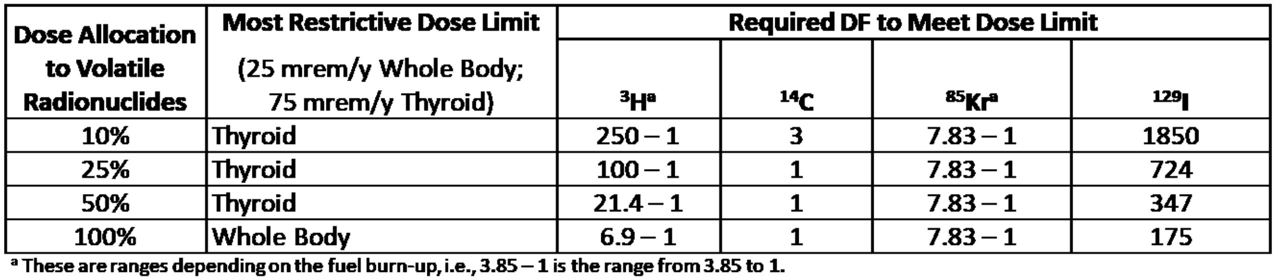
- Highest DF values required for ^{129}I
  - Scales with burn-up for PWR UOX, MOX and AHTGR
  - Scales with the particulate fraction
    - Main effect is on the thyroid
    - Vapor and organic forms contribute about 0.01 of the particulate dose
  - At full dose allocation, maximum DF values are ≈ 400 to 650
  - At 10% dose allocation, values are ≈ 4000 to 8000
- Other maximum DF values are
  - ^{3}H
    - Full dose allocation, 25 to 160
    - 10% dose allocation, 600 to 720
  - ^{14}C
    - 1 to 4
    - 10 to 30
  - ^{85}Kr
    - 4 to 9
    - 20 to 60
- DF requirements (dose contributions) most sensitive to stack height
  - Doubling stack height reduces dose to MEI by factor of ~4
- Most of our assumptions were on the conservative side
  - Alternate plant locations were an exception

Questions



Impact of Dose Allocation

DFs required to limit dose to limiting allocation for PWR UOX 30 GWd/tIHM



Dose Allocation to Volatile Radionuclides	Most Restrictive Dose Limit (25 mrem/y Whole Body; 75 mrem/y Thyroid)	Required DF to Meet Dose Limit			
		$^{3}H^{a}$	^{14}C	$^{85}Kr^{a}$	^{129}I
10%	Thyroid	250 – 1	3	7.83 – 1	1850
25%	Thyroid	100 – 1	1	7.83 – 1	724
50%	Thyroid	21.4 – 1	1	7.83 – 1	347
100%	Whole Body	6.9 – 1	1	7.83 – 1	175

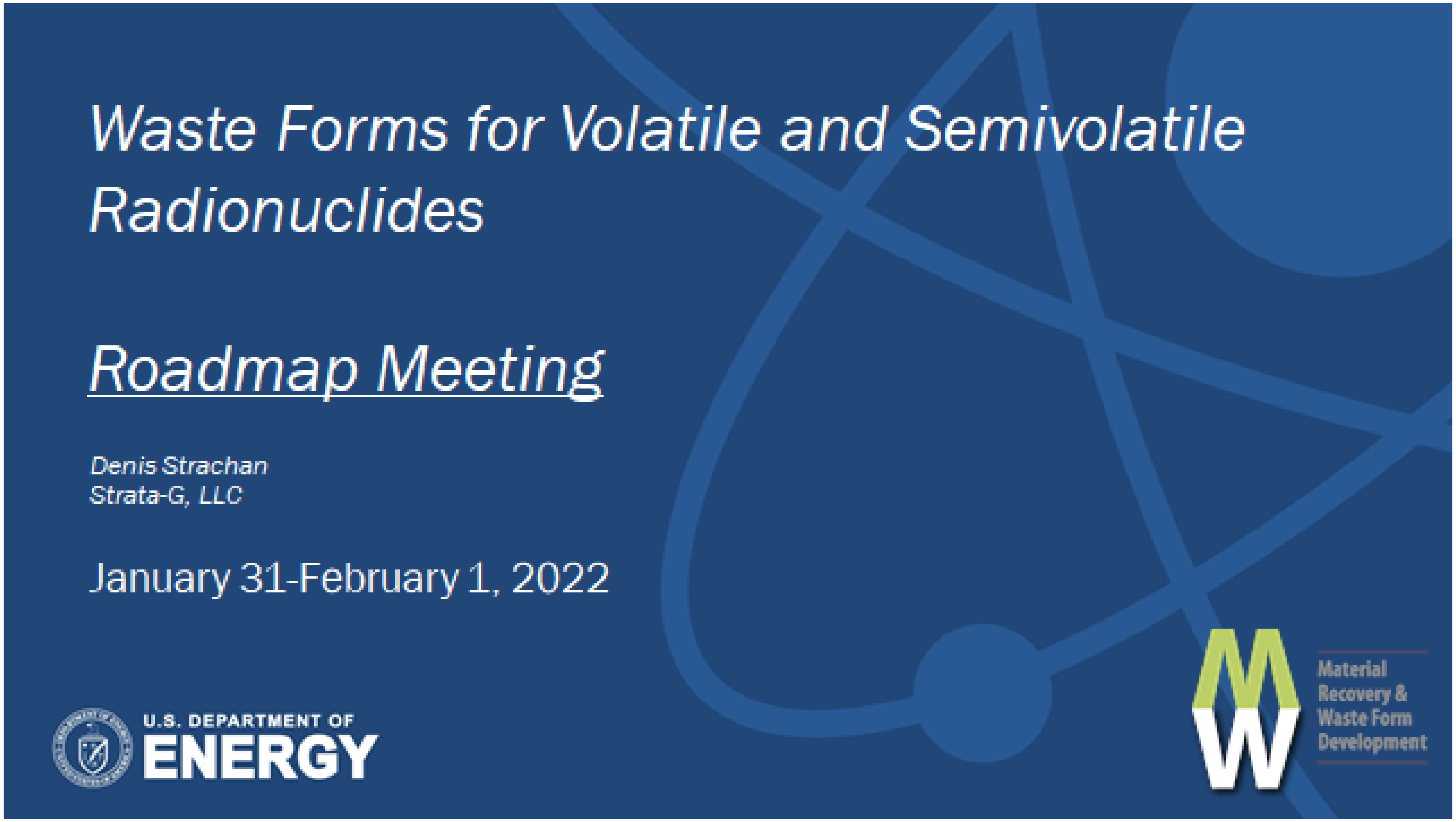
[a] These are ranges depending on the fuel burn-up, i.e., 3.85 – 1 is the range from 3.85 to 1.

Illustration case:
PWR used fuel; 1,000 t/yr; 36 m stack;
18 m/s stack gas velocity; conservative rural agriculture

Impact of Fuel Type

	Full dose allocation to volatile radionuclides			10% dose allocation to volatile radionuclides		
	PWR/UOX	PWR/MOX	AHTGR	PWR/UOX	PWR/MOX	AHTGR
^{3}H	25	160	42	600	720	585
^{14}C	1	1	4	10	15	30
^{85}Kr	9	4.2	9.2	18	13	62
^{129}I	380	630	650	3800	8000	6550

Illustration case:
1,000 t/yr; 36 m stack;
18 m/s stack gas velocity; conservative rural agriculture



Waste Forms for Volatile and Semivolatile Radionuclides

Roadmap Meeting

Denis Strachan
Strata-G, LLC

January 31-February 1, 2022

Semivolatile Radionuclides

- Semivolatile radionuclides were discussed in Jubin, et al 2014
- With the use of ORIGEN and SCALE for a PWR 60 GWd/tIHM fuel, 46 isotopes were identified
- With use of CAP88 (Rosnick 1992) to calculate the dose to the maximum exposed individual (MEI), 17 isotopes were identified for further consideration for 1000 tIHM/y
  - 0.025 mREM
  - Required DF > 1
- Process knowledge (known scrubber efficiencies, HEPA filtration, etc) eliminated all of these isotopes except those already being treated, e.g. ^{137}Cs, ^{99}Tc, ^{129}I

Volatile Radionuclides

- As covered already, these are ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I.
- The most intractable is ^{3}H
  - ^{3}H as $^{3}H_2O$ or ^{3}HHO could become mixed with process water and atmospheric H_2O
  - If this happens, then the volume of ^{3}H waste becomes very large
  - Limited contamination is feasible but difficult
- ^{14}C can be removed as $^{14}CO_2(g)$ along with atmospheric CO_2 at fuel dissolution
  - Slaked lime can be used remove CO_2 from process off-gas yielding $CaCO_3$
  - Lime and $Ba(OH)_2$ to yield $CaBa(CO_3)_2$ (Grandjean and Leturcq, 2005)
  - Solids can be mixed with cement or stored as a dense solid

Waste Form for ^{85}Kr

- There are two materials being investigated for removal
  - AgZ-PAN/HZ-PAN
  - MOF (CaSDB)
- Immobilization
  - Storage as a compressed gas
  - Storage in cannister with consolidation media (higher storage density; lower P)
  - Metal matrix
  - Consolidation of sorbent

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  - Storage in cannister with consolidation media (higher storage density; lower P)
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Waste Form for ^{129}I

- Removal from the dissolver off-gas
  - Traditional Ag-based materials, e.g. $AgNO_3$-coated beryl saddles
  - Ag-zeolites
  - Ag-Aerogel
- Immobilization
  - Separation of I from beryl saddles and conversion to a less soluble material – added unit operations.
  - Direct conversion of sorbants to final waste form
    - HIP
    - Other consolidation techniques

What Waste Form?

- We have no repository or candidate repository
- Based on past experience and the NRC regulations:
  - No free liquids
  - Unconsolidated powders are unlikely
    - Surface area is likely to be too high
    - Too easily dispersed in an unlikely accident
  - Minimize the dissolution rate
    - Need to meet drinking water standards at some distance from the repository horizon
    - Implies the waste form in combination with the engineered barriers must control the release such that those standards are met
  - We have borosilicate glass as a ‘model’ for release rates
    - There is already a significant stockpile of HLW glass

Previous Flowsheet Studies – Current Baseline, Plant Experiences, Opportunities, Needed Changes

Nick Soelberg
Argonne National Laboratory

Off-Gas and Waste Forms Strategy Meeting
Washington, DC
January 31-February 1, 2023

U.S. DEPARTMENT OF
ENERGY

Material
Recovery &
Waste Form
Development

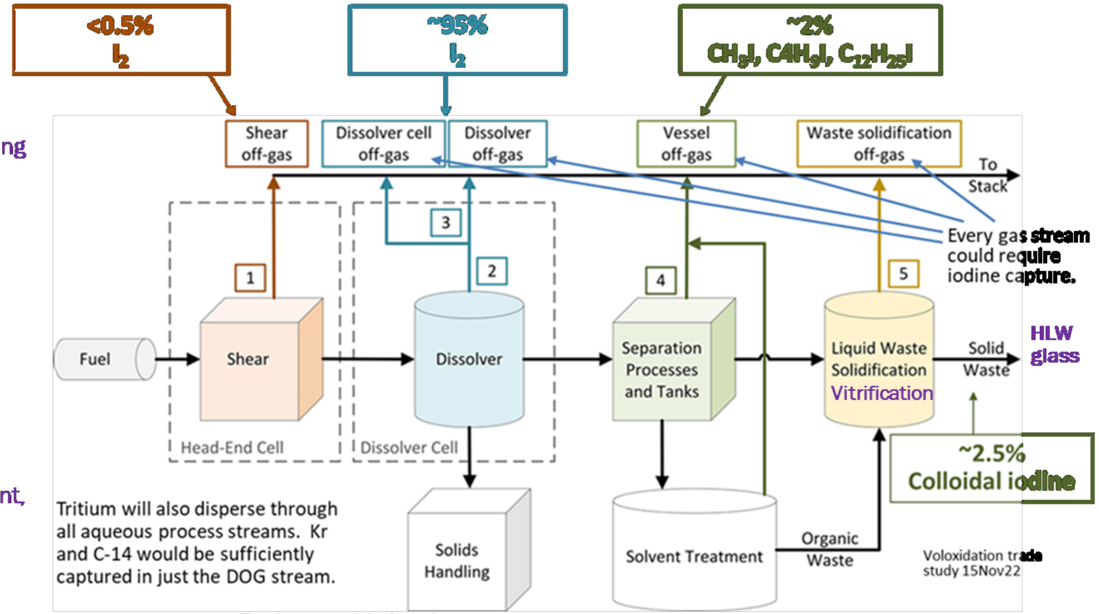
Aqueous* reprocessing facility experience and flowsheet studies

- 1970's - 1980's DOE and commercial separations processes at SRS, ORNL, INL, Hanford, West Valley, Barnwell
- ORNL "Hot Experimental Facility Reference Flowsheet" 1982
- Foreign - THORP in UK, LaHague in France, Tokai and Rokkasho in Japan, MAYAK in Russia
- Boston Consulting Group reprocessing facility design
- SRNL (WSRC) Engineering Alternative Studies (EAS) 2007
- SRNL (WSRC) Follow-on Engineering Alternative Studies (FOEAS) 2008
- Advanced Fuel Cycle Facility (AFCF) 2008
- Task Order 9 AREVA report 2013
- Task Order 9 Energy Solutions report 2013
- Case Study report 2015
- Engineering Evaluation reports 2016 and 2022
- Voloxidation, direct dissolution, advanced off-gas control trade study 2023

***Electrochemical reprocessing (pyroprocessing) is outside of this workshop scope.**

Subsystems not shown:

- Recycled product denitration and packaging
- Water recycle
- HNO_3 recycle
- Waste stream processes
  - Ru waste treatment and WF
  - Tritium waste treatment and WF
  - C-14 waste treatment and WF
  - Kr-85 waste treatment and WF
  - I-129 waste treatment and WF
- Chemical supply systems
  - Water, HNO_3, Ru sorbent, iodine sorbent, NaOH, $Ca(OH)_2$
  - Solvent extraction: solvent and other chemicals
  - Kr/Xe solid sorbent or else H_2 and NH_3
  - For voloxidation: source of O_2 and source of NO_2
  - Product denitration chemicals – such as formaldehyde, ammonium nitrate



Every gas stream could require iodine capture.

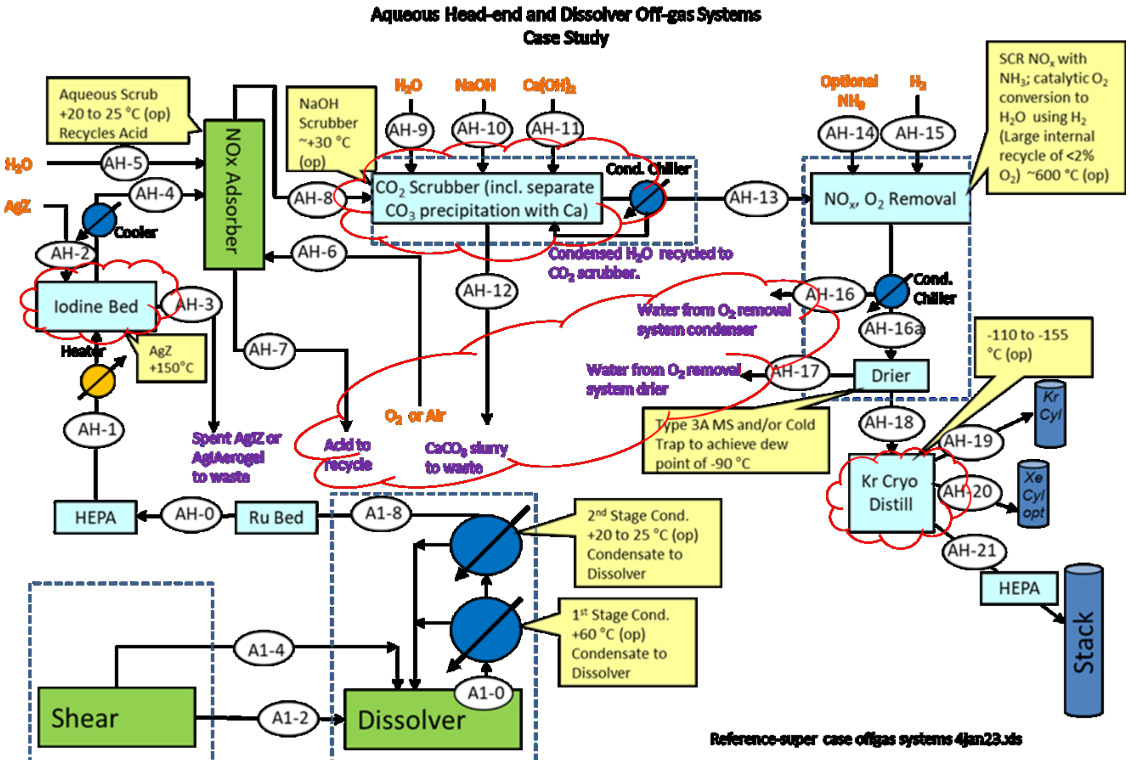
Tritium will also disperse through all aqueous process streams. Kr and C-14 would be sufficiently captured in just the DOG stream.

- Fuel assembly hardware management and WF
- Cladding hulls management and WF

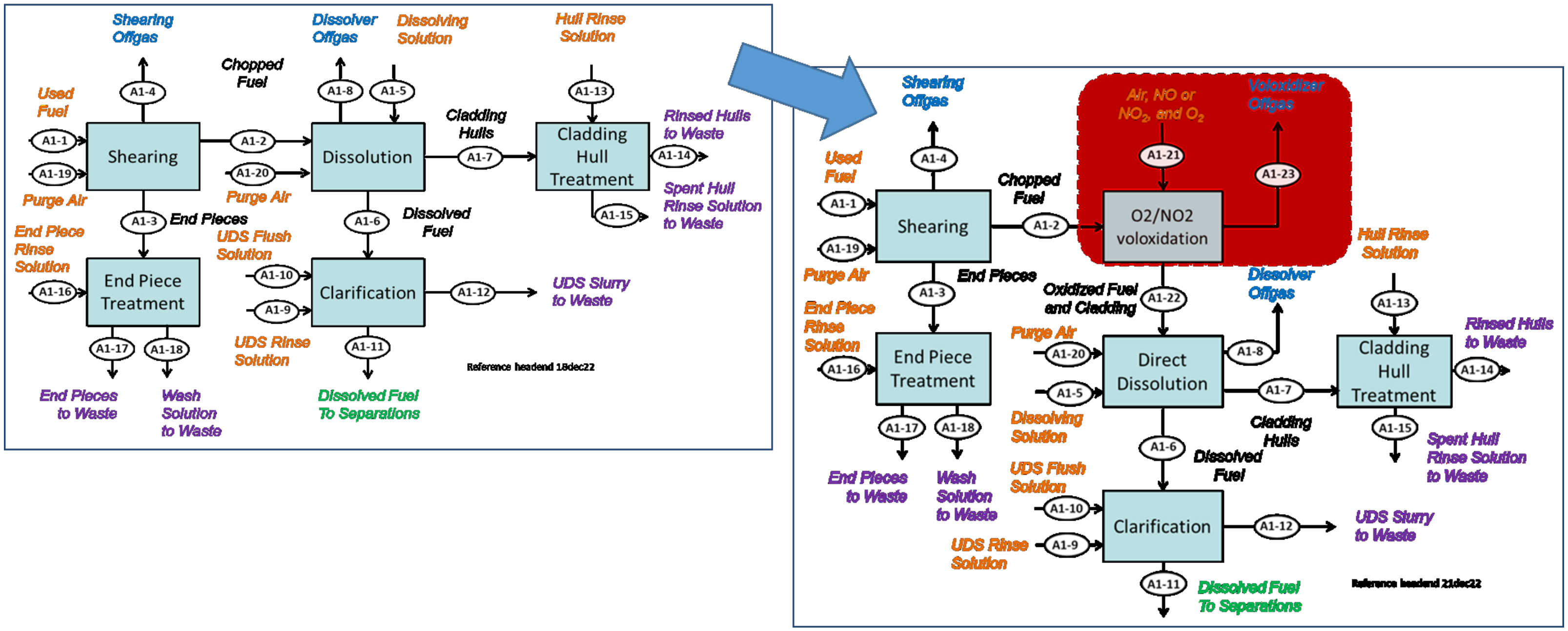
- Solvent recycle waste
- Solvent recycle salt waste

Case Study dissolver off-gas (DOG) system includes capture of semivolatile and volatile radionuclides

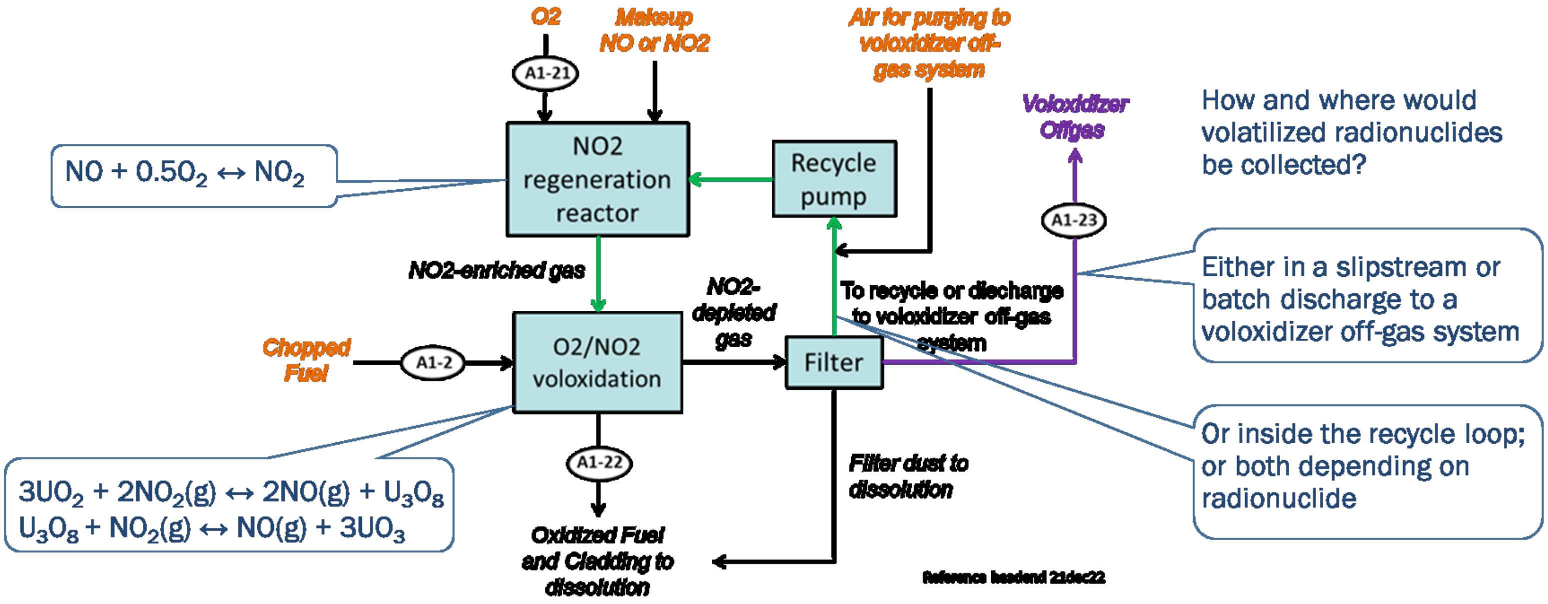
- AgZ iodine sorbent
- Wet scrub CO_2
- Tritiated water contaminates every aqueous waste stream (but eventually efficiently captured in front of cryogenic Kr/Xe capture
- Cryogenic Kr/Xe capture and separation



Adding voloxidation after used fuel rod shearing can potentially enable direct dissolution into organic solvent instead of dissolution into hot nitric acid, which eliminates solvent extraction



Voloxidizer gas recycle enables NO_2 (consumed during voloxidation) to be regenerated



$NO + 0.5O_2 \leftrightarrow NO_2$

$3UO_2 + 2NO_2(g) \leftrightarrow 2NO(g) + U_3O_8$
$U_3O_8 + NO_2(g) \leftrightarrow NO(g) + 3UO_3$

How and where would volatilized radionuclides be collected?

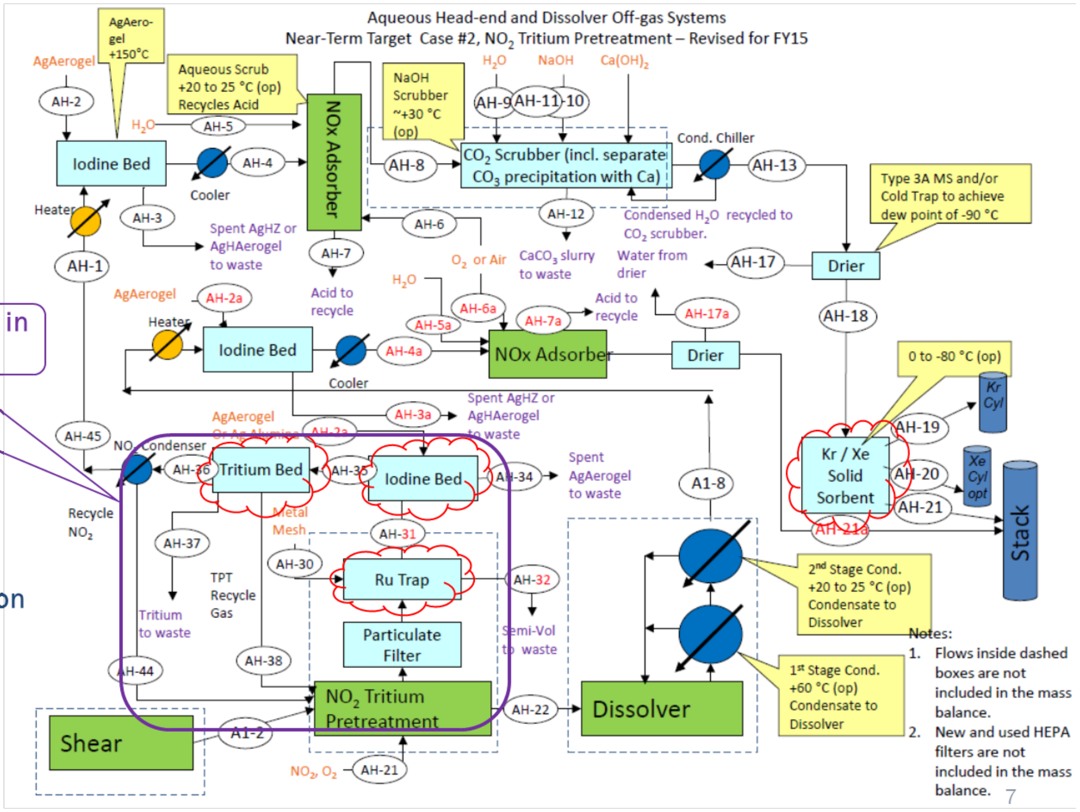
Either in a slipstream or batch discharge to a voloxidizer off-gas system

Or inside the recycle loop; or both depending on radionuclide

Case Study "Near-Term Target") Separate voloxidizer and DOG systems include capture of semivolatile and volatile radionuclides

- Ru, iodine, and tritiated water capture in the voloxidizer off-gas recycle system

- AgZ or Ag Aerogel iodine sorbent
- Same wet scrub for CO_2
- Same tritiated water capture
- Solid sorbent Kr/Xe capture, separation in the voloxidizer off-gas system

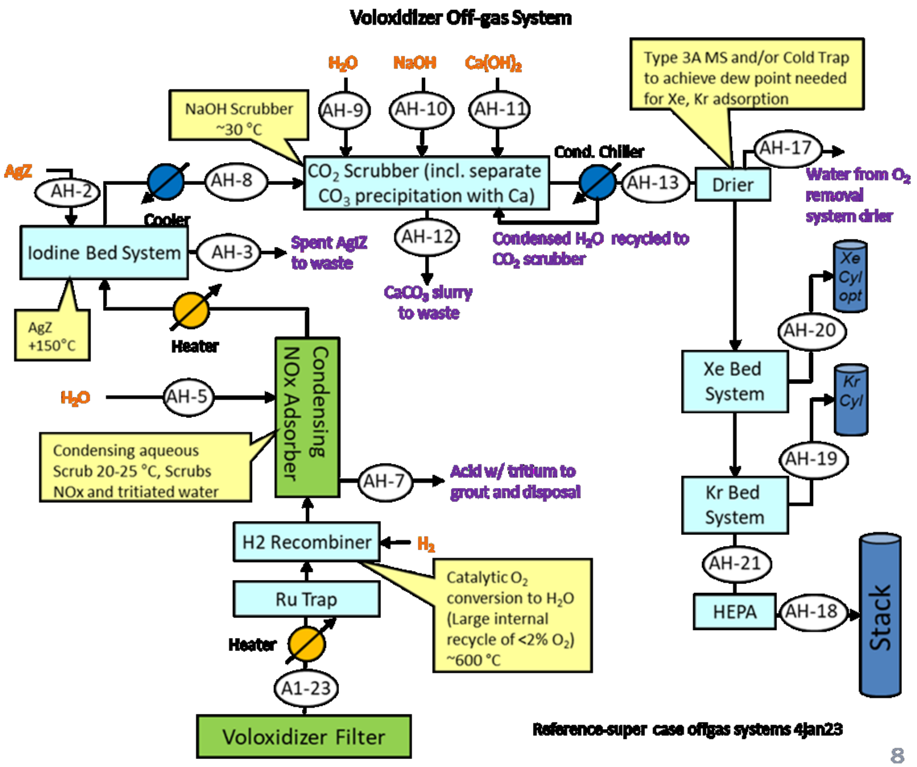


Notes:
1. Flows inside dashed boxes are not included in the mass balance.
2. New and used HEPA filters are not included in the mass balance.

Capture volatilized radionuclides inside the recycle loop or in the voloxidizer off-gas system?

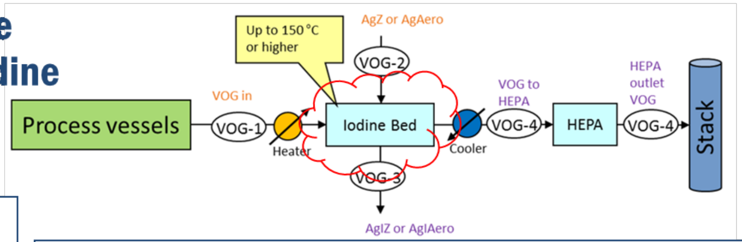
Depends on items that require further evaluation, development, demonstration:

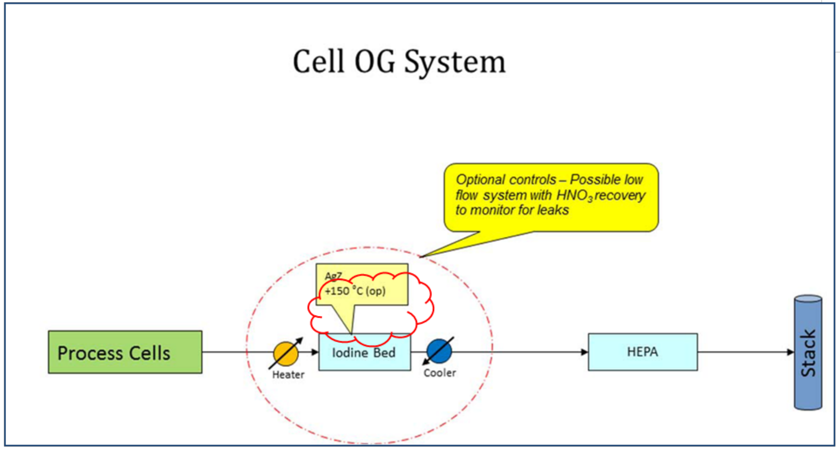
- Interferences from ~50% O_2, ~50% NO_x
- Footprint
- Control technology requirements and performance
- Operating conditions - temperature, pressure

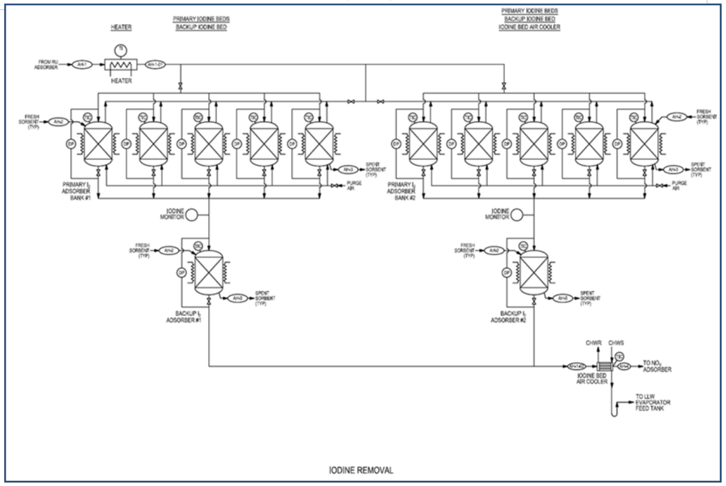


Some other off-gas systems can be simpler than DOG and voloxidizer off-gas systems but footprints can still be large due to large flowrates. Footprints can be reduced if voloxidation can eliminate need for iodine capture.

Case Study vessel off-gas (VOG) system
Ag Aerogel sorbent for iodine

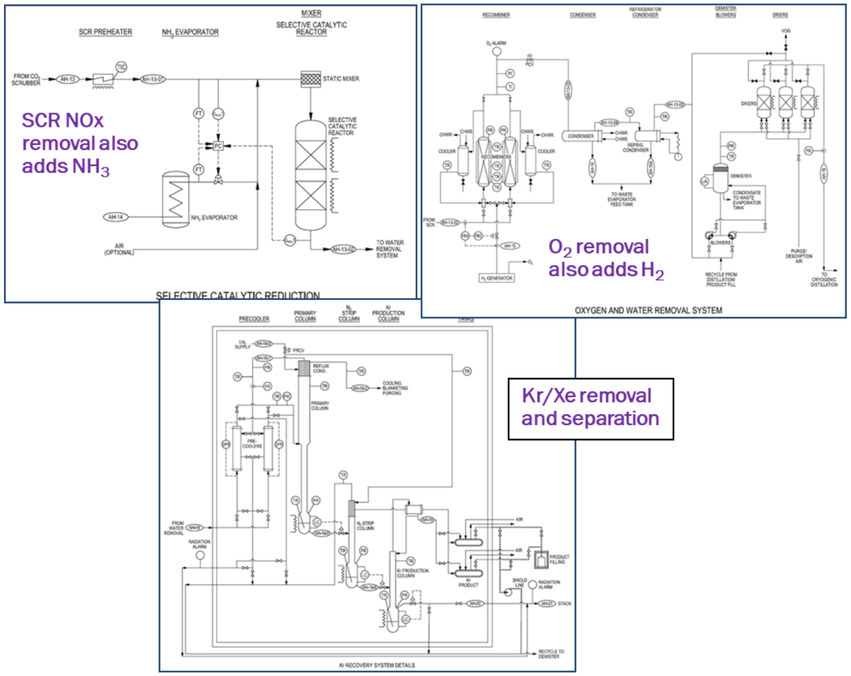






Kr/Xe capture and separation

Cryogenic: Need to remove gas impurities (NO_x, O_2, H_2O) before cryogenic capture and so complex with large footprint.

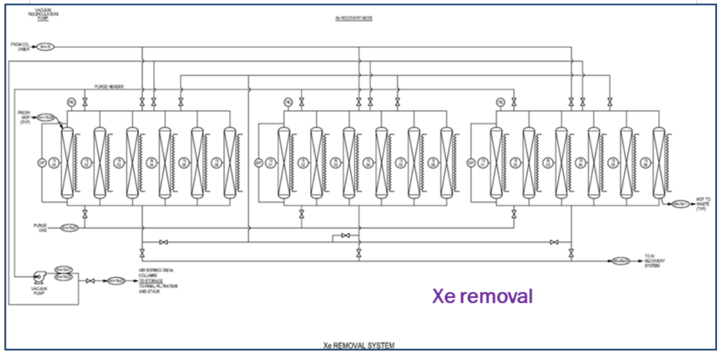


SCR NOx removal also adds NH_3

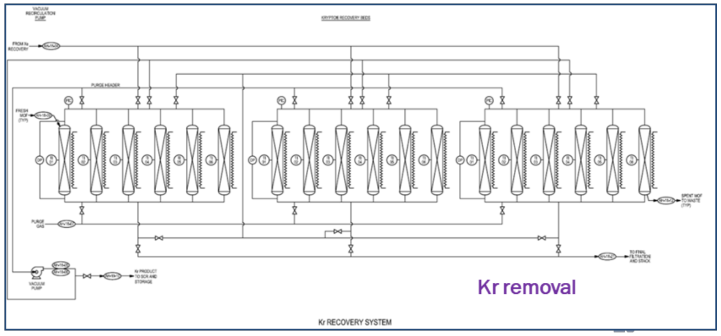
O_2 removal also adds H_2

Kr/Xe removal and separation

MOF sorbent: Still complex and needs large footprint based on current sorbent performance.

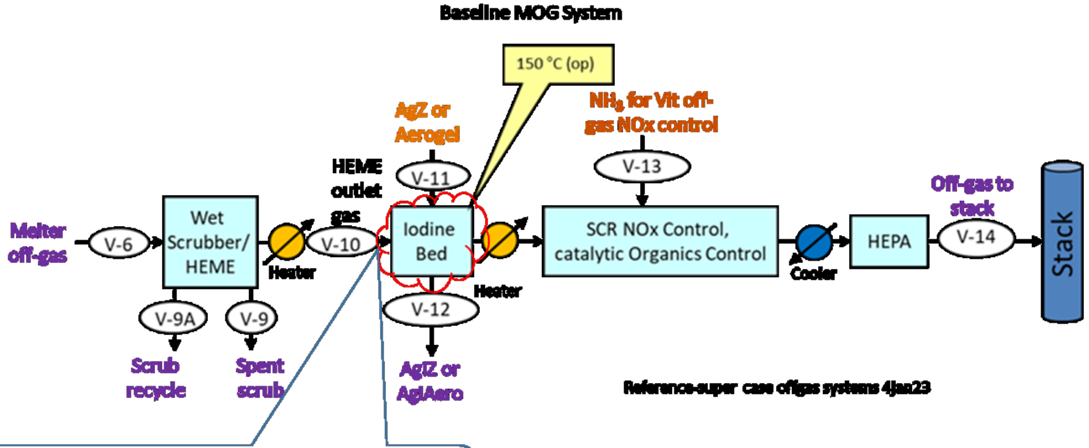


Xe removal



Kr removal

If iodine capture is needed for vitrification melter off-gas (MOG) then some interfering gas species may be different than for DOG, COG, and VOG systems



CO, volatile organic compounds (VOCs), submicron particulate matter ("fume"), acid gases (halogens, S species), NO$_x$

If iodine capture is needed for MOG then caustic wet scrubbing such as is designed for Hanford Waste Treatment Plant may be suitable depending on scrubber efficiency, spent scrubber solution management, and iodine WF.

Summary

- Conceptual flowsheet designs have been produced for capturing volatile radionuclides.
  - Engineering Evaluation and voloxidation/direct dissolution/and trade study reports include estimates of equipment designs and sizes.
- Capture technologies that have been used in aqueous reprocessing or in other full scale industrial processes include the following:
  - Iodine capture (such as $AgNO_3$ coated ceramic support). But higher-performance is needed to achieve the currently-needed DFs and WF.
  - Wet scrubbing for iodine or CO_2 capture. Other off-gas constituents can affect the scrubber performance and WF.
  - Water condensation and adsorption, which encompasses tritiated water capture. But potential impurities may interfere with or co-sorb with the water capture and impact water recycle or WF.
  - Cryogenic Kr/Xe capture (in aqueous reprocessing at INL and commercial air gas separations).
- Some volatile radionuclide capture technologies are:
  - Complex (such as Kr/Xe cryogenic capture).
  - Require high performance (such as for iodine capture).
  - Or are not yet developed and demonstrated for achieving the needed performance (especially Kr/Xe sorbents).

Off-Gas Treatment in Early Plants

R. T. Jubin
MCL-inc

Off-Gas and Waste Forms Strategy Meeting
Washington, DC
January 31-February 1, 2022

U.S. DEPARTMENT OF
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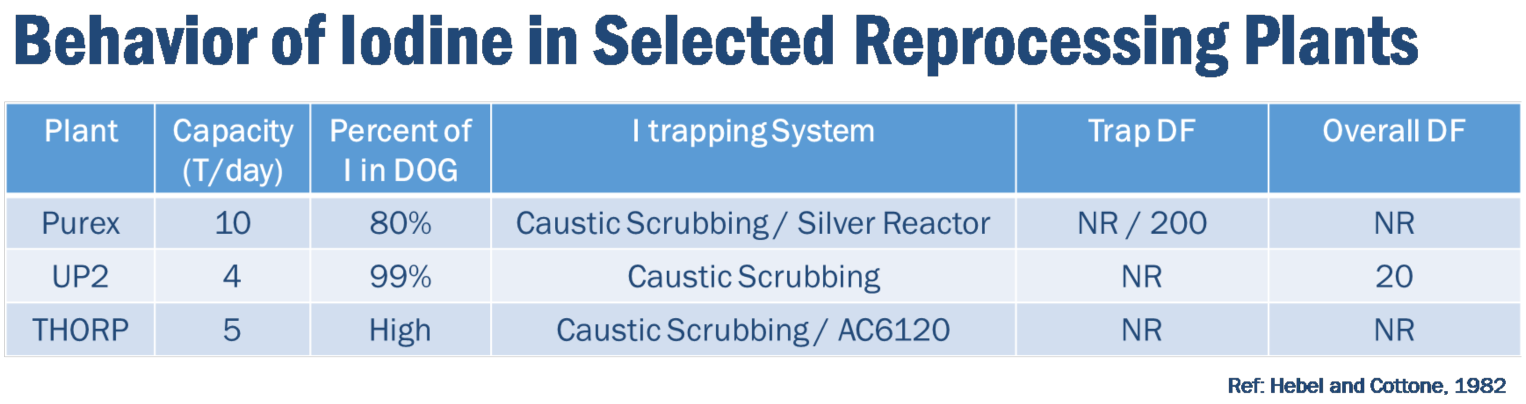


Behavior of Iodine in Selected Reprocessing Plants

Plant	Capacity (T/day)	Percent of I in DOG	I trapping System	Trap DF	Overall DF
Purex	10	80%	Caustic Scrubbing / Silver Reactor	NR / 200	NR
UP2	4	99%	Caustic Scrubbing	NR	20
THORP	5	High	Caustic Scrubbing / AC6120	NR	NR

Ref: Hebel and Cottone, 1982

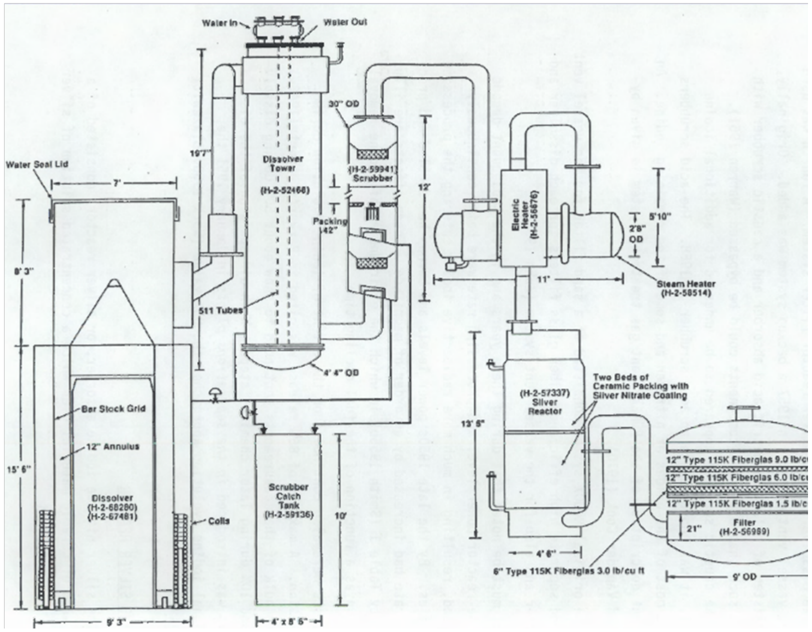
- Iodine control was expected to be a problem.
- Unfortunately, little was known of iodine behavior in the solutions and at the low concentrations involved
- Initial actions that could be taken were to
  - 1) locate the processing plants in the most favorable area with respect to dissipation and dilution by wind,
  - 2) maximize the decay of iodine-131 by storage of the irradiated fuel before processing,
  - 3) dilute the off gas at the plant stack, and
  - 4) carry out the dissolver operations during optimal atmospheric conditions.

Ref: Burger, PNL-7210 HEDR, 1991

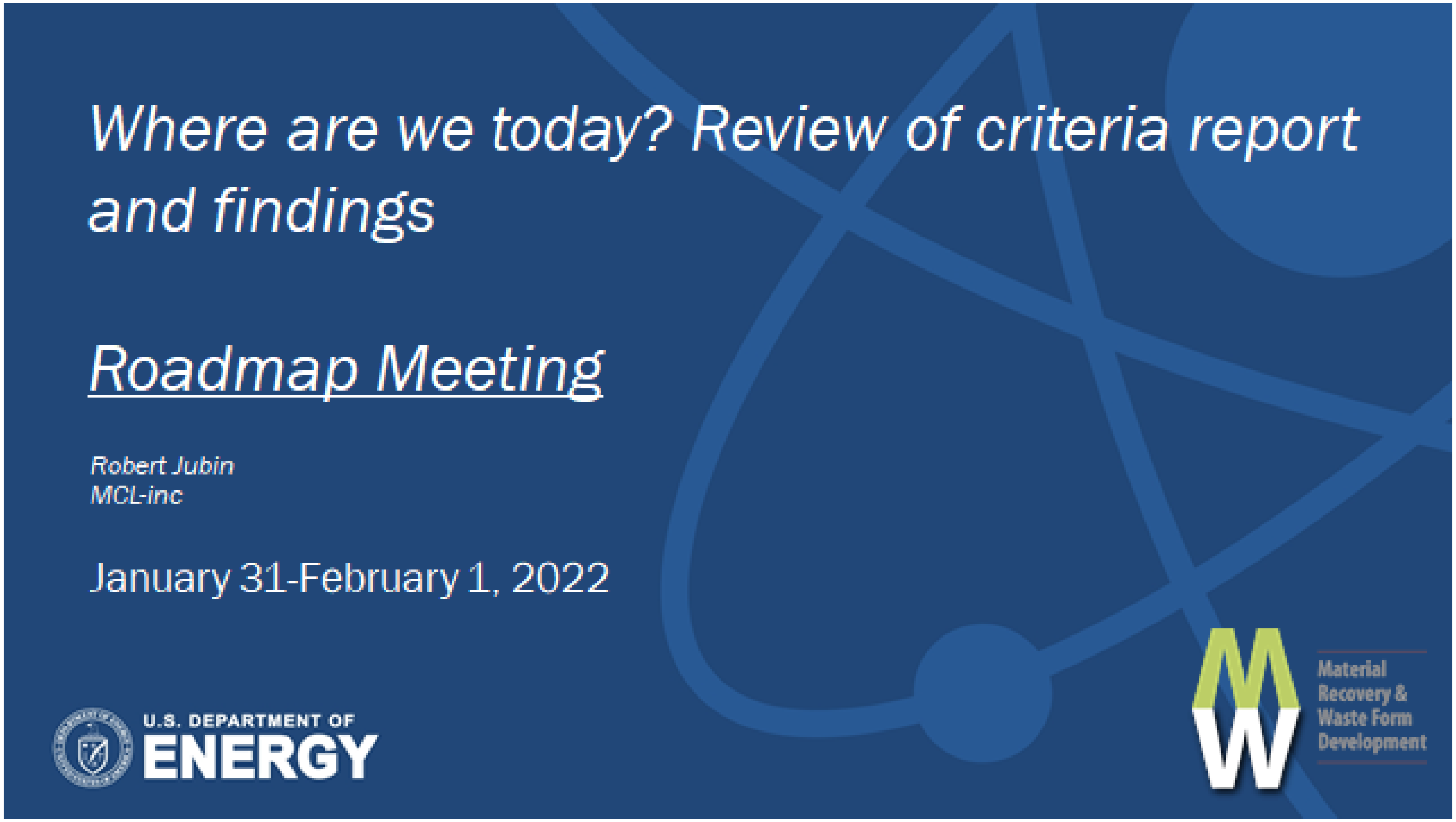
- The silver nitrate filter or "silver reactor" became the workhorse for iodine trapping and was applied to all the separations plants.
  - It was generally satisfactory, but suffered from occasional breakthroughs and deterioration with time, as well as from iodine release due to chlorine absorption.
- Acid absorbers were later installed as back-up devices in the REDOX and PUREX plants.
- The silver reactor used in the vessel vent system proved to be less efficient than those in the dissolver off-gas system.
- In retrospect it is likely that one of the more important contributions of the silver reactor was that the iodine residence time in the bed was long enough to permit the iodine-131 to decay.

Ref: Burger, PNL-7210 HEDR, 1991

- Packed bed of ceramic material
  - Silver Nitrate poured over bed.
- Operated at ~190C
- Regenerated by adding fresh silver nitrate.
- Key reactions
  - $0.5I_2 + AgNO_3 + O_2 \rightarrow AgIO_3 + NO_2$
  - $0.5I_2 + AgNO_3 \rightarrow AgI + NO_2 + 0.5O_2$
- Note the reactions are reversible



Ref: Burger, PNL-7210 HEDR, 1991



Where are we today? Review of criteria report and findings

Roadmap Meeting

Robert Jubin
MCL-inc

January 31-February 1, 2022

U.S. DEPARTMENT OF
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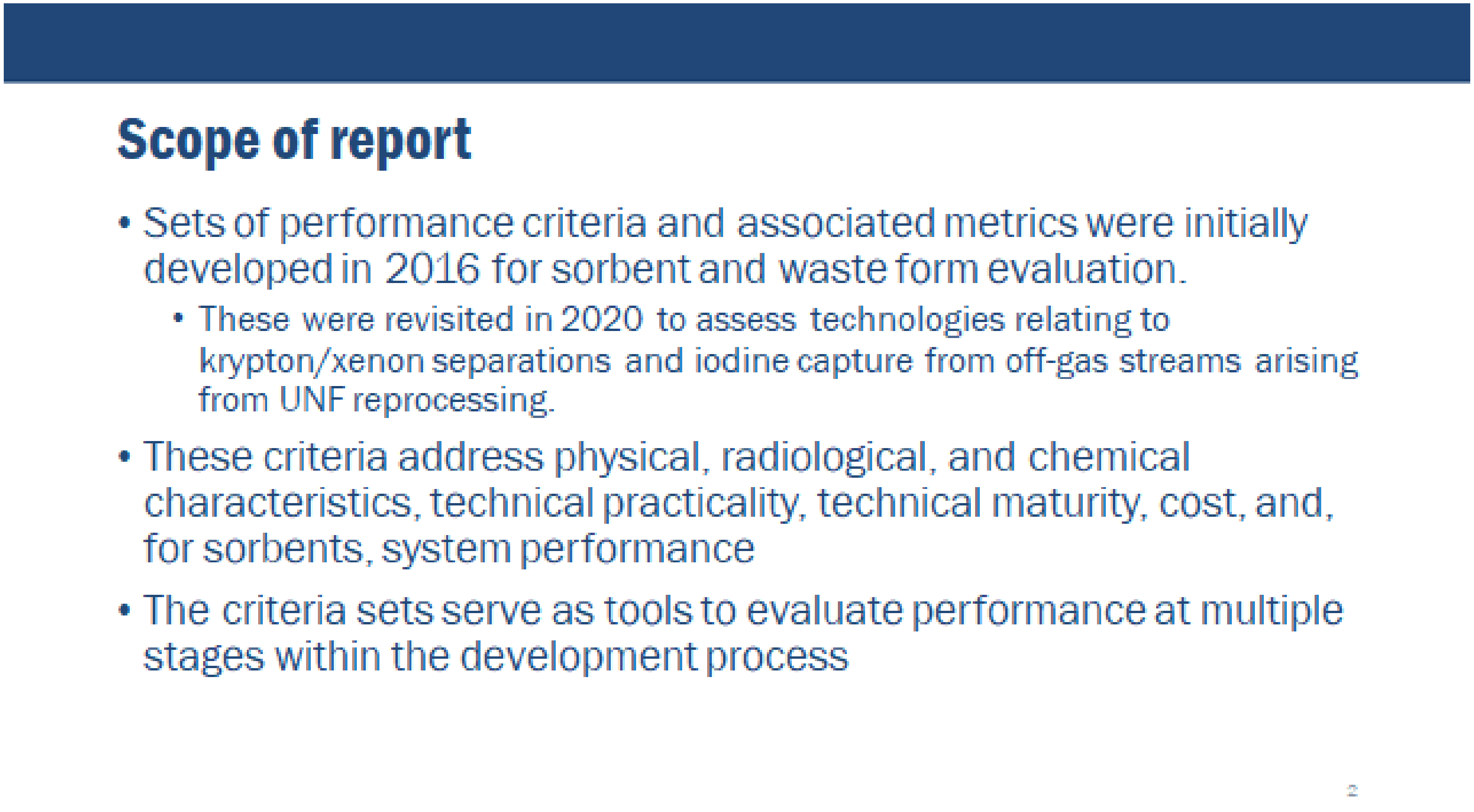
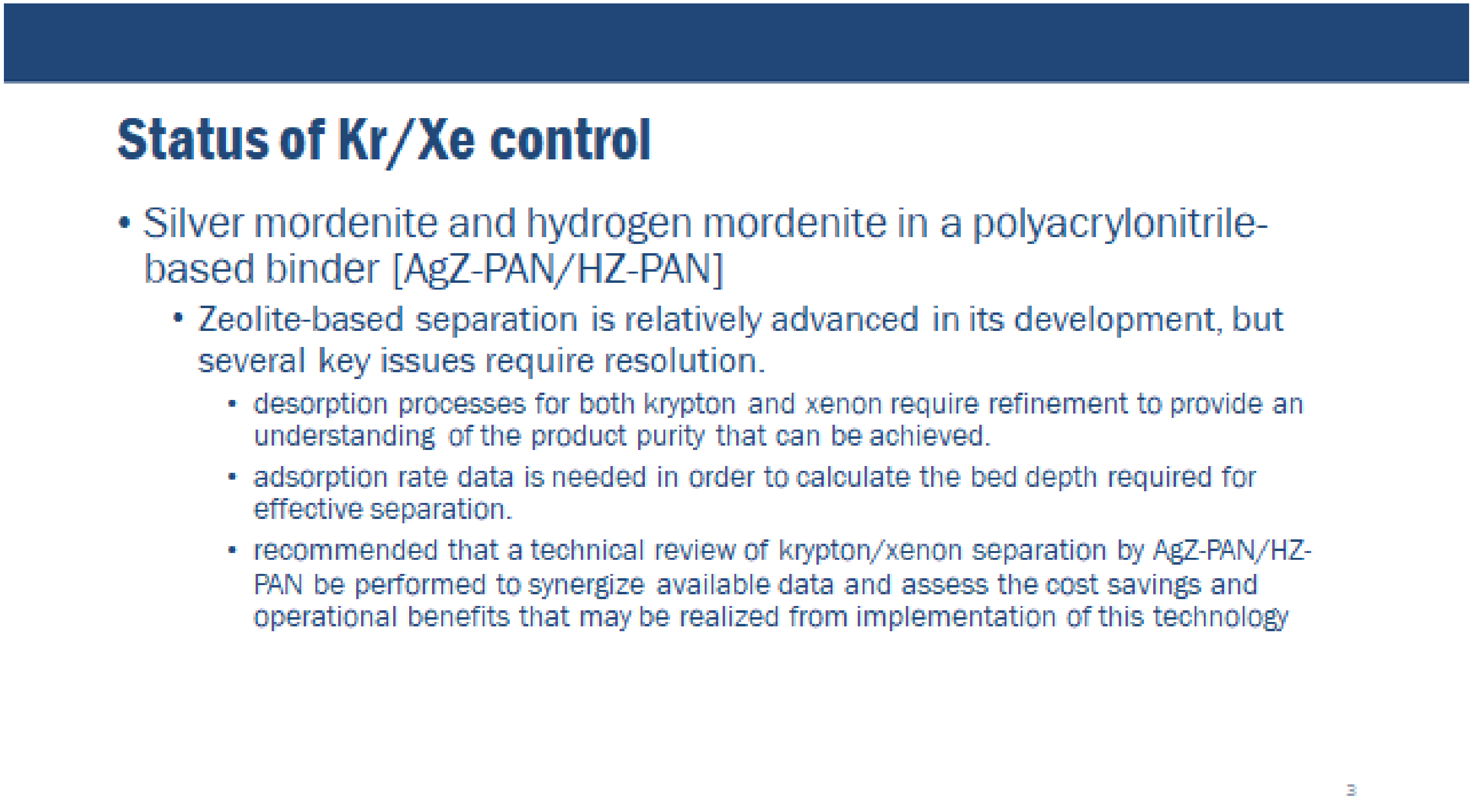


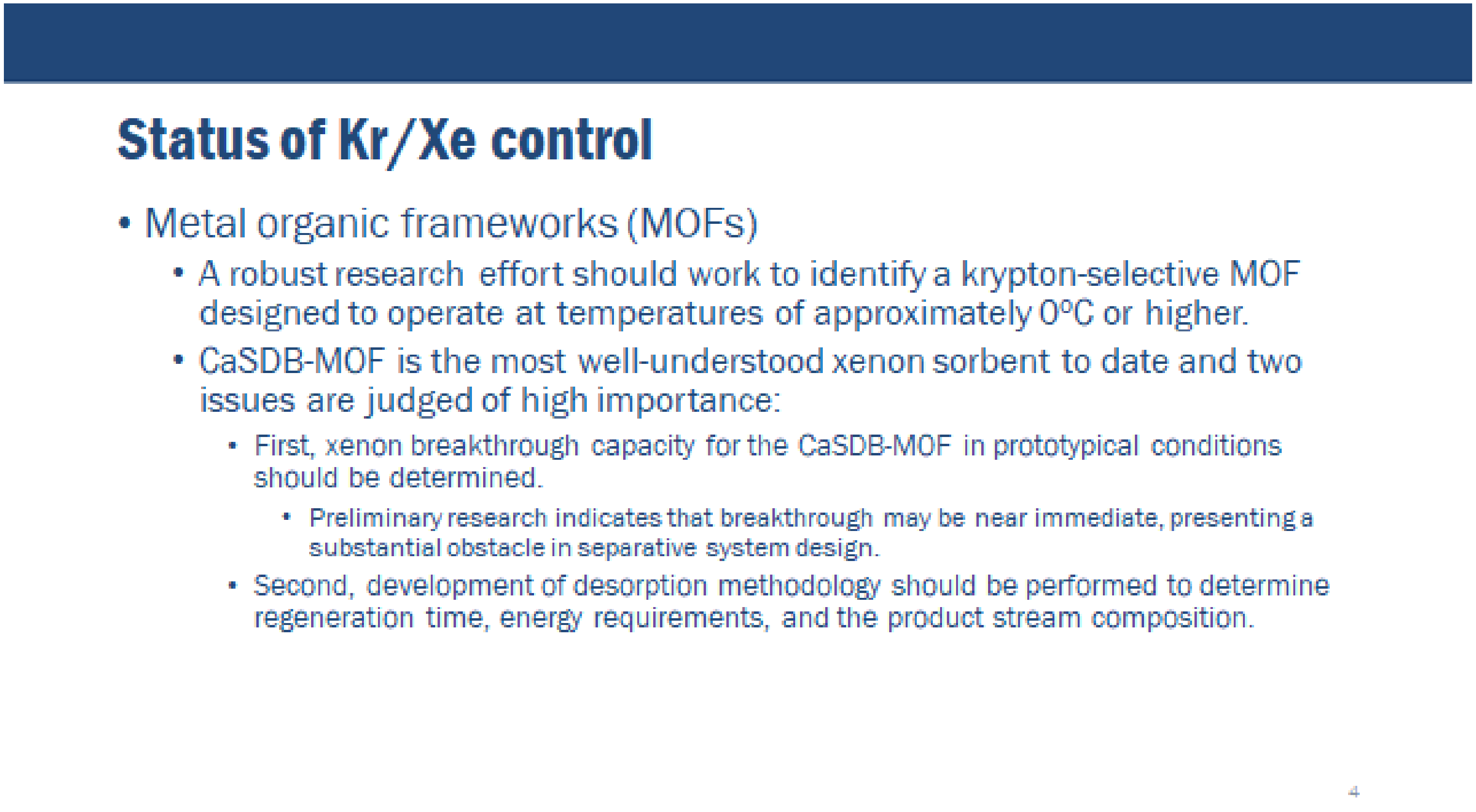
Scope of report

- Sets of performance criteria and associated metrics were initially developed in 2016 for sorbent and waste form evaluation.
    - These were revisited in 2020 to assess technologies relating to krypton/xenon separations and iodine capture from off-gas streams arising from UNF reprocessing.
- These criteria address physical, radiological, and chemical characteristics, technical practicality, technical maturity, cost, and, for sorbents, system performance
- The criteria sets serve as tools to evaluate performance at multiple stages within the development process



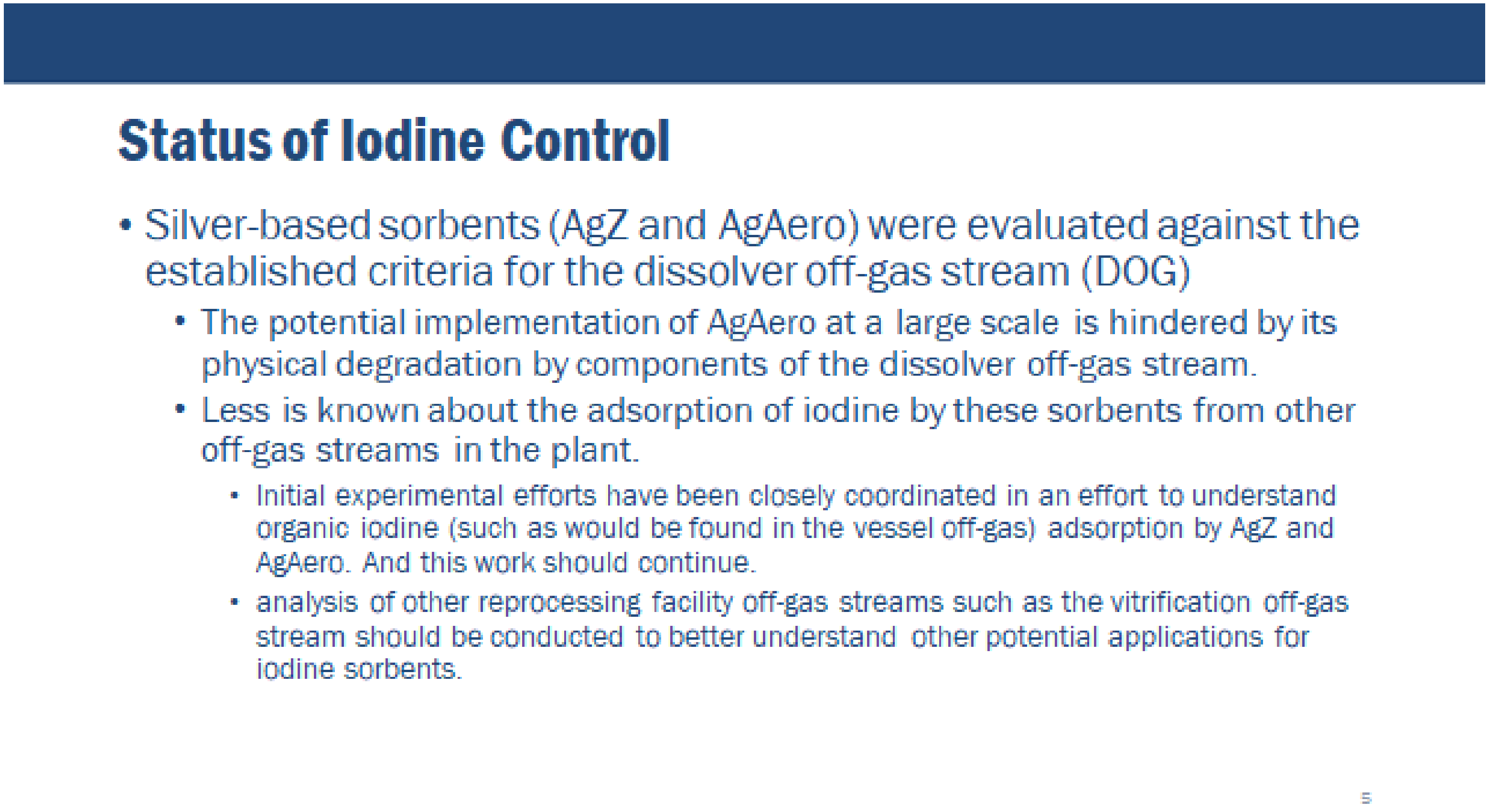
Status of Kr/Xe control

- Silver mordenite and hydrogen mordenite in a polyacrylonitrile-based binder [AgZ-PAN/HZ-PAN]
  - Zeolite-based separation is relatively advanced in its development, but several key issues require resolution.
    - desorption processes for both krypton and xenon require refinement to provide an understanding of the product purity that can be achieved.
    - adsorption rate data is needed in order to calculate the bed depth required for effective separation.
    - recommended that a technical review of krypton/xenon separation by AgZ-PAN/HZ-PAN be performed to synergize available data and assess the cost savings and operational benefits that may be realized from implementation of this technology



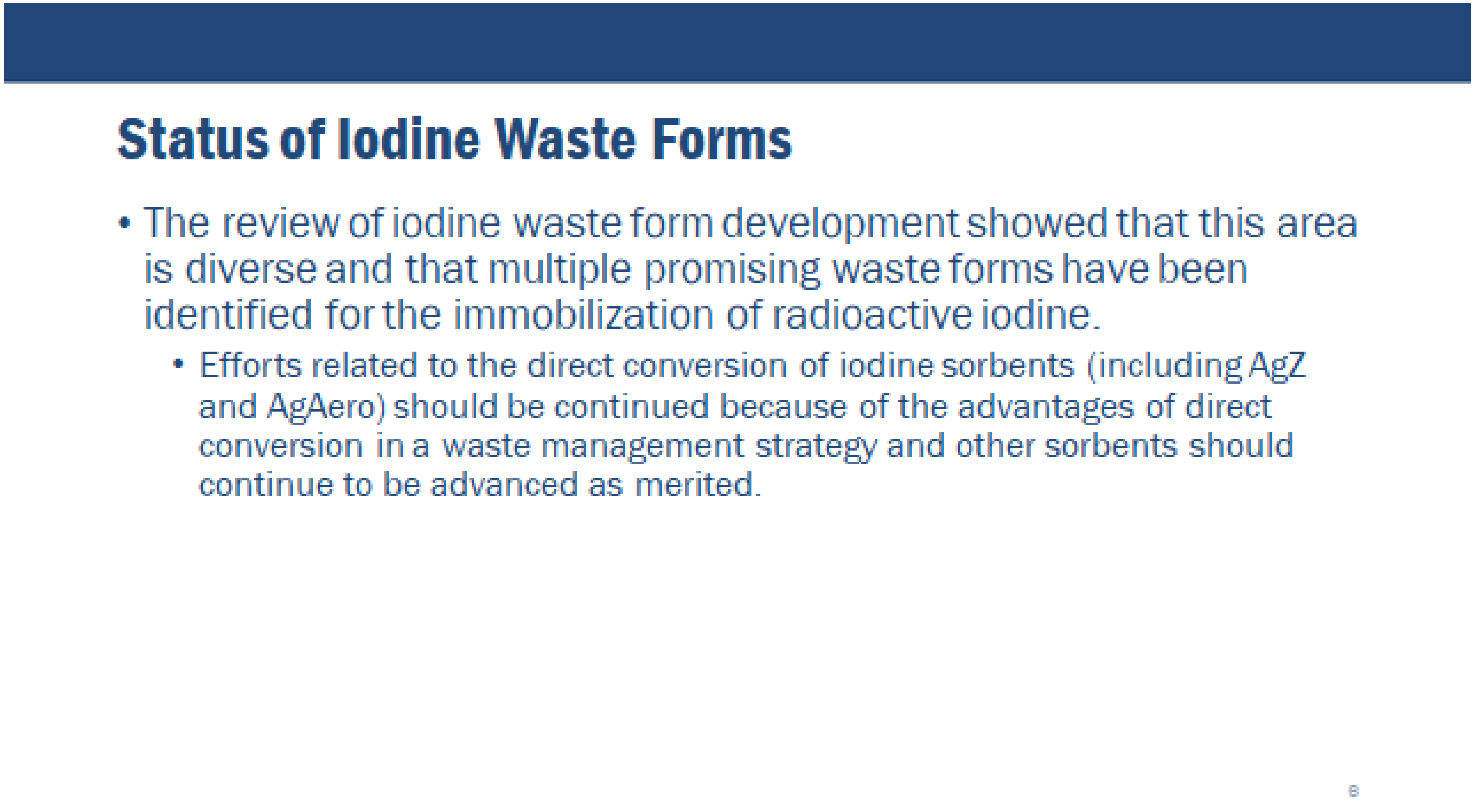
Status of Kr/Xe control

- Metal organic frameworks (MOFs)
  - A robust research effort should work to identify a krypton-selective MOF designed to operate at temperatures of approximately 0ºC or higher.
  - CaSDB-MOF is the most well-understood xenon sorbent to date and two issues are judged of high importance:
    - First, xenon breakthrough capacity for the CaSDB-MOF in prototypical conditions should be determined.
      - Preliminary research indicates that breakthrough may be near immediate, presenting a substantial obstacle in separative system design.
    - Second, development of desorption methodology should be performed to determine regeneration time, energy requirements, and the product stream composition.



Status of Iodine Control

- Silver-based sorbents (AgZ and AgAero) were evaluated against the established criteria for the dissolver off-gas stream (DOG)
  - The potential implementation of AgAero at a large scale is hindered by its physical degradation by components of the dissolver off-gas stream.
  - Less is known about the adsorption of iodine by these sorbents from other off-gas streams in the plant.
    - Initial experimental efforts have been closely coordinated in an effort to understand organic iodine (such as would be found in the vessel off-gas) adsorption by AgZ and AgAero. And this work should continue.
    - analysis of other reprocessing facility off-gas streams such as the vitrification off-gas stream should be conducted to better understand other potential applications for iodine sorbents.

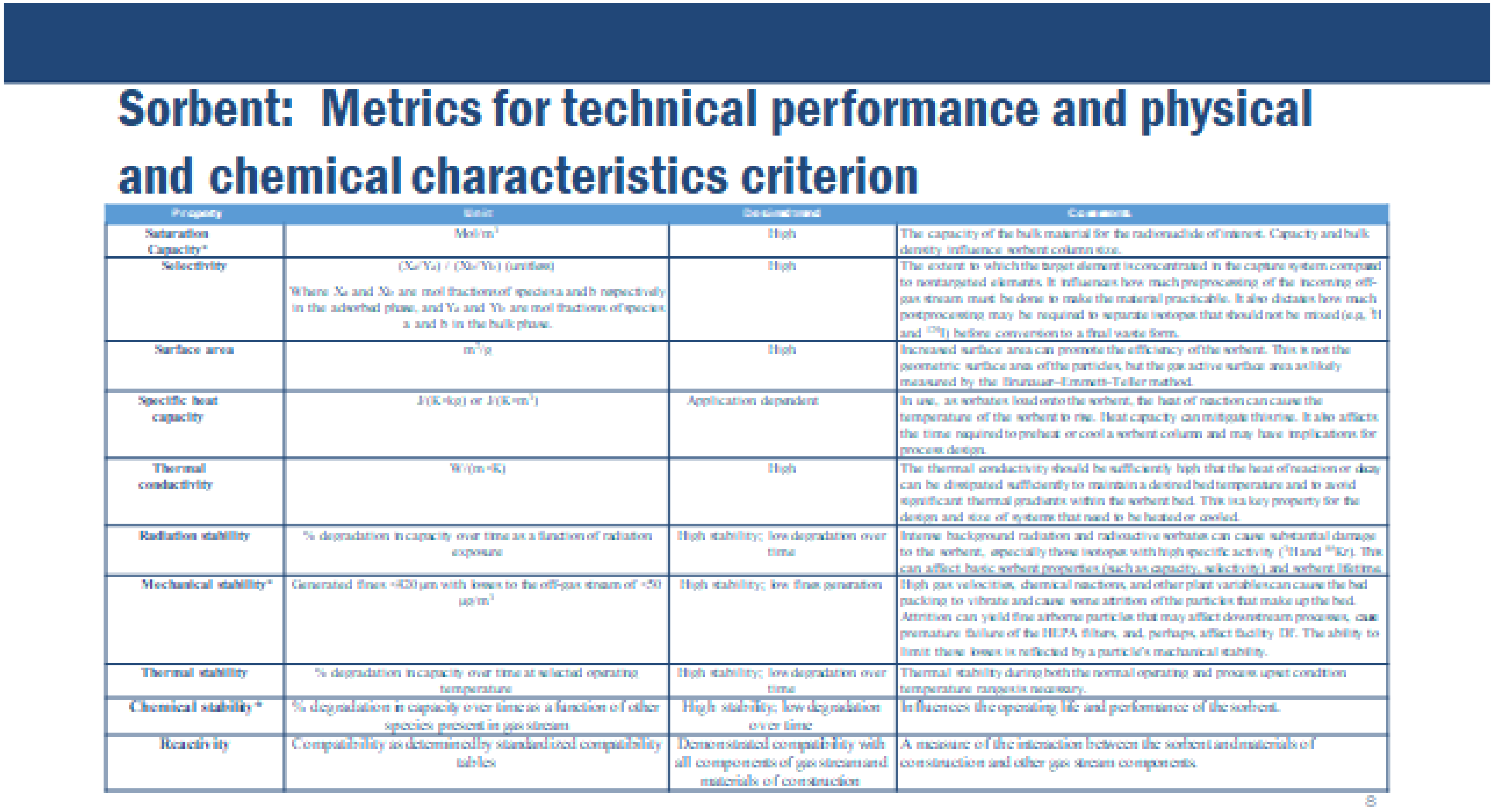


Status of Iodine Waste Forms

- The review of iodine waste form development showed that this area is diverse and that multiple promising waste forms have been identified for the immobilization of radioactive iodine.
  - Efforts related to the direct conversion of iodine sorbents (including AgZ and AgAero) should be continued because of the advantages of direct conversion in a waste management strategy and other sorbents should continue to be advanced as merited.

What was not addressed in this report

- Tritium recovery
- ^{14}C recovery
- Control of volatile species under high NOx conditions
- Semi-volatile control
- Scale-up



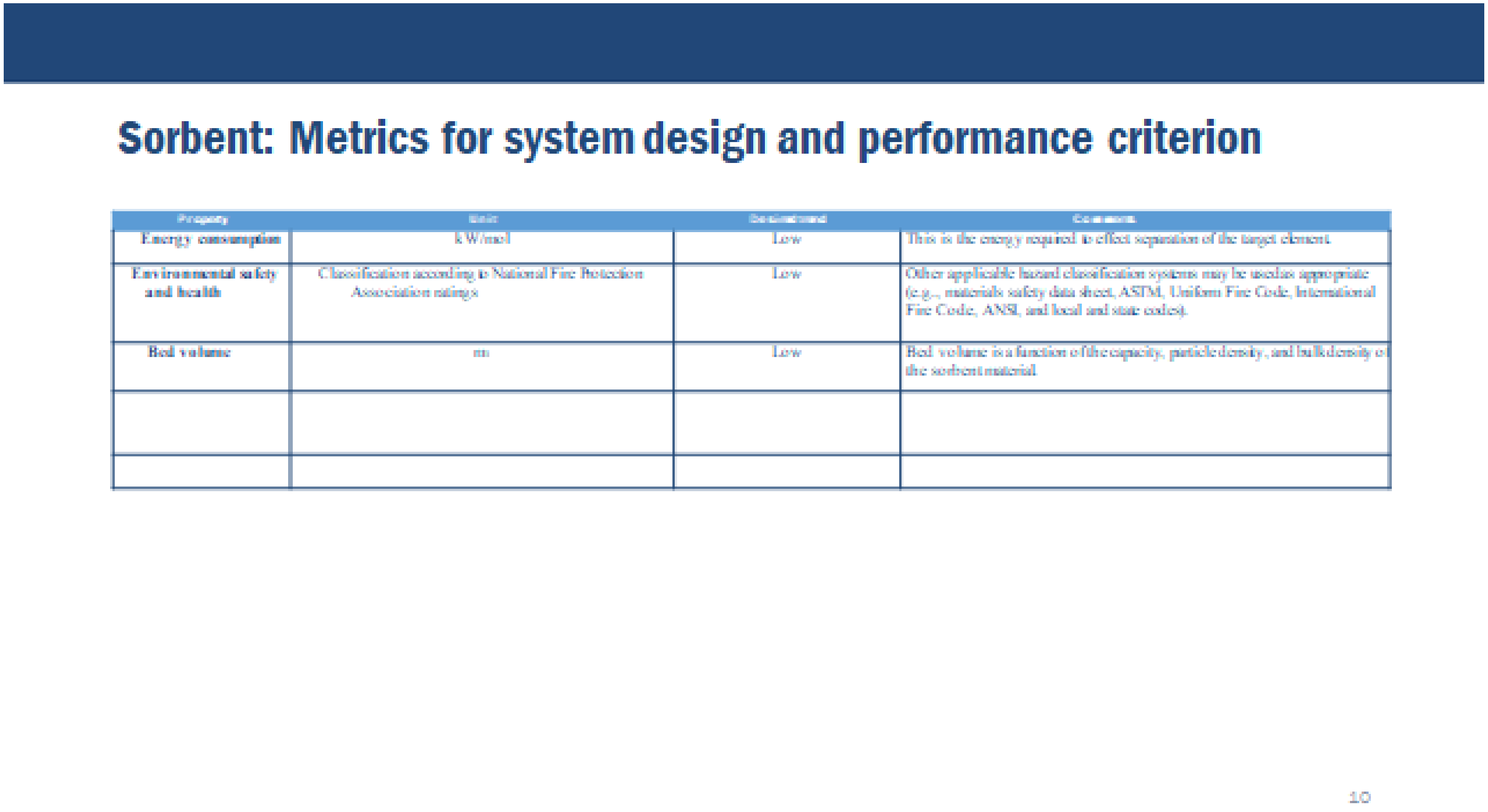
Sorbent: Metrics for technical performance and physical and chemical characteristics criterion

Property	Unit	Desired trend	Comments
Saturation Capacity*	Mol/m^3	High	The capacity of the bulk material for the radionuclide of interest. Capacity and bulk density influence sorbent column size.
Selectivity	(X_a/Y_a) / (X_b/Y_b) (unitless) Where X_a and X_b are mol fractions of species a and b respectively in the adsorbed phase, and Y_a and Y_b are mol fractions of species a and b in the bulk phase.	High	The extent to which the target element is concentrated in the capture system compared to nontargeted elements. It influences how much preprocessing of the incoming off-gas stream must be done to make the material practicable. It also dictates how much postprocessing may be required to separate isotopes that should not be mixed (e.g. ^{3}H and ^{129}I) before conversion to a final waste form.
Surface area	m^2/g	High	Increased surface area can promote the efficiency of the sorbent. This is not the geometric surface area of the particles, but the gas active surface area as likely measured by the Brunauer–Emmett–Teller method.
Specific heat capacity	J/(K•kg) or J/(K•m^3)	Application dependent	In use, as sorbates load onto the sorbent, the heat of reaction can cause the temperature of the sorbent to rise. Heat capacity can mitigate this rise. It also affects the time required to preheat or cool a sorbent column and may have implications for process design.
Thermal conductivity	W/(m•K)	High	The thermal conductivity should be sufficiently high that the heat of reaction or decay can be dissipated sufficiently to maintain a desired bed temperature and to avoid significant thermal gradients within the sorbent bed. This is a key property for the design and size of systems that need to be heated or cooled.
Radiation stability	% degradation in capacity over time as a function of radiation exposure	High stability; low degradation over time	Intense background radiation and radioactive sorbates can cause substantial damage to the sorbent, especially those isotopes with high specific activity (^{3}H and ^{85}Kr). This can affect basic sorbent properties (such as capacity, selectivity) and sorbent lifetime.
Mechanical stability*	Generated fines <420 µm with losses to the off-gas stream of <50 µg/m^3	High stability; low fines generation	High gas velocities, chemical reactions, and other plant variables can cause the bed packing to vibrate and cause some attrition of the particles that make up the bed. Attrition can yield fine airborne particles that may affect downstream processes, cause premature failure of the HEPA filters, and, perhaps, affect facility DF. The ability to limit these losses is reflected by a particle's mechanical stability.
Thermal stability	% degradation in capacity over time at selected operating temperature	High stability; low degradation over time	Thermal stability during both the normal operating and process upset condition temperature ranges is necessary.
Chemical stability*	% degradation in capacity over time as a function of other species present in gas stream	High stability; low degradation over time	Influences the operating life and performance of the sorbent.
Reactivity	Compatibility as determined by standardized compatibility tables	Demonstrated compatibility with all components of gas stream and materials of construction	A measure of the interaction between the sorbent and materials of construction and other gas stream components.

8

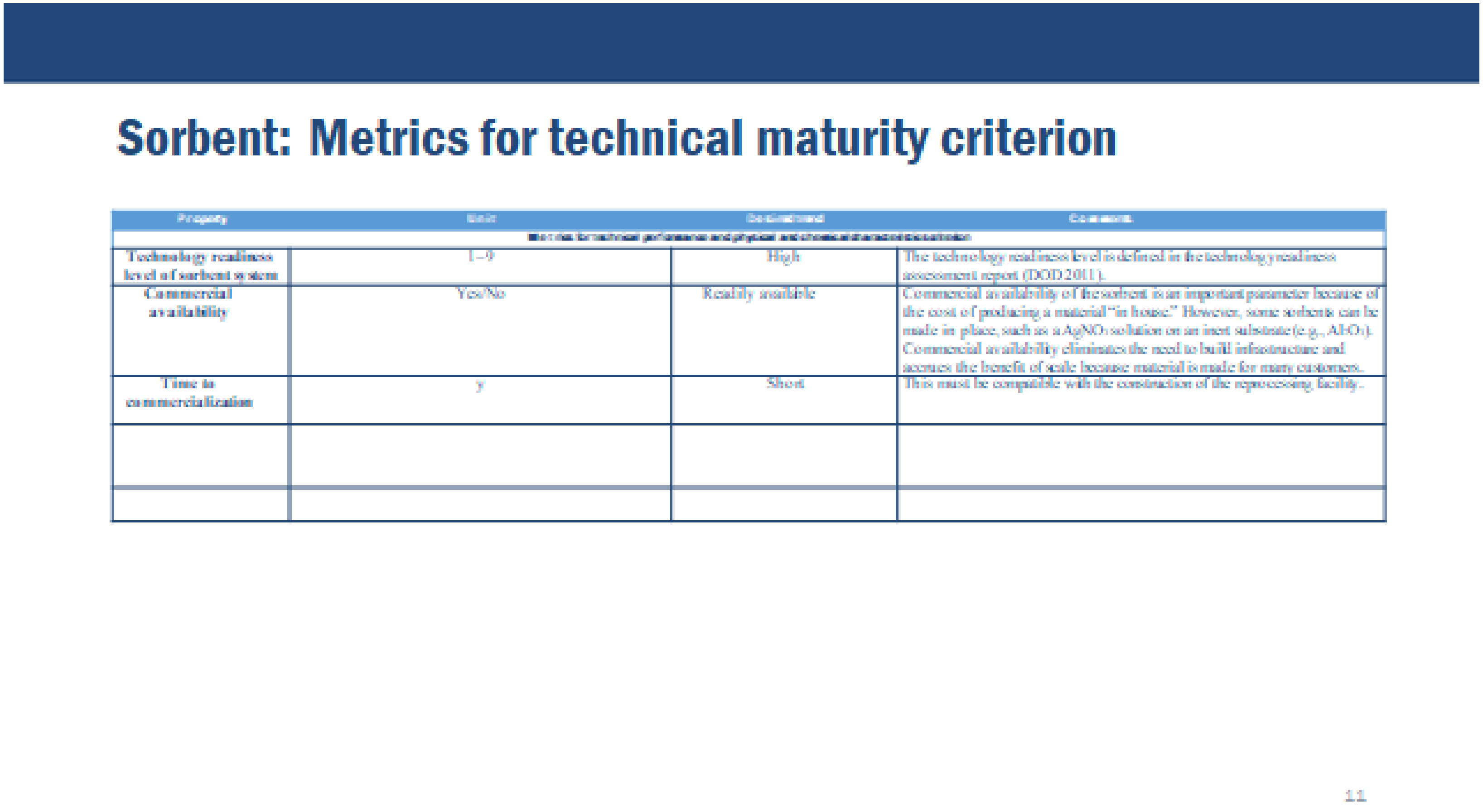
Sorbent: Metrics for technical practicality criterion

Property	Unit	Desired trend	Comments
Regeneration*	No. of cycles before degrading to 80% of capacity for the target element	High	This property affects the overall plant design and cost of operation. Some materials may not be regenerated (i.e., they are single use).
Bulk density	kg/m^3	High	Bulk density is the average density of the sorbent bed taking into account the particle density and the intra-particle void volume (i.e., the mass of the sorbent [kg] divided by the volume of the packed bed [m^3]). Bulk density influences bed size, pressure drop, and surface area available for reaction. Increases in bulk density approaching the particle density in the limiting case will result in the smallest bed size but excessive pressure drop.
Co-adsorbed species*	Mol/kg	Small in number of species and quantity	Indicates how much the overall capacity of the sorbent is affected by sorption of nontargeted elements. Tramp elements or isotopes (e.g., Cl, ^{14}C, Xe) fall into this category.
Robustness	% variation in operating parameters tolerated without deleterious effects	High	Tolerance to process upset conditions.
Flexibility and pretreatment*	Operating ranges; no. of unit operations for pretreatment	High flexibility; minimal pretreatment	The width of the sorbent standard operating envelope.
Process complexity	Number and type of control systems and unit operations required.	Low	Affects the cost, volume, and footprint of the treatment system.
Energy consumption	kW/mol	Low	This is the energy required to effect separation of the target element.
Environmental safety and health	Classification according to National Fire Protection Association ratings	Low	Other applicable hazard classification systems may be used as appropriate (e.g., materials safety data sheet, ASTM, Uniform Fire Code, International Fire Code, ANSI, and local and state codes).



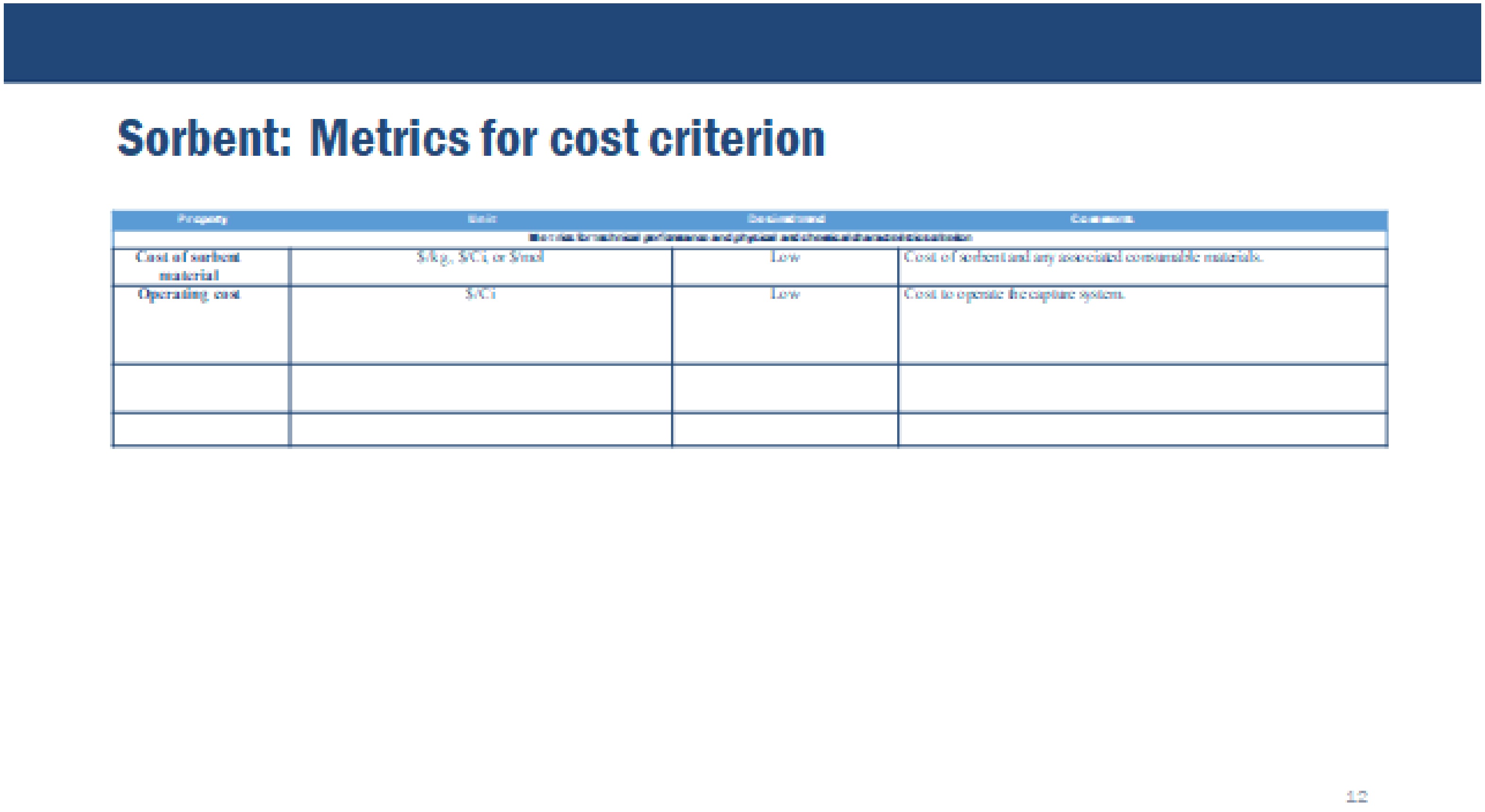
Sorbent: Metrics for system design and performance criterion

Property	Unit	Desired trend	Comments
Energy consumption	kW/mol	Low	This is the energy required to effect separation of the target element.
Environmental safety and health	Classification according to National Fire Protection Association ratings	Low	Other applicable hazard classification systems may be used as appropriate (e.g., materials safety data sheet, ASTM, Uniform Fire Code, International Fire Code, ANSI, and local and state codes).
Bed volume	m	Low	Bed volume is a function of the capacity, particle density, and bulk density o the sorbent material.



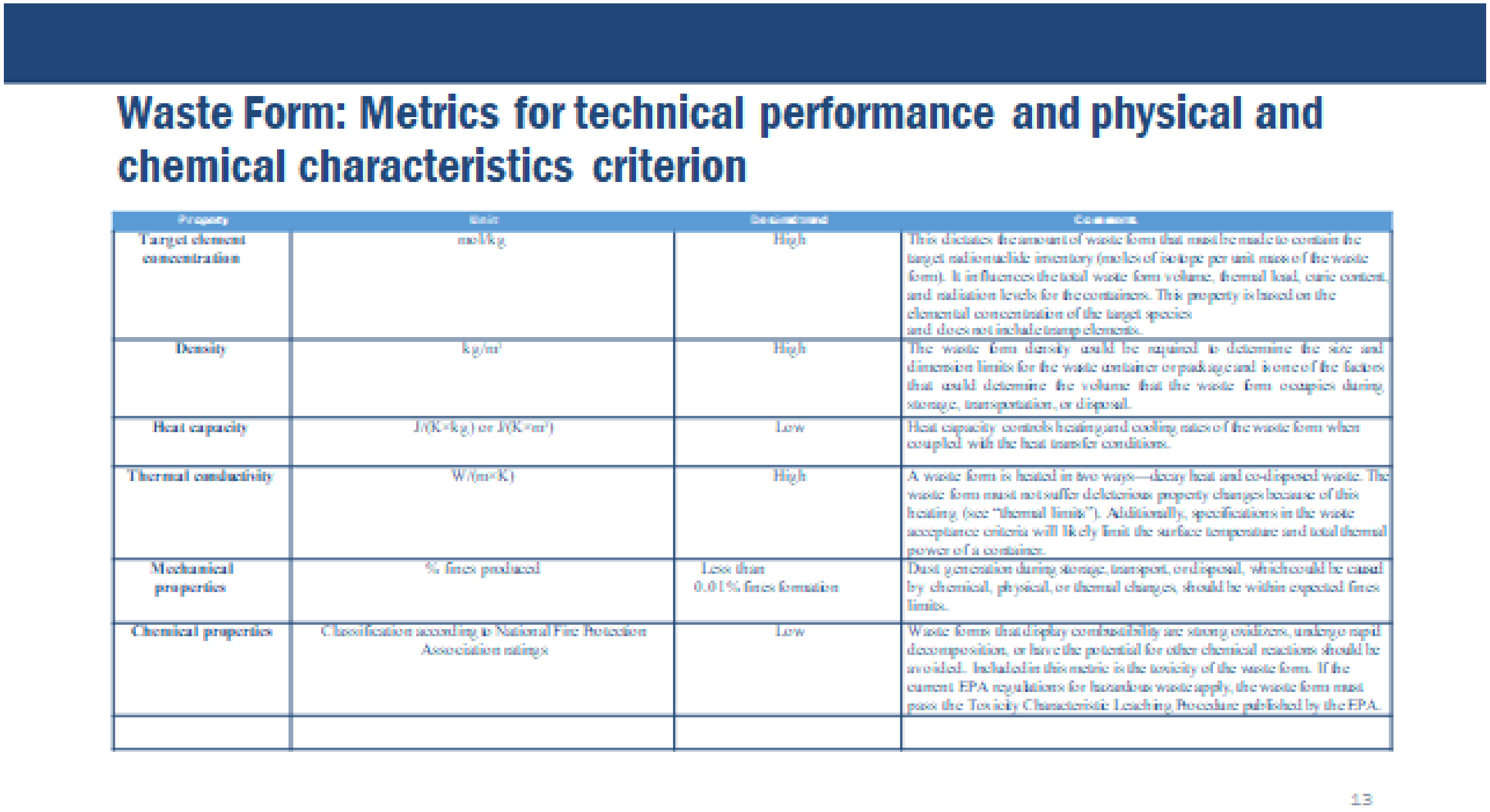
Sorbent: Metrics for technical maturity criterion

Property	Unit	Desired trend	Comments
[illegible]			
Technology readiness level of sorbent system	1–9	High	The technology readiness level is defined in the technology readiness assessment report (DOD 2011).
Commercial availability	Yes/No	Readily available	Commercial availability of the sorbent is an important parameter because of the cost of producing a material "in house." However, some sorbents can be made in place, such as a $AgNO_3$ solution on an inert substrate (e.g., Al_2O_3). Commercial availability eliminates the need to build infrastructure and accrues the benefit of scale because material is made for many customers.
Time to commercialization	y	Short	This must be compatible with the construction of the reprocessing facility.



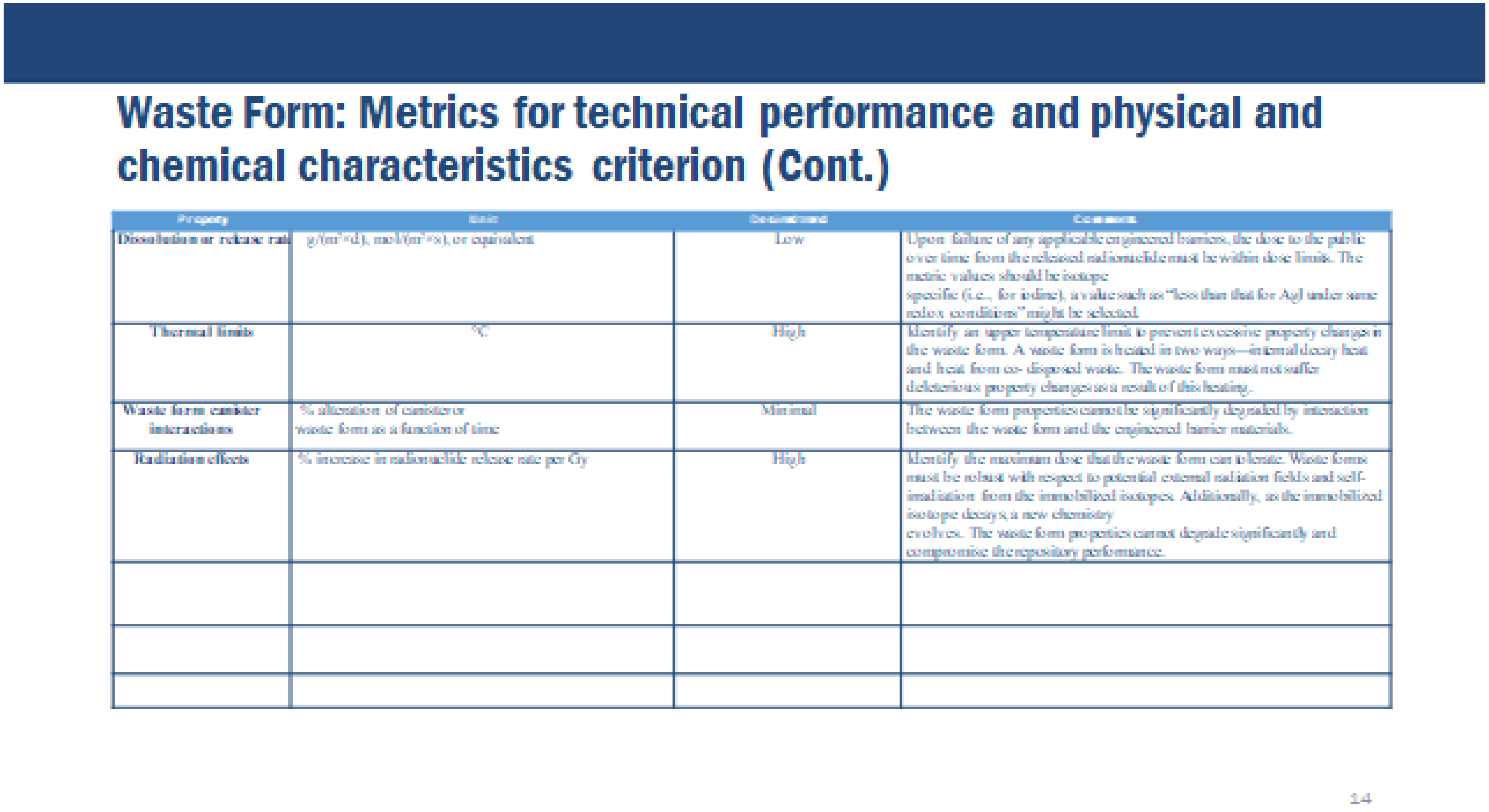
Sorbent: Metrics for cost criterion

Property	Unit	Desired trend	Comments
Metrics for technical performance and physical and chemical characterization			
Cost of sorbent material	$/kg, $/Ci, or $/mol	Low	Cost of sorbent and any associated consumable materials.
Operating cost	$/Ci	Low	Cost to operate the capture system.



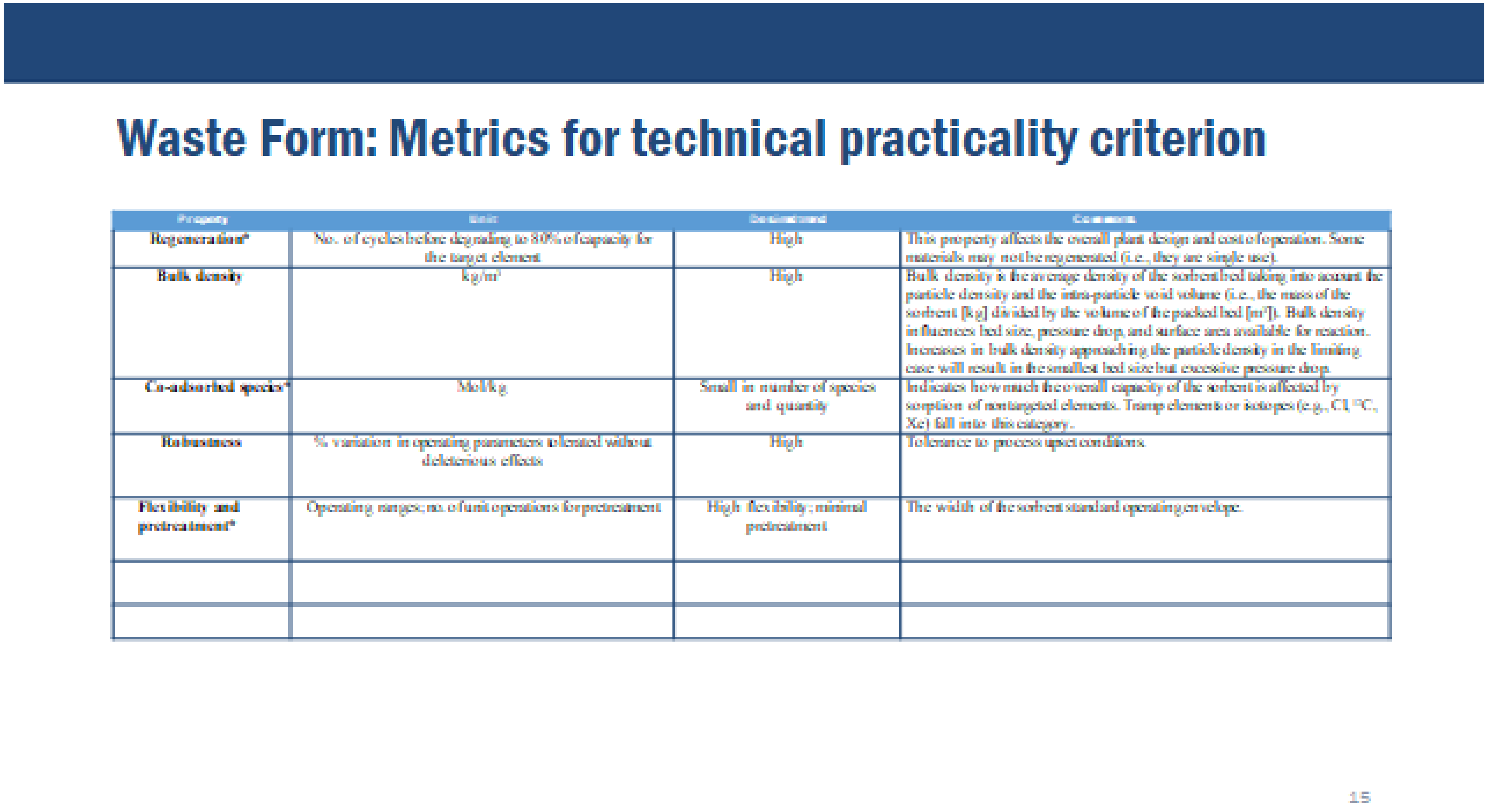
Waste Form: Metrics for technical performance and physical and chemical characteristics criterion

Property	Unit	Desired trend	Comments
Target element concentration	mol/kg	High	This dictates the amount of waste form that must be made to contain the target radionuclide inventory (moles of isotope per unit mass of the waste form). It influences the total waste form volume, thermal load, curie content, and radiation levels for the containers. This property is based on the elemental concentration of the target species and does not include tramp elements.
Density	kg/m^3	High	The waste form density could be required to determine the size and dimension limits for the waste container or package and is one of the factors that could determine the volume that the waste form occupies during storage, transportation, or disposal.
Heat capacity	J/(K×kg) or J/(K×m^3)	Low	Heat capacity controls heating and cooling rates of the waste form when coupled with the heat transfer conditions.
Thermal conductivity	W/(m×K)	High	A waste form is heated in two ways—decay heat and co-disposed waste. The waste form must not suffer deleterious property changes because of this heating (see "thermal limits"). Additionally, specifications in the waste acceptance criteria will likely limit the surface temperature and total thermal power of a container.
Mechanical properties	% fines produced	Less than 0.01% fines formation	Dust generation during storage, transport, or disposal, which could be caused by chemical, physical, or thermal changes, should be within expected fines limits.
Chemical properties	Classification according to National Fire Protection Association ratings	Low	Waste forms that display combustibility are strong oxidizers, undergo rapid decomposition, or have the potential for other chemical reactions should be avoided. Included in this metric is the toxicity of the waste form. If the current EPA regulations for hazardous waste apply, the waste form must pass the Toxicity Characteristic Leaching Procedure published by the EPA.



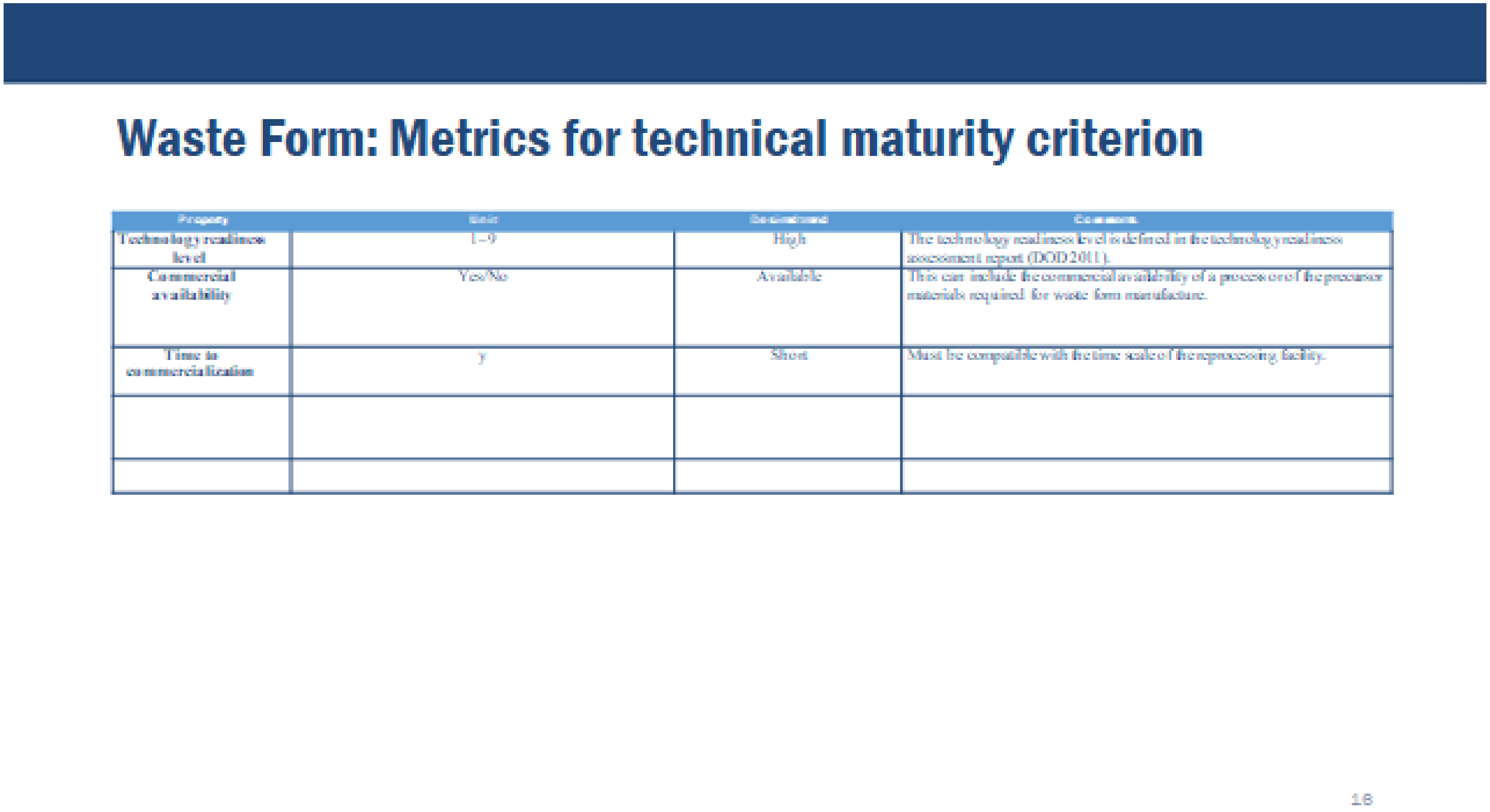
Waste Form: Metrics for technical performance and physical and chemical characteristics criterion (Cont.)

Property	Unit	Desired trend	Comments
Dissolution or release rat	g/(m^2×d), mol/(m^2×s), or equivalent	Low	Upon failure of any applicable engineered barriers, the dose to the public over time from the released radionuclide must be within dose limits. The metric values should be isotope specific (i.e., for iodine), a value such as "less than that for AgI under same redox conditions" might be selected.
Thermal limits	°C	High	Identify an upper temperature limit to prevent excessive property changes in the waste form. A waste form is heated in two ways—internal decay heat and heat from co- disposed waste. The waste form must not suffer deleterious property changes as a result of this heating.
Waste form canister interactions	% alteration of canister or waste form as a function of time	Minimal	The waste form properties cannot be significantly degraded by interaction between the waste form and the engineered barrier materials.
Radiation effects	% increase in radionuclide release rate per Gy	High	Identify the maximum dose that the waste form can tolerate. Waste forms must be robust with respect to potential external radiation fields and self-irradiation from the immobilized isotopes. Additionally, as the immobilized isotope decays, a new chemistry evolves. The waste form properties cannot degrade significantly and compromise the repository performance.



Waste Form: Metrics for technical practicality criterion

Property	Unit	Desired trend	Comments
Regeneration*	No. of cycles before degrading to 80% of capacity for the target element	High	This property affects the overall plant design and cost of operation. Some materials may not be regenerated (i.e., they are single use).
Bulk density	kg/m³	High	Bulk density is the average density of the sorbent bed taking into account the particle density and the intra-particle void volume (i.e., the mass of the sorbent [kg] divided by the volume of the packed bed [m³]). Bulk density influences bed size, pressure drop, and surface area available for reaction. Increases in bulk density approaching the particle density in the limiting case will result in the smallest bed size but excessive pressure drop.
Co-adsorbed species*	Mol/kg	Small in number of species and quantity	Indicates how much the overall capacity of the sorbent is affected by sorption of nontargeted elements. Tramp elements or isotopes (e.g., Cl, ^{14}C, Xe) fall into this category.
Robustness	% variation in operating parameters tolerated without deleterious effects	High	Tolerance to process upset conditions.
Flexibility and pretreatment*	Operating ranges; no. of unit operations for pretreatment	High flexibility; minimal pretreatment	The width of the sorbent standard operating envelope.

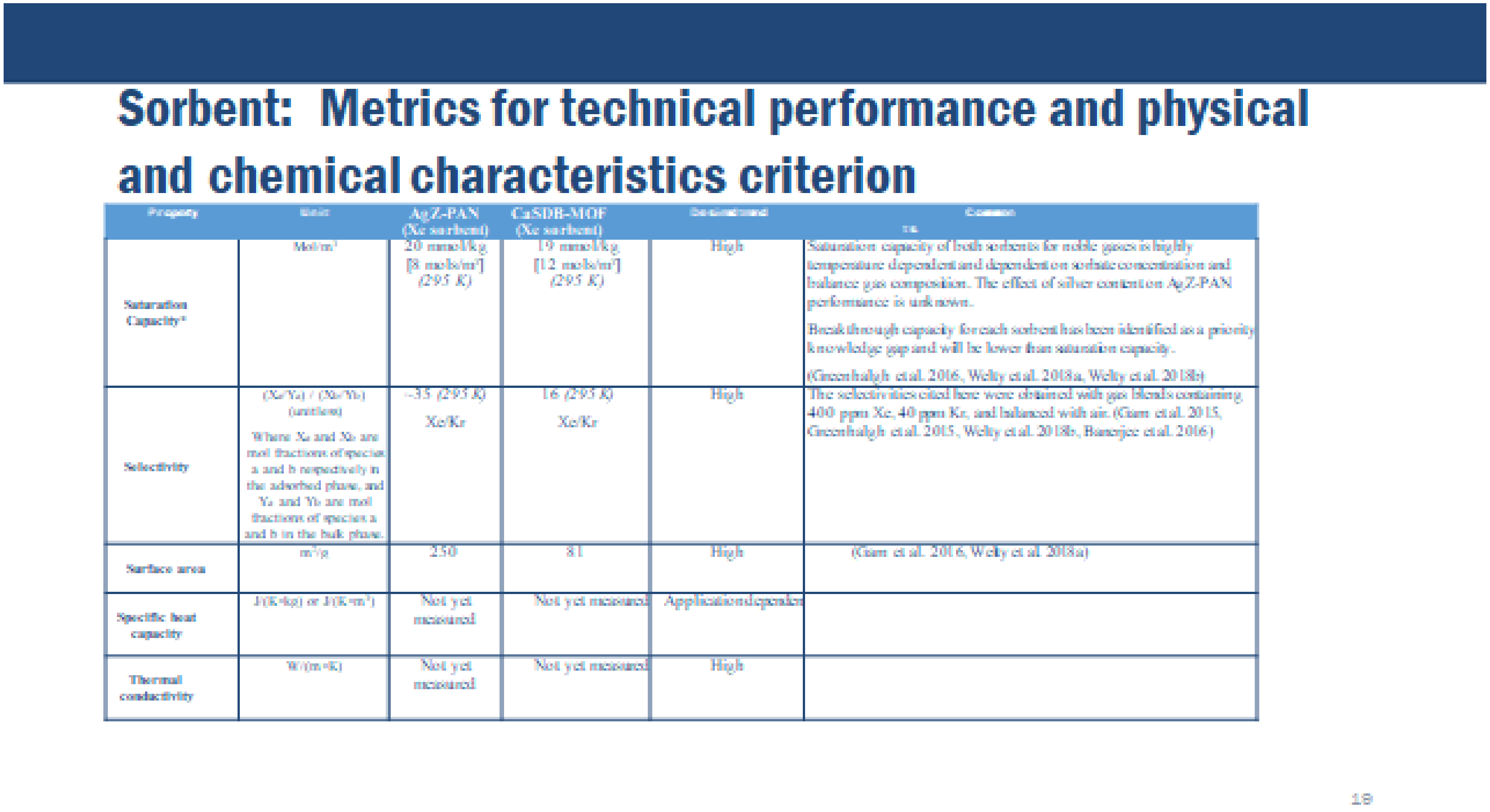


Waste Form: Metrics for technical maturity criterion

Property	Unit	Desired trend	Comments
Technology readiness level	1–9	High	The technology readiness level is defined in the technology readiness assessment report (DOD 2011).
Commercial availability	Yes/No	Available	This can include the commercial availability of a process or of the precursor materials required for waste form manufacture.
Time to commercialization	y	Short	Must be compatible with the time scale of the reprocessing facility.

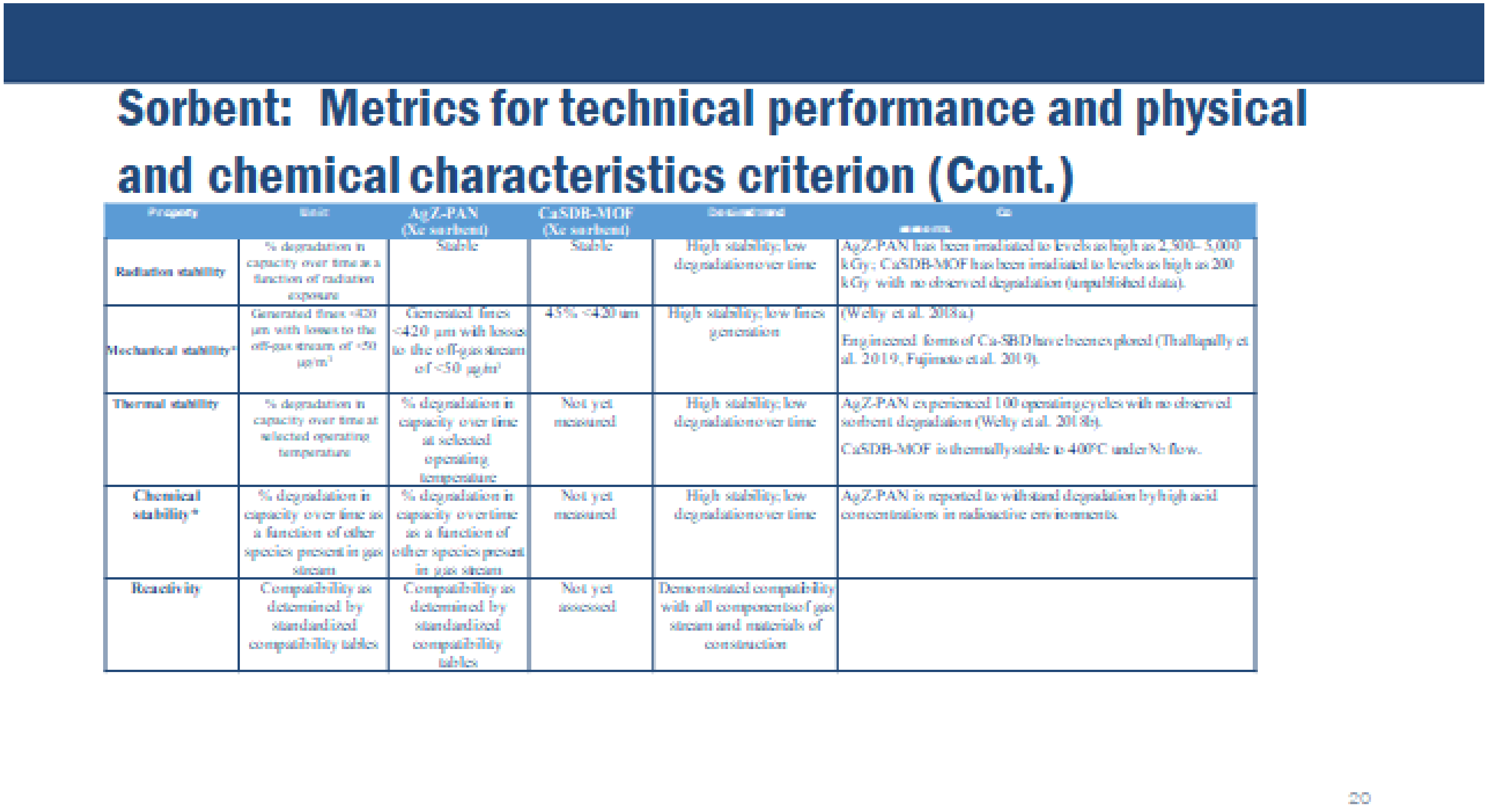
Waste Form: Metrics for cost criterion

Property	Unit	Desired trend	Comments
[illegible]			
Cost of materials	$/kg	Low	Cost of consumable materials.
Operating cost	$/Ci	Low	Processing cost less consumables.



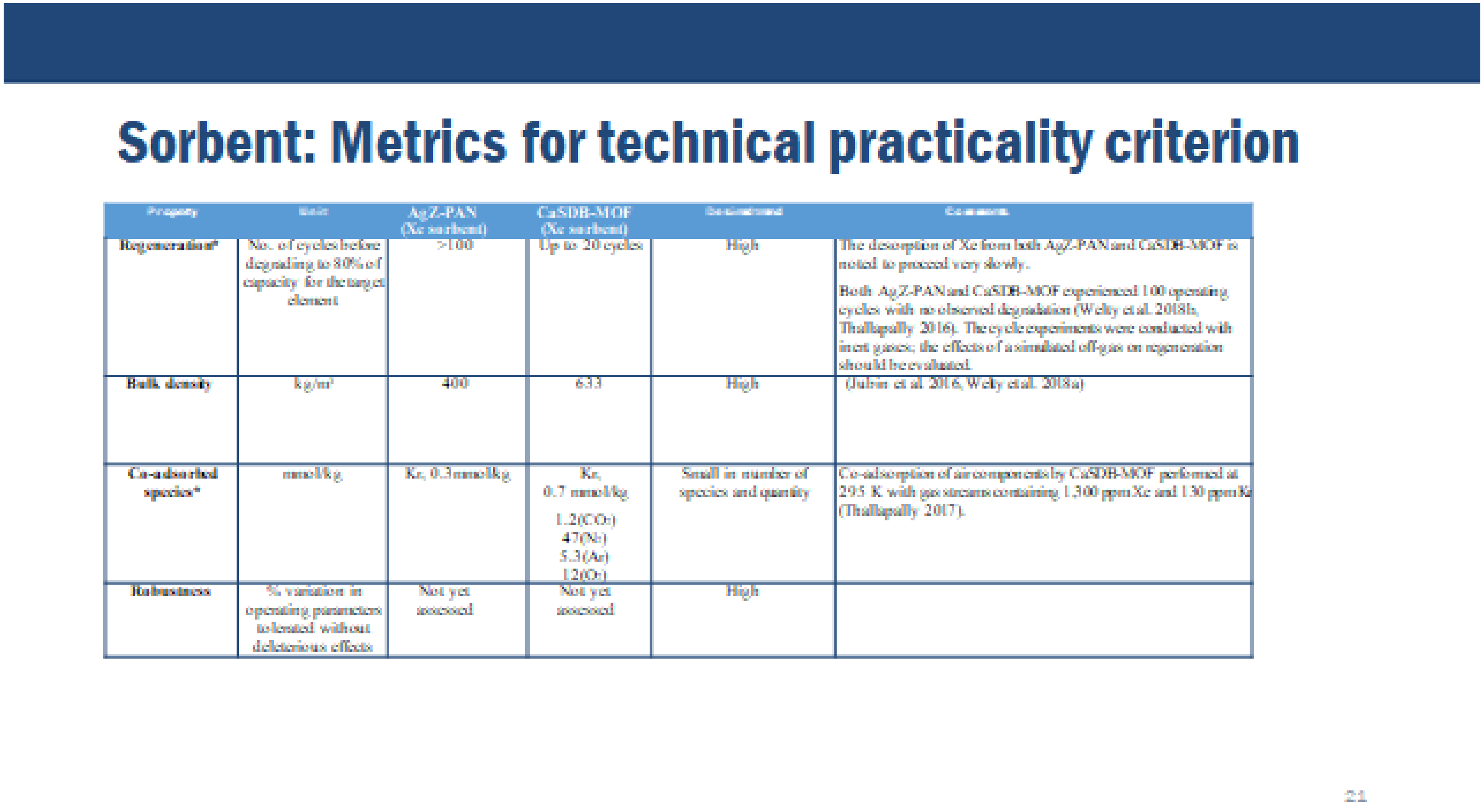
Sorbent: Metrics for technical performance and physical and chemical characteristics criterion

Property	Unit	AgZ-PAN (Xe sorbent)	CaSDB-MOF (Xe sorbent)	Desired trend	Comments
Saturation Capacity*	Mol/m^3	20 mmol/kg [8 mols/m^3] (295 K)	19 mmol/kg [12 mols/m^3] (295 K)	High	Saturation capacity of both sorbents for noble gases is highly temperature dependent and dependent on sorbate concentration and balance gas composition. The effect of silver content on AgZ-PAN performance is unknown. Breakthrough capacity for each sorbent has been identified as a priority knowledge gap and will be lower than saturation capacity. (Greenhalgh et al. 2016, Welty et al. 2018a, Welty et al. 2018b)
Selectivity	$(X_a/Y_a) / (X_b/Y_b)$ (unitless) Where X_a and X_b are mol fractions of species a and b respectively in the adsorbed phase, and Y_a and Y_b are mol fractions of species a and b in the bulk phase.	~35 (295 K) Xe/Kr	16 (295 K) Xe/Kr	High	The selectivities cited here were obtained with gas blends containing 400 ppm Xe, 40 ppm Kr, and balanced with air. (Garn et al. 2015, Greenhalgh et al. 2015, Welty et al. 2018b, Banerjee et al. 2016)
Surface area	m^2/g	250	81	High	(Garn et al. 2016, Welty et al. 2018a)
Specific heat capacity	J/(K·kg) or J/(K·m^3)	Not yet measured	Not yet measured	Application dependent	
Thermal conductivity	W/(m·K)	Not yet measured	Not yet measured	High	



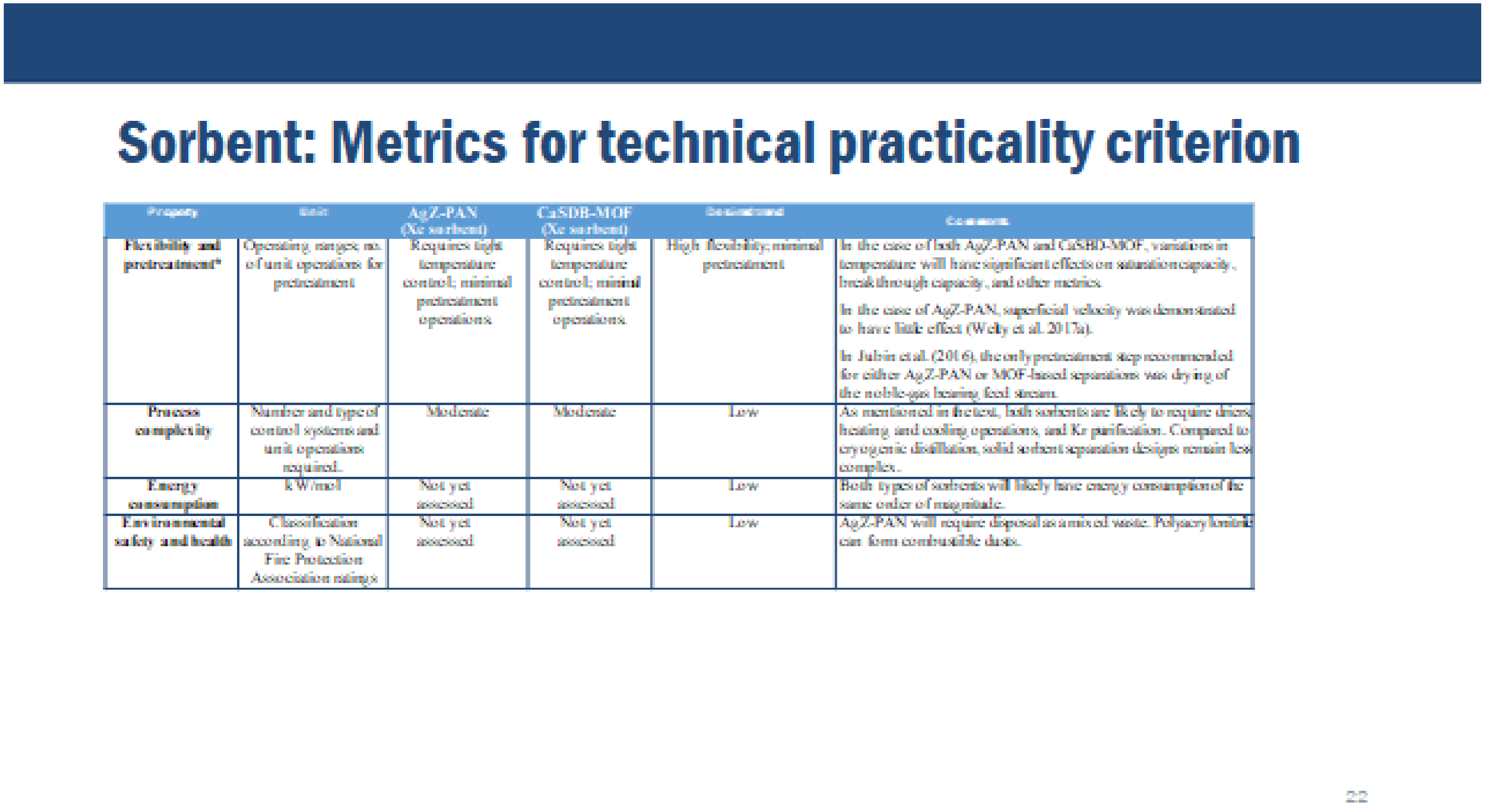
Sorbent: Metrics for technical performance and physical and chemical characteristics criterion (Cont.)

Property	Unit	AgZ-PAN (Xe sorbent)	CaSDB-MOF (Xe sorbent)	Desired trend	Comments
Radiation stability	% degradation in capacity over time as a function of radiation exposure	Stable	Stable	High stability; low degradation over time	AgZ-PAN has been irradiated to levels as high as 2,300– 5,000 kGy; CaSDB-MOF has been irradiated to levels as high as 200 kGy with no observed degradation (unpublished data).
Mechanical stability*	Generated fines <420 μm with losses to the off-gas stream of <50 μg/m^3	Generated fines <420 μm with losses to the off-gas stream of <50 μg/m^3	45% <420 um	High stability; low fines generation	(Welty et al. 2018a.) Engineered forms of Ca-SBD have been explored (Thallapally et al. 2019, Fujimoto et al. 2019).
Thermal stability	% degradation in capacity over time at selected operating temperature	% degradation in capacity over time at selected operating temperature	Not yet measured	High stability; low degradation over time	AgZ-PAN experienced 100 operating cycles with no observed sorbent degradation (Welty et al. 2018b). CaSDB-MOF is thermally stable to 400°C under N_2 flow.
Chemical stability*	% degradation in capacity over time as a function of other species present in gas stream	% degradation in capacity over time as a function of other species present in gas stream	Not yet measured	High stability; low degradation over time	AgZ-PAN is reported to withstand degradation by high acid concentrations in radioactive environments.
Reactivity	Compatibility as determined by standardized compatibility tables	Compatibility as determined by standardized compatibility tables	Not yet assessed	Demonstrated compatibility with all components of gas stream and materials of construction	



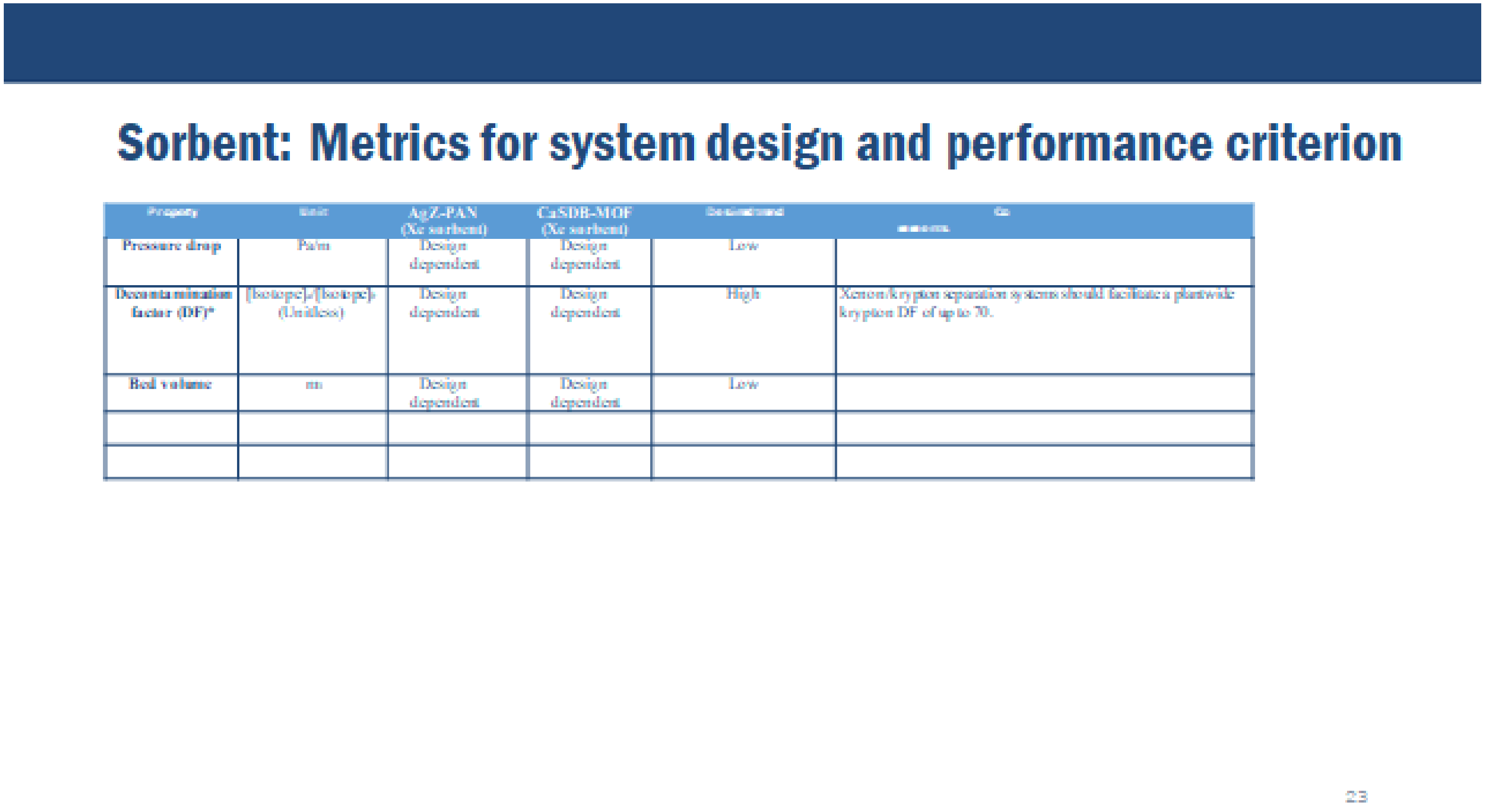
Sorbent: Metrics for technical practicality criterion

Property	Unit	AgZ-PAN (Xe sorbent)	CaSDB-MOF (Xe sorbent)	Desired trend	Comments
Regeneration*	No. of cycles before degrading to 80% of capacity for the target element	>100	Up to 20 cycles	High	The desorption of Xe from both AgZ-PAN and CaSDB-MOF is noted to proceed very slowly. Both AgZ-PAN and CaSDB-MOF experienced 100 operating cycles with no observed degradation (Welty et al. 2018b, Thallapally 2016). The cycle experiments were conducted with inert gases; the effects of a simulated off-gas on regeneration should be evaluated.
Bulk density	kg/m³	400	633	High	(Jubin et al. 2016, Welty et al. 2018a)
Co-adsorbed species*	mmol/kg	Kr, 0.3 mmol/kg	Kr, 0.7 mmol/kg 1.2(CO_2) 47(N_2) 5.3(Ar) 12(O_2)	Small in number of species and quantity	Co-adsorption of air components by CaSDB-MOF performed at 295 K with gas streams containing 1,300 ppm Xe and 130 ppm K (Thallapally 2017).
Robustness	% variation in operating parameters tolerated without deleterious effects	Not yet assessed	Not yet assessed	High	



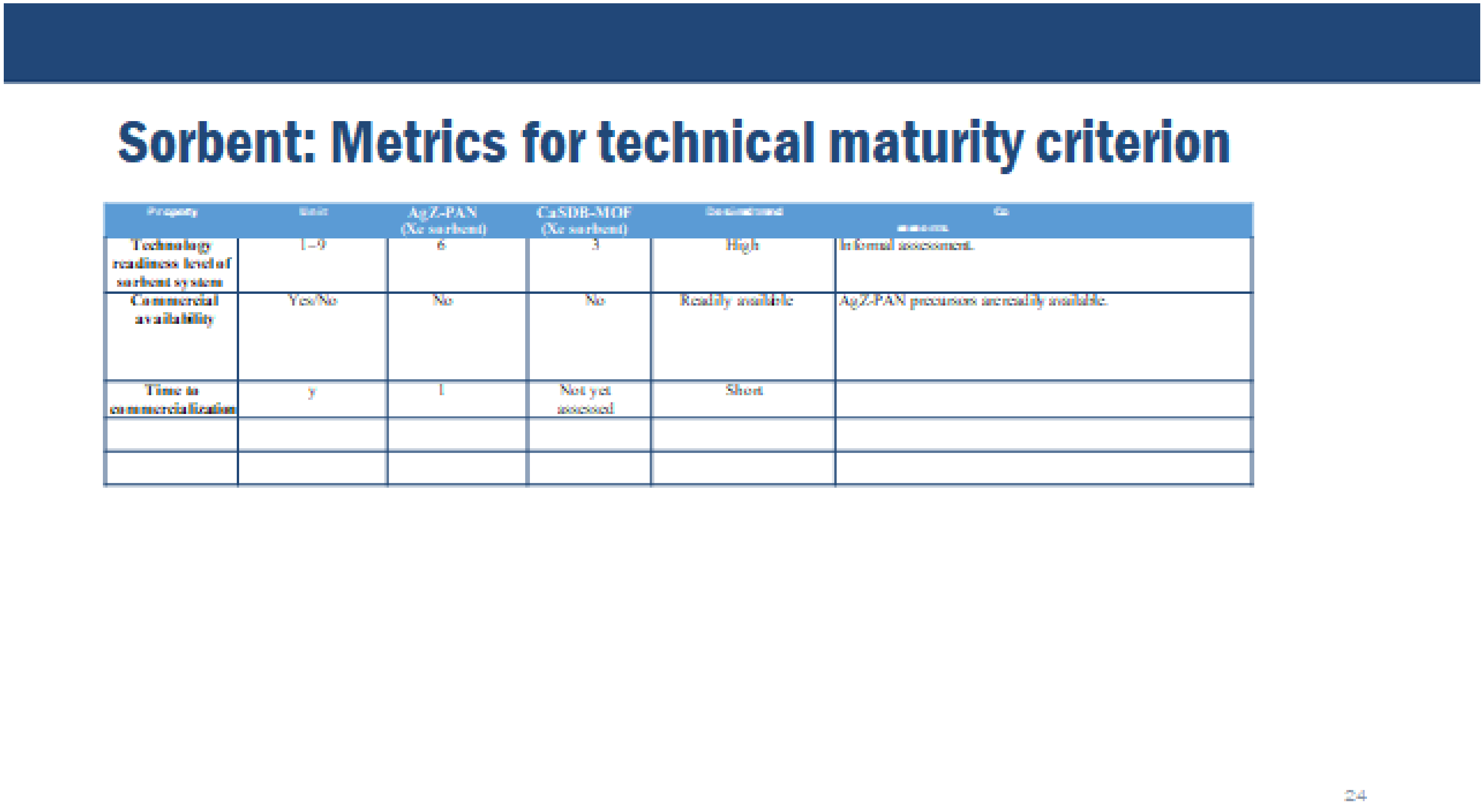
Sorbent: Metrics for technical practicality criterion

Property	Unit	AgZ-PAN (Xe sorbent)	CaSDB-MOF (Xe sorbent)	Desired trend	Comments
Flexibility and pretreatment*	Operating ranges; no. of unit operations for pretreatment	Requires tight temperature control; minimal pretreatment operations.	Requires tight temperature control; minimal pretreatment operations.	High flexibility; minimal pretreatment	In the case of both AgZ-PAN and CaSBD-MOF, variations in temperature will have significant effects on saturation capacity, breakthrough capacity, and other metrics. In the case of AgZ-PAN, superficial velocity was demonstrated to have little effect (Welty et al. 2017a). In Jubin et al. (2016), the only pretreatment step recommended for either AgZ-PAN or MOF-based separations was drying of the noble-gas bearing feed stream.
Process complexity	Number and type of control systems and unit operations required.	Moderate	Moderate	Low	As mentioned in the text, both sorbents are likely to require driers, heating and cooling operations, and Kr purification. Compared to cryogenic distillation, solid sorbent separation designs remain less complex.
Energy consumption	kW/mol	Not yet assessed	Not yet assessed	Low	Both types of sorbents will likely have energy consumption of the same order of magnitude.
Environmental safety and health	Classification according to National Fire Protection Association ratings	Not yet assessed	Not yet assessed	Low	AgZ-PAN will require disposal as a mixed waste. Polyacrylonitrile can form combustible dusts.



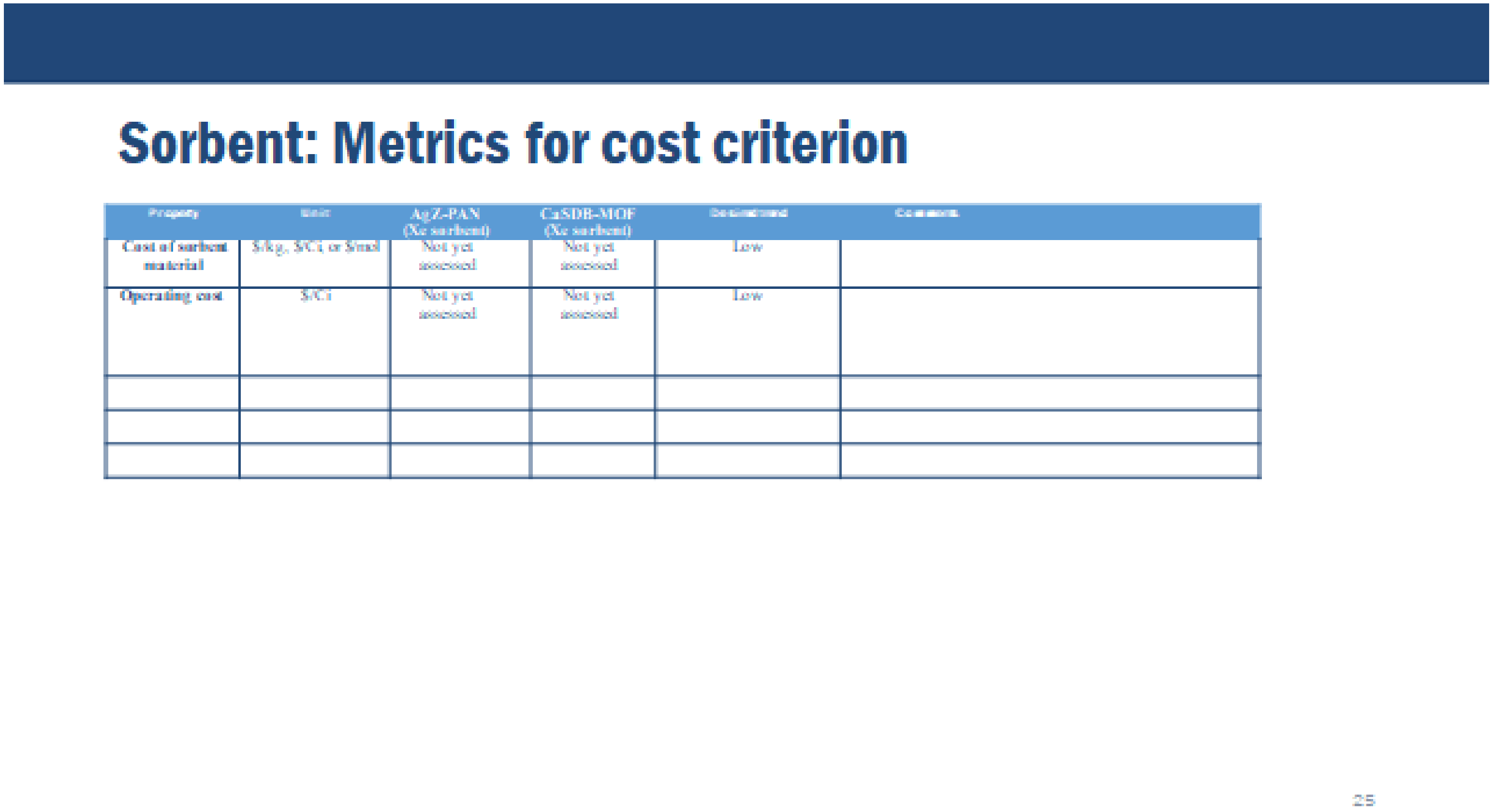
Sorbent: Metrics for system design and performance criterion

Property	Unit	AgZ-PAN (Xe sorbent)	CaSDB-MOF (Xe sorbent)	Desired trend	Comments
Pressure drop	Pa/m	Design dependent	Design dependent	Low	
Decontamination factor (DF)*	[Isotope]$_i$/[Isotope]$_f$ (Unitless)	Design dependent	Design dependent	High	Xenon/krypton separation systems should facilitate a plantwide krypton DF of up to 70.
Bed volume	m	Design dependent	Design dependent	Low	



Sorbent: Metrics for technical maturity criterion

Property	Unit	AgZ-PAN (Xe sorbent)	CaSDB-MOF (Xe sorbent)	Desired trend	Comments
Technology readiness level of sorbent system	1–9	6	3	High	Informal assessment.
Commercial availability	Yes/No	No	No	Readily available	AgZ-PAN precursors are readily available.
Time to commercialization	y	1	Not yet assessed	Short	

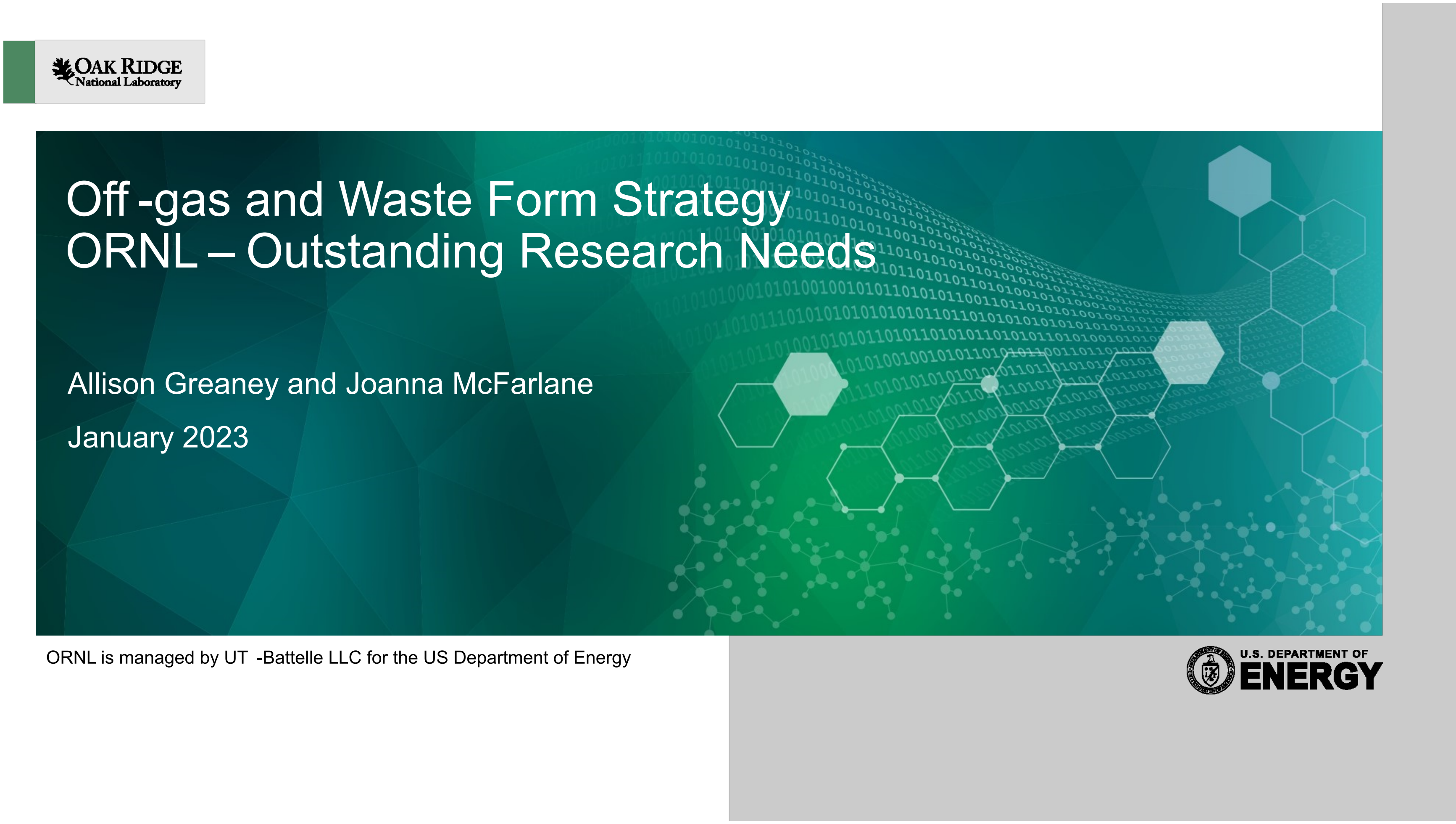


Sorbent: Metrics for cost criterion

Property	Unit	AgZ-PAN (Xe sorbent)	CaSDB-MOF (Xe sorbent)	Desired trend	Comments
Cost of sorbent material	$/kg, $/Ci, or $/mol	Not yet assessed	Not yet assessed	Low	
Operating cost	$/Ci	Not yet assessed	Not yet assessed	Low	

APPENDIX D

WORKSHOP RAPID-FIRE PRESENTATIONS

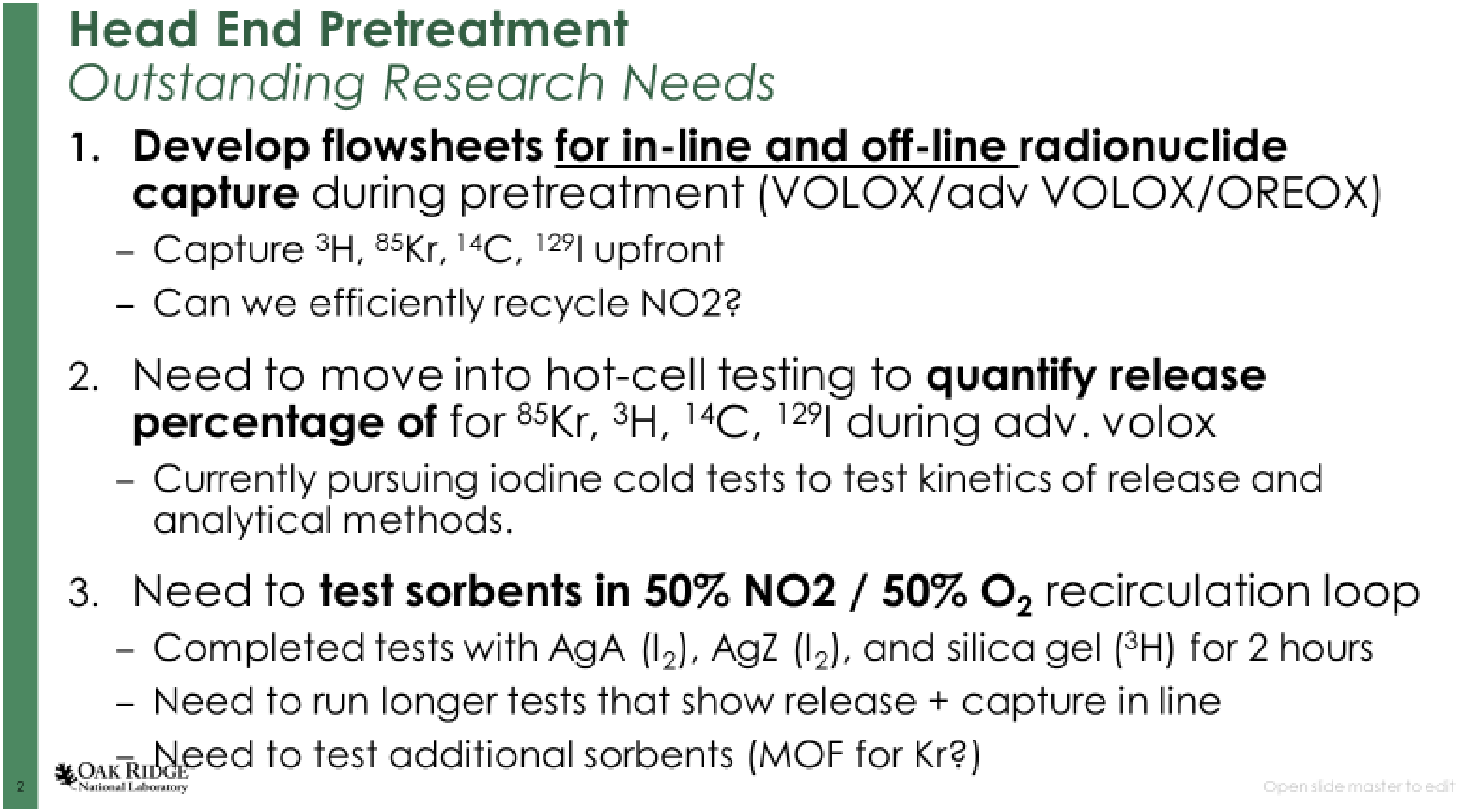


Off-gas and Waste Form Strategy ORNL – Outstanding Research Needs

Allison Greaney and Joanna McFarlane

January 2023

ORNL is managed by UT-Battelle LLC for the US Department of Energy



Head End Pretreatment
Outstanding Research Needs

1. **Develop flowsheets for in-line and off-line radionuclide capture** during pretreatment (VOLOX/adv VOLOX/OREOX)
   - Capture ^{3}H, ^{85}Kr, ^{14}C, ^{129}I upfront
   - Can we efficiently recycle NO2?
2. Need to move into hot-cell testing to **quantify release percentage of** for ^{85}Kr, ^{3}H, ^{14}C, ^{129}I during adv. volox
   - Currently pursuing iodine cold tests to test kinetics of release and analytical methods.
3. Need to **test sorbents in 50% NO2 / 50% O_2** recirculation loop
   - Completed tests with AgA (I_2), AgZ (I_2), and silica gel (^{3}H) for 2 hours
   - Need to run longer tests that show release + capture in line
   - Need to test additional sorbents (MOF for Kr?)

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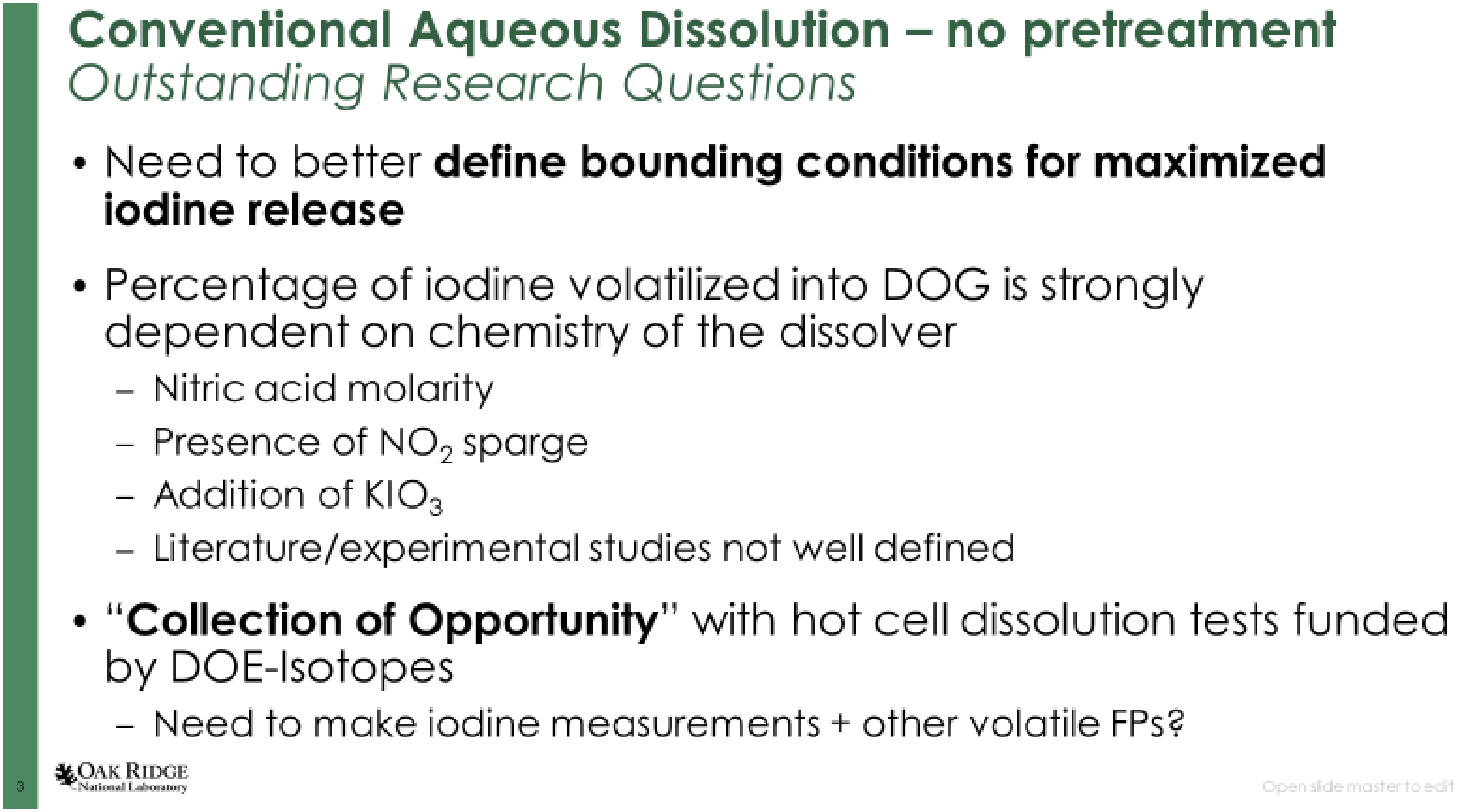
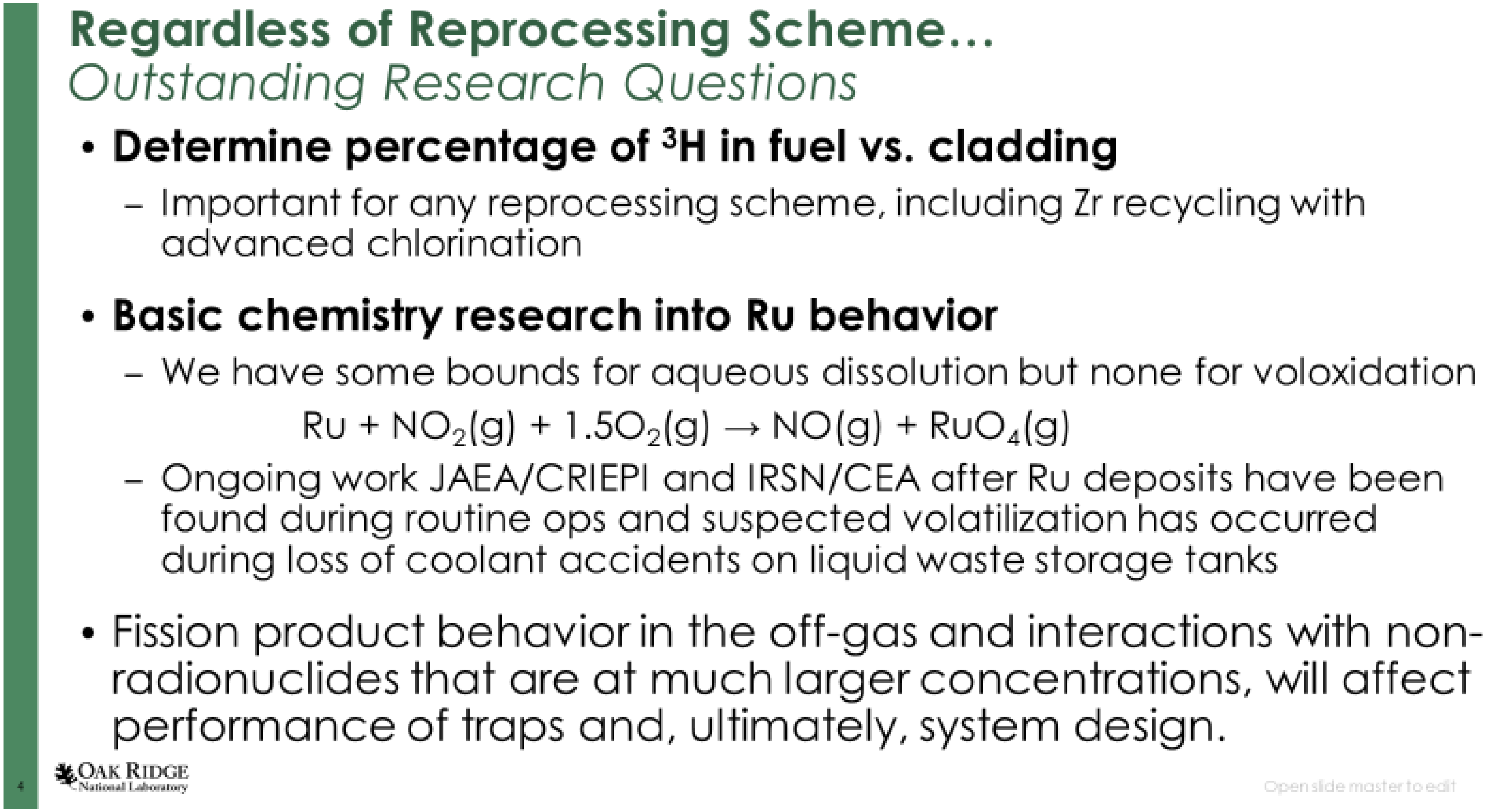


Conventional Aqueous Dissolution – no pretreatment

Outstanding Research Questions

- Need to better **define bounding conditions for maximized iodine release**
- Percentage of iodine volatilized into DOG is strongly dependent on chemistry of the dissolver
  - Nitric acid molarity
  - Presence of NO_2 sparge
  - Addition of KIO_3
  - Literature/experimental studies not well defined
- "**Collection of Opportunity**" with hot cell dissolution tests funded by DOE-Isotopes
  - Need to make iodine measurements + other volatile FPs?



Regardless of Reprocessing Scheme…
Outstanding Research Questions

- **Determine percentage of ^3H in fuel vs. cladding**
  - Important for any reprocessing scheme, including Zr recycling with advanced chlorination
- **Basic chemistry research into Ru behavior**
  - We have some bounds for aqueous dissolution but none for voloxidation

$$Ru + NO_2(g) + 1.5O_2(g) \rightarrow NO(g) + RuO_4(g)$$

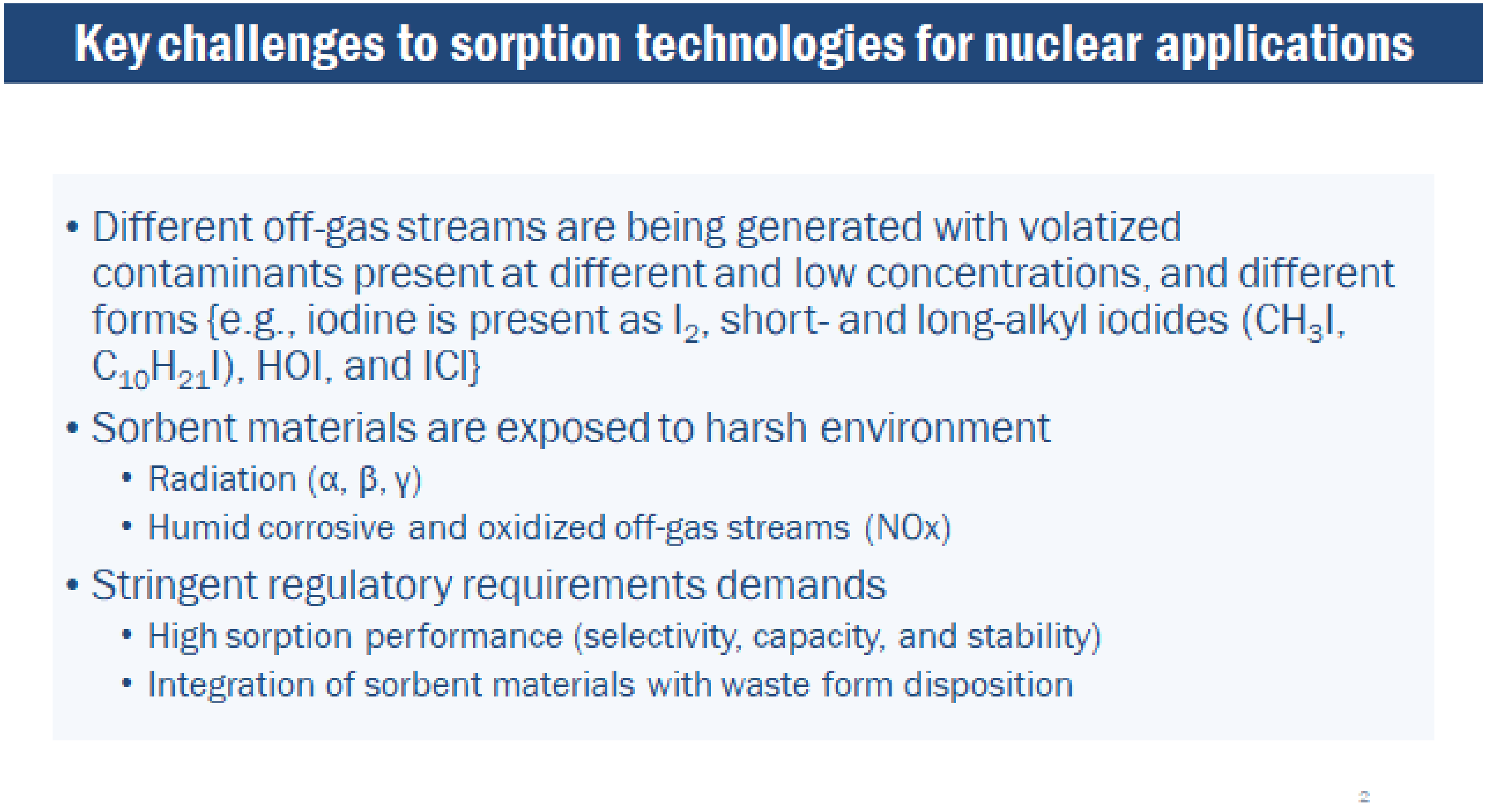
  - Ongoing work JAEA/CRIEPI and IRSN/CEA after Ru deposits have been found during routine ops and suspected volatilization has occurred during loss of coolant accidents on liquid waste storage tanks
- Fission product behavior in the off-gas and interactions with non-radionuclides that are at much larger concentrations, will affect performance of traps and, ultimately, system design.

Sorption Technologies for Nuclear Applications

Josef Matyáš
Pacific Northwest National Laboratory

Off-Gas and Waste Forms Strategy Workshop
Jan 31 –Feb 1, 2023
Washington, D.C.

U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY



Key challenges to sorption technologies for nuclear applications

- Different off-gas streams are being generated with volatized contaminants present at different and low concentrations, and different forms {e.g., iodine is present as I_2, short- and long-alkyl iodides (CH_3I, $C_{10}H_{21}I$), HOI, and ICl}
- Sorbent materials are exposed to harsh environment
  - Radiation (α, β, γ)
  - Humid corrosive and oxidized off-gas streams (NOx)
- Stringent regulatory requirements demands
  - High sorption performance (selectivity, capacity, and stability)
  - Integration of sorbent materials with waste form disposition

Knowledge gaps

- *Material discovery through "Hierarchical Methodology Design"*
  - The focus should be on synthesis and application of multifunctional and sustainable sorbents from natural and engineered materials with high specific surface area, tunable structures, and tailorable surface chemistry
  - Machine learning
- *Development of performance criteria and associated metrics to objectively evaluate sorbent technologies*
- *Development of low-cost and easily employed processes to produce durable waste forms*

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My Thoughts

May 16, 2023

B Riley

U.S. DEPARTMENT OF ENERGY BATTELLE

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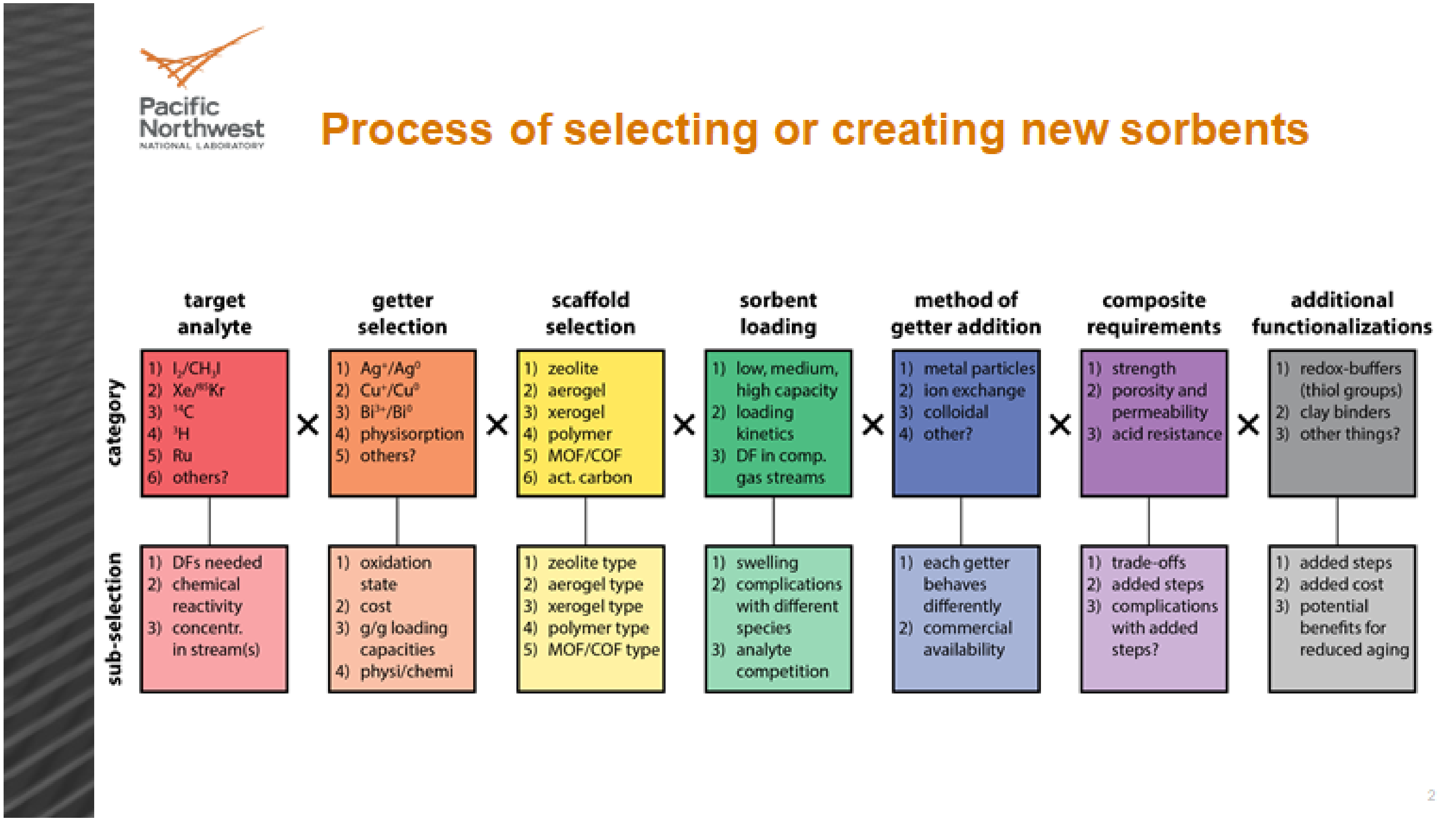

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Process of selecting or creating new sorbents

	target analyte		getter selection		scaffold selection		sorbent loading		method of getter addition		composite requirements		additional functionalizations
category	1) I_2/CH_3I 2) $Xe/^{85}Kr$ 3) ^{14}C 4) ^{3}H 5) Ru 6) others?	×	1) Ag^+/Ag^0 2) Cu^+/Cu^0 3) Bi^{3+}/Bi^0 4) physisorption 5) others?	×	1) zeolite 2) aerogel 3) xerogel 4) polymer 5) MOF/COF 6) act. carbon	×	1) low, medium, high capacity 2) loading kinetics 3) DF in comp. gas streams	×	1) metal particles 2) ion exchange 3) colloidal 4) other?	×	1) strength 2) porosity and permeability 3) acid resistance	×	1) redox-buffers (thiol groups) 2) clay binders 3) other things?
sub-selection	1) DFs needed 2) chemical reactivity 3) concentr. in stream(s)		1) oxidation state 2) cost 3) g/g loading capacities 4) physi/chemi		1) zeolite type 2) aerogel type 3) xerogel type 4) polymer type 5) MOF/COF type		1) swelling 2) complications with different species 3) analyte competition		1) each getter behaves differently 2) commercial availability		1) trade-offs 2) added steps 3) complications with added steps?		1) added steps 2) added cost 3) potential benefits for reduced aging

Recommendations and Data Gaps

Integrated off-gas system

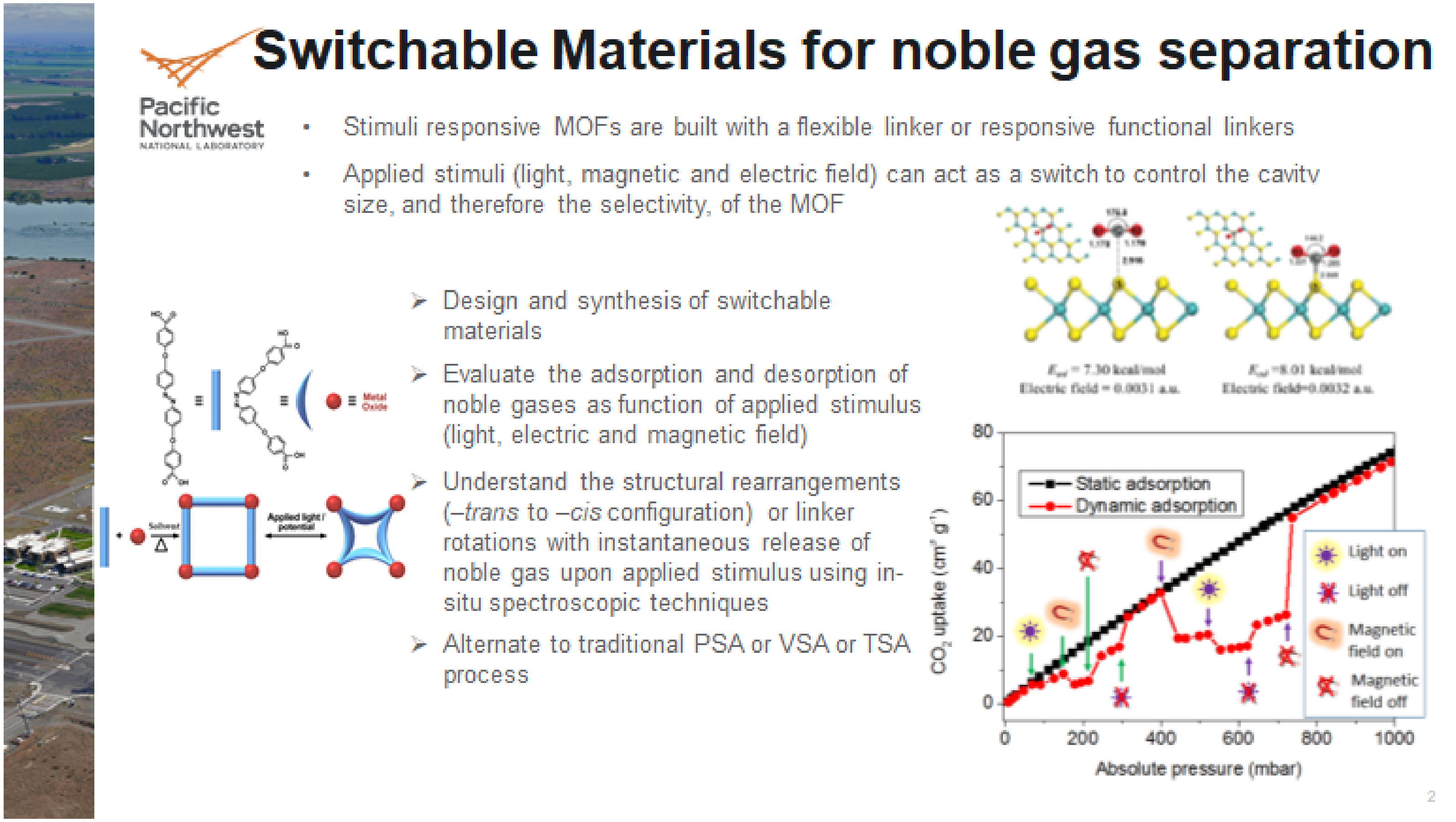
Praveen K. Thallapally

Pacific Northwest National Laboratory
Richland, Washington 99352

INNOVATIVE SEPARATIONS RESEARCH AND DEVELOPMENT NEEDS FOR
Advanced Fuel Cycles

Science-Based Technology Directions for Accelerating Nuclear Fuel Recycle

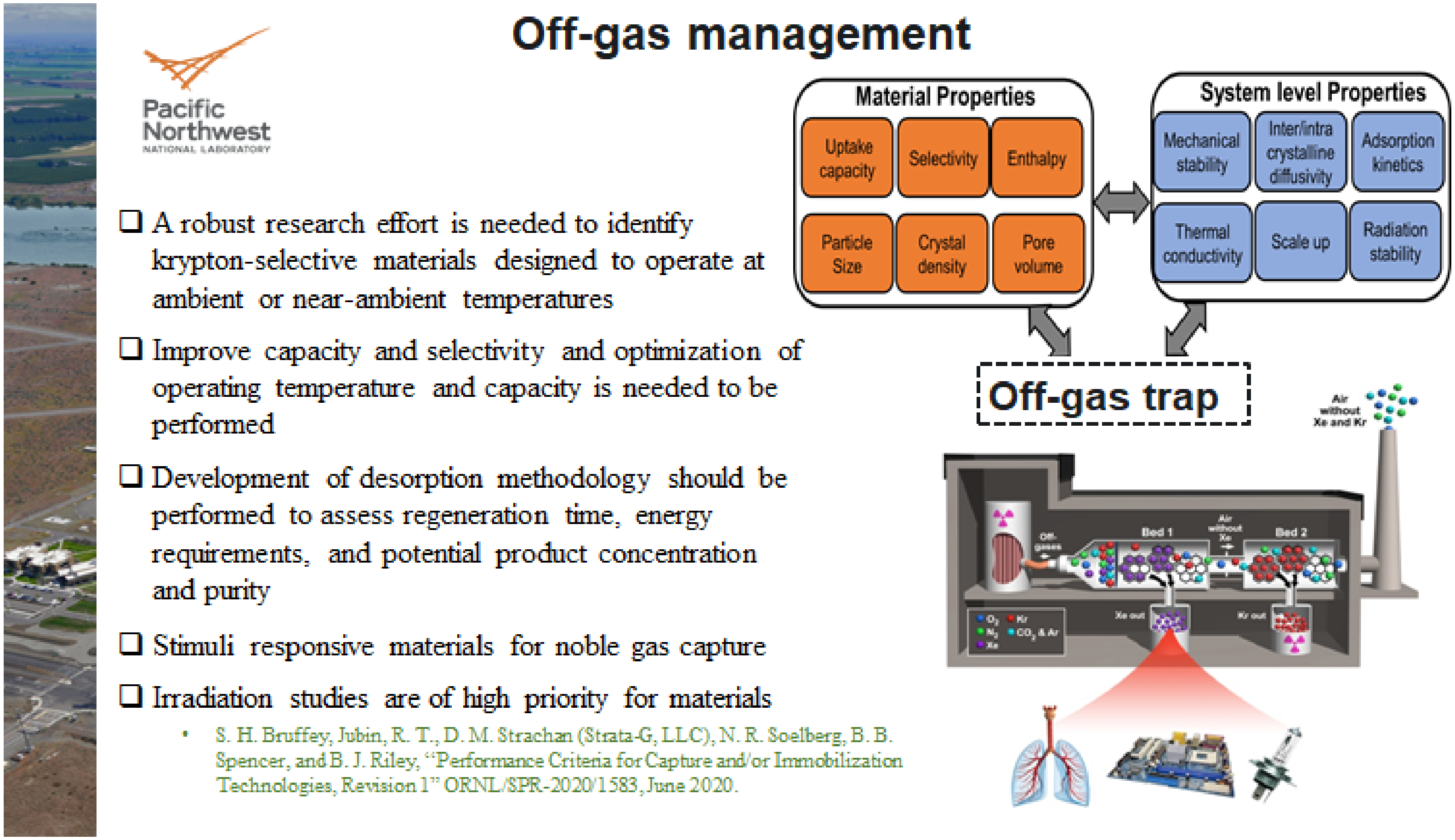
DOE NE Report



Switchable Materials for noble gas separation

- Stimuli responsive MOFs are built with a flexible linker or responsive functional linkers
- Applied stimuli (light, magnetic and electric field) can act as a switch to control the cavitv size, and therefore the selectivity, of the MOF

- ➢ Design and synthesis of switchable materials
- ➢ Evaluate the adsorption and desorption of noble gases as function of applied stimulus (light, electric and magnetic field)
- ➢ Understand the structural rearrangements (–*trans* to –*cis* configuration) or linker rotations with instantaneous release of noble gas upon applied stimulus using in-situ spectroscopic techniques
- ➢ Alternate to traditional PSA or VSA or TSA process



Off-gas management

- ❑ A robust research effort is needed to identify krypton-selective materials designed to operate at ambient or near-ambient temperatures
- ❑ Improve capacity and selectivity and optimization of operating temperature and capacity is needed to be performed
- ❑ Development of desorption methodology should be performed to assess regeneration time, energy requirements, and potential product concentration and purity
- ❑ Stimuli responsive materials for noble gas capture
- ❑ Irradiation studies are of high priority for materials
    - S. H. Bruffey, Jubin, R. T., D. M. Strachan (Strata-G, LLC), N. R. Soelberg, B. B. Spencer, and B. J. Riley, "Performance Criteria for Capture and/or Immobilization Technologies, Revision 1" ORNL/SPR-2020/1583, June 2020.

Material Properties

Uptake capacity
Selectivity
Enthalpy
Particle Size
Crystal density
Pore volume

System level Properties

Mechanical stability
Inter/intra crystalline diffusivity
Adsorption kinetics
Thermal conductivity
Scale up
Radiation stability

Off-gas trap

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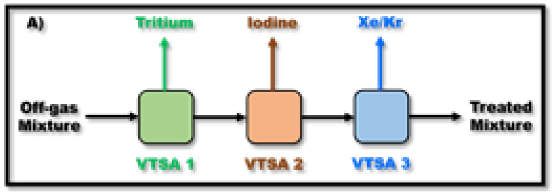
Instrumentation

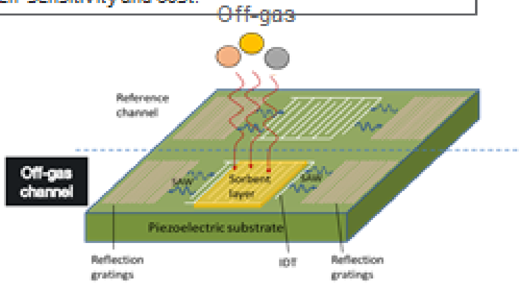
- ☐ Lack of advanced instrumentation to detect gases at low concentrations
- ☐ Integrated off-gas system to demonstrate the off-gas management
- ☐ Sensors



Surface Acoustic Wave Sensor for Noble Gas Detection

Technology Summary

- PNNL design, demonstrate, and prepare metal-organic framework (MOF) based SAW sensor for noble gas detection and monitoring. A selective MOF sensor film is deposited on a surface acoustic wave (SAW) active substrate to form the sensor. The SAW sensor's principle of operation involves monitoring the frequency shift of the surface acoustic waves on a piezoelectric substrate due to the increased mass or stress loading after noble gas molecules attach to a MOF sensor film bonded to the substrate. SAW sensors are selected because they offer a good balance between sensitivity and cost.



Highly selective, sensitivity SAW senor coated with a selective MOF thin film for noble gas detection and monitoring.

Technology Impact

The ability to develop fast and reliable sensor is an important new direction in advanced reactor program with the goal of overcoming short falls of current sensor technologies such as reliability, fast and cost. The information obtained from this project will not only provide a next generation of SAW sensors that are durable, stable and reliable. These sensors could play a major role in other applications such as methane sensing, humidity sensing, CO_2 sensing and so on.

1. Banerjee *et. al.*, Surface acoustic wave sensors for leak detection" *USPTO WO2021/041359 A1*

Overarching Ideas from Amy Welty:

1. Criteria:
    a. No-go criteria – couple with revisiting sorbent performance criteria
    b. Efficient information/data sharing
    c. Failure sharing!!!
    d. Create a healthy balance of research ranging from the outlandish notion to the applied pilot scale
2. Fundamental:
    a. Sorbent development for multi-component capture
    b. Sorbent development for singular selectivity
3. Applied:
    a. Leveraging existing test beds – at INL alone, we have Moran, MRPP, Beartooth, Pyro, and others. Utilize each other’s strengths
    b. Design and build a modular, coupled, mobile testbed

APPENDIX E

TECHNOLOGY READINESS LEVEL TABLES

Table E-1. Technology Readiness Levels (from Table 1 of DOE 2015).

Relative Level of Technology Development	Technology Readiness Level	TRL Definition	Description
System Operations	**TRL 9**	Actual system operated over the full range of expected mission conditions.	The technology is in its final form and operated under the full range of operating mission conditions. Examples include using the actual system with the full range of wastes in hot operations.
System Commissioning	**TRL 8**	Actual system completed and qualified through test and demonstration.	The technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental testing and evaluation of the system with actual waste in hot commissioning. Supporting information includes operational procedures that are virtually complete. An Operational Readiness Review (ORR) has been successfully completed prior to the start of hot testing.
	TRL 7	Full-scale, similar (prototypical) system demonstrated in relevant environment	This represents a major step up from TRL 6, requiring demonstration of an actual system prototype in a relevant environment. Examples include testing full-scale prototype in the field with a range of simulants in cold commissioning[1]. Supporting information includes results from the full-scale testing and analysis of the differences between the test environment, and analysis of what the experimental results mean for the eventual operating system/environment. Final design is virtually complete.
Technology Demonstration	**TRL 6**	Engineering/pilot-scale, similar (prototypical) system validation in relevant environment	Engineering-scale models or prototypes are tested in a relevant environment. This represents a major step up in a technology's demonstrated readiness. Examples include testing an engineering scale prototypical system with a range of simulants.[1] Supporting information includes results from the engineering scale testing and analysis of the differences between the engineering scale, prototypical system/environment, and analysis of what the experimental results mean for the eventual operating system/environment. TRL 6 begins true engineering development of the technology as an operational system. The major difference between TRL 5 and 6 is the step up from laboratory scale to engineering scale and the determination of scaling factors that will enable design of the operating system. The prototype should be capable of performing all the functions that will be required of the operational system. The operating environment for the testing should closely represent the actual operating environment.
Technology Development	**TRL 5**	Laboratory scale, similar system validation in relevant environment	The basic technological components are integrated so that the system configuration is similar to (matches) the final application in almost all respects. Examples include testing a high-fidelity, laboratory scale system in a simulated environment with a range of simulants[1] and actual waste[2]. Supporting information includes results from the laboratory scale testing, analysis of the differences between the laboratory and eventual operating system/ environment, and analysis of what the experimental results mean for the eventual operating system/environment. The major difference between TRL 4 and 5 is the increase in the fidelity of the system and environment to the actual application. The system tested is almost prototypical.

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

[1] Simulants should match relevant chemical and physical properties.

[2] Testing with as wide a range of actual waste as practicable and consistent with waste availability, safety, ALARA, cost and project risk is highly desirable.

Table E-2. DOE Technology Readiness Levels (from Table 4 of DOE 2015).

Relative Level of Technology Development	Technology Readiness Level	TRL Definition	Description
System Operations	TRL 9	Actual system operated over the full range of expected conditions.	Actual operation of the technology in its final form, under the full range of operating conditions. Examples include using the actual system with the full range of wastes.
System Commissioning	TRL 8	Actual system completed and qualified through test and demonstration.	Technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental testing and evaluation of the system with real waste in hot commissioning.
	TRL 7	Full-scale, similar (prototypical) system demonstrated in a relevant environment.	Prototype full-scale system. Represents a major step up from TRL 6, requiring demonstration of an actual system prototype in a relevant environment. Examples include testing the prototype in the field with a range of simulants and/or real waste and cold commissioning.
Technology Demonstration	TRL 6	Engineering/pilot-scale, similar (prototypical) system demonstrated in a relevant environment.	Representative engineering scale model or prototype system, which is well beyond the lab scale tested for TRL 5, is tested in a relevant environment. Represents a major step up in a technology's demonstrated readiness. Examples include testing a prototype with real waste and a range of simulants.
Technology Development	TRL 5	Laboratory scale, similar system validation in relevant environment.	The basic technological components are integrated so that the system configuration is similar to (matches) the final application in almost all respects. Examples include testing a high-fidelity system in a simulated environment and/or with a range of real waste and simulants.
	TRL 4	Component and/or system validation in laboratory environment.	Basic technological components are integrated to establish that the pieces will work together. This is relatively "low fidelity" compared with the eventual system. Examples include integration of "ad hoc" hardware in a laboratory and testing with a range of simulants.
Research to Prove Feasibility	TRL 3	Analytical and experimental critical function and/or characteristic proof of concept.	Active research and development is initiated. This includes analytical studies and laboratory scale studies to physically validate the analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representative. Components may be tested with simulants.
Basic Technology Research	TRL 2	Technology concept and/or application formulated.	Invention begins. Once basic principles are observed, practical applications can be invented. Applications are speculative, and there may be no proof or detailed analysis to support the assumptions. Examples are still limited to analytic studies.
	TRL 1	Basic principles observed and reported.	Lowest level of technology readiness. Scientific research begins to be translated into applied research and development (R&D). Examples might include paper studies of a technology's basic properties.