Assessments and Options for Removal and Immobilization of Volatile Radionuclides from the Processing of Used Nuclear Fuel

Fuel Cycle Research & Development

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Material Recovery and Waste Form Development Campaign

RT Jubin (ORNL) and DM Strachan (Strata-G) (Principal Authors) and Authors from ORNL, PNNL, INL, and SNL

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SUMMARY

Nuclear fuel reprocessing is being considered in the US as part of an effort to help meet the nation's energy needs. Various options are available to meet these needs (DOE 2010). The recent Fuel Options Study indicated that fuel cycles that utilize continuous recycling are among the "most promising" (Wigeland et al. 2014). After the valuable components have been extracted from the irradiated UO_2 during reprocessing, the remaining waste must be immobilized and sent to a repository. Some of the radionuclides in the fuel are short-lived isotopes that decay to innocuous levels soon after reactor discharge, e.g., ^{127}Xe ($t_{1/2}$ = 36.4 d). However, the preponderance of radionuclides requires long-term, geological storage. In this report, we assess options for capturing and immobilizing radionuclides expected to volatilize during aqueous reprocessing of used nuclear fuel. This document is an update to a previous report prepared in 2011 that was only released as a draft (FCR&D-SWF-2011-000305).

Several radionuclides that require intermediate- to long-term storage become volatile during the processing of the fuel. These include ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I. These radionuclides are released into the gas streams associated with processing the nuclear fuel and are particularly difficult to remove because of their chemical state and very low concentrations.

The SCALE code version 6.0 (ORNL 2009) was used to calculate the masses and activities of these volatile radionuclides in representative used commercial light water reactor (LWR) fuels that could be reprocessed for recycling. Two levels of fuel burnup, 30 GWd/tIHM (gigawatt-days per metric ton initial heavy metal) and 60 GWd/tIHM with 5- and 30-year cooling periods (time out of reactor) were selected as reference cases for the these SCALE calculations.

A number of the capture methods are reviewed in this study. Although many appear promising, significant research and development remains to be completed to advance them from the laboratory or bench scale to a level suitable for use in commercial facilities. Likewise, significant development and performance testing is needed for waste forms, particularly for iodine.

Waste volumes for each of the four primary volatile radionuclides (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I) were estimated. Included in these estimates were the nonradioactive isotopes and "tramp" elements found in air (e.g., Kr and Xe) and process chemicals (e.g., I and Cl) that would be present in the resulting waste form. The resulting waste volume for iodine was found to be highly dependent on the final waste form selected and increased by a factor of 2 to 4 by tramp halogens that were released into the off-gas stream from the process chemicals. The volume of tritiated water from the fuel was quite small but was increased by a factor of 4 to 7 by the air in-leakage to the head-end even at very low humidity (-60 °C dew point). The deliberate addition of water to the ^{3}H pretreatment off-gas has been suggested as a possible requirement to ensure the recovery of the tritiated water. However, this increased the waste volume by another factor of 10. The Kr waste volume was calculated assuming pure Kr, i.e., complete separation from the Xe and Ar. If Xe separation was not performed, the Kr and Xe waste volume increased by factor of ~10. Argon from the air, if not removed, increased the Kr waste volume by a factor of 425. The volume of carbon waste was dominated by the CO_2 from the air in-leakage from the processing cell.

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CONTENTS

FIGURES

TABLES

ACRONYMS AND ABBREVIATIONS

3AMS	Type 3A molecular sieve adsorbent
AgX	Silver faujasite
AgZ	Silver mordenite or zeolite
ANL	Argonne National Laboratory
CANDU	Canada Deuterium-Uranium (a Canadian design nuclear reactor)
CEA	Commissariat à l'énergie atomique et aux énergies alternatives
CETE	Coupled End-to-End
COG	Cell off-gas
DF	Decontamination factor
DOE	US Department of Energy
DOG	Dissolver off-gas
EPA	US Environmental Protection Agency
FRP	Fuel reprocessing plant
GCM	Glass composite material
GNEP	Global Nuclear Energy Partnership or Program
GWd/t	Gigawatt-days per tonne
GWd/tIHM	Gigawatt-days per tonne initial heavy metal
HIP	Hot isostatic press
HLLW	High level liquid waste
HTO	Hydrogen-tritium oxide (tritiated water)
HUP	Hot uniaxial press
HZ	Hydrogen mordenite or zeolite
IODOX	Iodine oxidation process
KfK	Kernforschungszentrum Karlsruhe
L/t	Liters per tonne
Mercurex	Mercury extraction (a process for extracting iodine)
MOF	Metal organic framework

MPa	Megapascal
MW	Megawatt
MWd	Megawatt-day
MWd/t	Megawatt-day per tonne
Nm^3/h	"Normal" cubic metres per hour ("Normal" refers to the volume of gas measured at 25 °C as compared with standard temperature and pressure)
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
Pa	Pascals
PAN	polyacrylonitrile
PNC	Power Reactor and Nuclear Fuel Development Corporation
PNNL	Pacific Northwest National Laboratory
SCK·CEN	Studiecentrum voor Kernenergie Centre d'Etude de l'Energie Nucleaire
SNL	Sandia National Laboratories
t	Metric tons, aka tonne; 1000 kg
t(U)/y	tonne(uranium) per year
t/y	tonne per year
TBq/y	Terrabecquerel per year
TGA	Thermal gravimetric analysis
tHM/y	tonne heavy metal per year
TPT	Tritium pretreatment
TPTOG	Tritium pretreatment off-gas
TRISO	tri-structural-isotropic
UK	United Kingdom
UNF	Used nuclear fuel
VOG	Vessel off-gas
W	Watts
W/Ci	Watts per curie
WOG	Waste systems off-gas

SEPARATIONS AND WASTE FORMS CAMPAIGN / OFF-GAS SIGMA TEAM

ASSESSMENTS AND OPTIONS FOR REMOVAL AND IMMOBILIZATION OF VOLATILE RADIONUCLIDES FROM THE PROCESSING OF USED NUCLEAR FUEL

1. INTRODUCTION

Nuclear fuel reprocessing is being considered in the US as part of an effort to help meet the nation's energy needs. Various options are available to meet these needs (DOE 2010). The recent Fuel Options Study indicated that fuel cycles that utilize continuous recycling are among the "most promising" (Wigeland et al. 2014). After the valuable components have been extracted from the irradiated UO_2 during reprocessing, the remaining waste must be immobilized and sent to a repository. Some of the radionuclides in the fuel are short-lived isotopes that decay to innocuous levels soon after reactor discharge, e.g., ^{127}Xe ($t_{1/2}$ = 36.4 d). However, the preponderance of radionuclides requires long-term, geological storage. In this report, we assess options for capturing and immobilizing radionuclides expected to volatilize during aqueous reprocessing of used nuclear fuel (UNF). This document is an update to a previous report prepared in 2011 that was only released as a draft (FCR&D-SWF-2011-000305).

Several radionuclides that require intermediate- to long-term storage become volatile during the processing of the fuel. These include ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I. These radionuclides are released into the gas streams associated with reprocessing the nuclear fuel and are particularly difficult to remove because of their chemical state and very low concentrations.

1.1 Purpose

The processing or treatment of UNF will result in the release of a number of volatile and semivolatile species. Under current US regulations, ^{129}I and ^{14}C, if captured, must be sequestered essentially indefinitely (EPA 2010a) because of their long half-lives, but ^{3}H and ^{85}Kr, if captured, can potentially be managed in decay storage because of their relatively short half-lives. Currently, ^{14}C and ^{3}H releases are not regulated to specific curie levels by 40 CFR 190 (EPA 2010b). Over the past two to three decades, a number of capture and immobilization technologies for these four elements have been developed to various stages of maturity. Each of the technologies results in different storage densities (mass of target radionuclide per cubic meter of storage space) for the target radionuclide because of the bulk density of the waste form and radionuclide content. The waste volumes are significantly influenced by the radioactive gas capture technology because that technology ultimately affects the content of the target radionuclide in the waste form. The effect that the process used to remove the target radionuclide has on the volume of waste is often overlooked. The analyses performed in this study provide an initial look at waste volumes resulting from off-gas treatment.

1.2 Need

In 2011 the Off-Gas Sigma Team[a] was asked to perform an evaluation of the amounts (volumes and masses) of potential waste forms for volatile radionuclides along with estimates of radionuclide inventories in these waste forms. This study supported systems engineering studies being performed by several groups supported by DOE as part of the consideration of nuclear fuel reprocessing. Special attention was placed on the order of separations processes (e.g., I before or after ^{3}H) and the options for Kr and CO_2 removal and/or release. The technical problems relevant to the capture and immobilization of the volatile radionuclides were also evaluated. This document is an update to the previous report prepared in 2011, which was only released as a draft (FCR&D-SWF-2011-000305).

1.3 Scope

The scope of this study is to provide an initial estimate of the volumes and masses of the materials needed to remove ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I from fuel reprocessing off-gas and to estimate the volumes and types of secondary wastes associated with these technologies. This study was performed early in the development of some removal and immobilization technologies, and therefore, the estimates of the volumes and masses are very preliminary and may change as more information becomes available.

1.4 Assumptions and Caveats

Calculations with the ORIGEN code (Croff 1983) were used to quantify the mass and activity of the radionuclides expected in the off-gas streams from reprocessing. Two levels of fuel burnup, 30 GWd/tIHM and 60 GWd/tIHM with 5- and 30-year cooling periods, were selected as reference cases for the these calculations. Calculations were performed with the SCALE code version 6.0 (ORNL 2009) for the following irradiations:

Case 1: Burnup = 30 GWd/tIHM; Power = 35.00 MW; Flux= 4.88×10^{17} neutrons/($m^2 \cdot s$)
Case 2: Burnup = 60 GWd/tIHM; Power = 35.00 MW; Flux= 3.54×10^{17} neutrons/($m^2 \cdot s$)

Volatile gas emissions from a nuclear fuel reprocessing facility are addressed in several regulatory documents. The US Environmental Protection Agency (EPA) has established annual dose limits resulting from nuclear fuel cycle facilities in the commercial sector through 40 CFR 190 (EPA 2010b). The dose limits for specific organs and for the whole body are provided in 40 CFR 190.10. Specific release limits for ^{85}Kr, ^{129}I, and ^{239}Pu in terms of curies released per unit of power produced are also defined in 40 CFR 190 (EPA 2010b). The dose limits for both workers and individual members of the public are provided in 10 CFR 20 (NRC 2011). Table 1 summarizes regulatory ambient air and water concentration limits, emission limits specific to ^{85}Kr and ^{129}I, and dose limits that apply to all four of the volatile radionuclides. Table 2 summarizes the required decontamination factors (DFs) for ^{85}Kr and ^{129}I to meet the curie release limits specified in 40 CFR 190. The release limits and required DFs to meet these regulations are shown in Tables 1 and 2.

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[a] The Off-Gas Sigma Team is composed of scientists from the DOE National Laboratories, Argonne National Laboratory (ANL), Idaho National Laboratory (INL), Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratories (SNL).

Comparison of the data in Table 2 clearly shows the relatively small impact of burnup on the required DFs for both ^{85}Kr and ^{129}I based on release per GW(e), because as burnup increases, so does the power generated, and the amounts of ^{129}I and ^{85}Kr generated in the fuel are roughly proportional to the power generated. It should be noted that the DF values in Table 2 contain no engineering allowance or safety margin.

The Off-gas Sigma team examined the impacts of fuel age on the DF requirements for the four radionuclides of interest (Jubin et al. 2012a). The impact of the relatively short half-life of ^{85}Kr and the length of time the fuel is cooled after reactor discharge prior to processing on the required DFs relative to this regulation can be seen in Table 2. Note that while the mathematics of calculating DF values for ^{85}Kr in UNF cooled 30 years results in values less than 1, this simply implies that the curie content is such that controls may not be needed based solely on the EPA requirement and no engineering and safety margins.

Depending on the age of the fuel, the required DFs are such that the capture of a significant fraction of ^{3}H, ^{85}Kr, and ^{129}I is required, and in some cases, ^{14}C capture is also required. For purposes of this report, it is assumed that near complete capture of each of the volatile radionuclides is required, as this results in an upper bounding condition.

Table 1. Key release and exposure limits.

	10 CFR 20			40 CFR 190		40 CFR 61
	Air (Ci/m^3) at site boundary	Water (Ci/m^3)	Dose to member of the public (mrem/y)	Discharge (Ci/GW(e)-y)	Annual dose (mrem)	Effective dose to any member of the public (mrem/y)
^{3}H	1.0 x 10^{-7}	1.0 x 10^{-3}				
^{14}C (as CO$_2$)	3.0 x 10^{-5}	--				
^{85}Kr	7.0 x 10^{-7}	N/A		50,000		
^{129}I	4.0 x 10^{-11}	2.0 x 10^{-7}		0.005		
Whole body			100		25	10
Thyroid					75	
Other organs					25	

Table 2. Decontamination factors (DFs) required to meet 40 CFR 190 (EPA 2010b).

Isotope	Ci/tIHM	Ci/GW(e)-y[1]	Minimum required DFs
Burnup = 30 GWd/tIHM			
^{129}I	0.02497	0.92	184
^{85}Kr (5-yr cooled)	6375	235,000	4.70
^{85}Kr (10-yr cooled)	4614	170,000	3.40
^{85}Kr (30-yr cooled)	1266	47,000	<1.0[2] (No control needed)
Burnup = 60 GWd/tIHM			
^{129}I	0.04866	0.90	179
^{85}Kr (5-yr cooled)	11,590	214,000	4.27
^{85}Kr (10-yr cooled)	8388	155,000	3.09
^{85}Kr (30-yr cooled)	2301	42,000	<1.0[2] (No control needed)

[1] Thermal-to-electric conversion efficiency of 33% was used.

[2] No trapping or abatement required.

2. SOURCE TERMS

2.1 Estimation of Stream Compositions

2.1.1 Volatile Radionuclides in Used Fuel

Calculations with the SCALE code version 6.0 (ORNL 2009) were used to quantify the mass and activity of the radionuclides expected in the off-gas streams for four base cases: 30 GWd/tIHM and 60 GWd/tIHM fuel burnups with 5- and 30-year cooling periods. Tables 3 to 6 summarize the results for the four volatile radionuclides in terms of mass (g/tIHM), activity (ci/tIHM) and power (watt/tIHM or W/tIHM). Additionally, any nonradioactive elements in the off-gas streams whose chemistry was similar to the targeted radionuclides would also be removed. Removal of these “tramp” elements would have an impact on the removal and immobilization processes. For example, Cl^- is a typical trace contaminant of HNO_3. During fuel dissolution, the Cl^- is released to the gas stream as HCl or other Cl species. The chlorides would be removed along with and compete with the iodides in the iodine removal process, reducing the sorption capacity of the sorbent for iodine and would be incorporated into the iodine waste form. Likewise, air contains Ar (0.93 volume %), Kr (1.1×10^{-4} volume %), and Xe (9×10^{-6} volume %). These gases would be removed from air in the cryogenic process that is the current process for the removal of Kr. Even if a more selective, non-cryogenic process is used, the Kr and Xe from air would be removed along with the Kr and Xe from UNF and would be included in the Kr and Xe waste forms. This is discussed in more detail in Section 2.2.

Table 3. Volatile fission and activation product estimates[1] for 30 GWd/tIHM cooled 5 years

Isotopes	g/tIHM	Ci/tIHM	W/tIHM
Krypton			
^{82}Kr	0.4705		
^{83}Kr	37.26		
^{84}Kr	102.4		
^{85}Kr	16.24	6375	9.561
^{86}Kr	161.1		
Kr Total	**317**	**6375**	**9.561**
Xenon			
^{128}Xe	2.261		
^{129}Xe	0.01255		
^{130}Xe	5.481		
^{131}Xe	397.3		
^{132}Xe	991.8		
^{134}Xe	1381		
^{136}Xe	2138		
Xe Total	**4916**		
Carbon			
^{12}C	0.0008224		
^{13}C	9.628		
^{14}C	0.4194	1.870	0.0005448
C Total	**10.05**	**1.870**	**0.0005448**
Iodine			
^{127}I	43.90		
^{129}I	141.4	0.02497	0.00001168
I Total	**185.3**	**0.02497**	**0.00001168**
Tritium			
^{1}H	0.1382		
^{2}H	0.003368		
^{3}H	0.03984	384.5	0.01299
H Total	**0.181**	**384.5**	**0.01299**
Fluorine			
^{19}F	0.0001454		
F Total	**0.0001454**		
Bromine			
^{79}Br	0.00007063		
^{81}Br	18.86		
Br Total	**18.86**		
Helium			
^{3}He	0.01346		
^{4}He	4.735		
He Total	**4.748**		
Neon			
^{21}Ne	0.003608		
Ne Total	**0.003608**		

[1] Values in table have been rounded to the nearest fourth significant figure. Therefore, round-off errors are likely to occur.

Table 4. Volatile fission and activation product estimates[1] for 30 GWd/tIHM cooled 30 years.

Isotopes	g/tIHM	Ci/tIHM	W/tIHM
Krypton			
^{82}Kr	0.4705		
^{83}Kr	37.26		
^{84}Kr	102.4		
^{85}Kr	3.225	1266	1.898
^{86}Kr	161.1		
Kr Total	304.5	1266	**1.898**
Xenon			
^{128}Xe	2.261		
^{129}Xe	0.01271		
^{130}Xe	5.481		
^{131}Xe	397.3		
^{132}Xe	991.8		
^{134}Xe	1381		
^{136}Xe	2138		
Xe Total	4916		
Carbon			
^{12}C	0.0008224		
^{13}C	9.628		
^{14}C	0.4181	1.864	0.0005432
C Total	**10.05**	1.864	**0.0005432**
Iodine			
^{127}I	43.90		
^{129}I	141.4	0.02497	0.00001168
I Total	**185.3**	0.02497	**0.00001168**
Tritium			
^{1}H	0.1382		
^{2}H	0.003368		
^{3}H	0.009769	94.47	0.003186
H Total	**0.152**	**94.47**	**0.003186**
Fluorine			
^{19}F	0.0001454		
F Total	0.0001454		
Bromine			
^{79}Br	0.0003220		
^{81}Br	18.86		
Br Total	**18.86**		
Helium			
^{3}He	0.04346		
^{4}He	5.934		
He Total	**5.98**		
Neon			
^{21}Ne	0.003608		
Ne Total	**0.003608**		

[1] Values in table have been rounded to the nearest fourth significant figure. Therefore, round-off errors are likely to occur.

Table 5. Volatile fission and activation product estimates[1] for 60 GWd/tIHM cooled 5 years.

Isotopes	g/tIHM	Ci/tIHM	W/tIHM
Krypton			
^{82}Kr	1.619		
^{83}Kr	64.77		
^{84}Kr	211.5		
^{85}Kr	29.53	11590	17.38
^{86}Kr	318.6		
Kr Total	626		
Xenon			
^{128}Xe	8.605		
^{129}Xe	0.08011		
^{130}Xe	17.09		
^{131}Xe	626.7		
^{132}Xe	2140		
^{134}Xe	2760		
^{136}Xe	4064		
Xe Total	**9616**		
Carbon			
^{12}C	0.001767		
^{13}C	19.11		
^{14}C	0.643	2.87	8.41×10^{-4}
C Total	**19.75**		
Iodine			
^{127}I	82.49		
^{129}I	275.5	0.04866	2.276×10^{-4}
I Total	**358**		
Tritium			
^{1}H	0.2611		
^{2}H	0.00673		
^{3}H	0.08173	790.3	0.02666
H Total	0.3496		
Fluorine			
^{19}F	0.0002195		
F Total	**0.0002195**		
Bromine			
^{79}Br	0.0001596		
^{81}Br	36.42		
Br Total	**36.42**		
Helium			
^{3}He	0.02788		
^{4}He	11.05		
He Total	11.08		
Neon			
^{21}Ne	0.007086		
Ne Total	**0.007086**		

[1] Values in table have been rounded to the nearest fourth significant figure. Therefore, round-off errors are likely to occur.

Table 6. Volatile fission and activation product estimates[1] for 60 GWd/tIHM cooled 30 years.

Isotopes	**g/tIHM**	**Ci/tIHM**	**W/tIHM**
Krypton			
^{82}Kr	1.619		
^{83}Kr	64.77		
^{84}Kr	211.5		
^{85}Kr	5.863	2301	3.451
^{86}Kr	318.6		
Kr Total	**602.4**	**2301**	**3.451**
Xenon			
^{128}Xe	8.605		
^{129}Xe	0.08041		
^{130}Xe	17.09		
^{131}Xe	626.7		
^{132}Xe	2140		
^{134}Xe	2760		
^{136}Xe	4064		
Xe Total	**9616**		
Carbon			
^{12}C	0.001767		
^{13}C	19.11		
^{14}C	0.6410	2.858	0.000838
C Total	**19.75**	**2.858**	**0.000838**
Iodine			
^{127}I	82.49		
^{129}I	275.5	0.04866	2.276×10^{-4}
I Total	**358.0**	**0.04866**	$\mathbf{2.276 \times 10^{-4}}$
Tritium			
^{1}H	0.2511		
^{2}H	0.00673		
^{3}H	0.02004	193.8	0.006537
H Total	**0.2779**	**193.8**	**0.006537**
Fluorine			
^{19}F	0.0002195		
F Total	**0.0002195**		
Bromine			
^{79}Br	0.0006488		
^{81}Br	36.42		
Br Total	**36.42**		
Helium			
^{3}He	0.08944		
^{4}He	14.84		
He Total	**14.93**		
Neon			
^{21}Ne	0.007086		
Ne Total	**0.007086**		

[1] Values in table have been rounded to the nearest fourth significant figure. Therefore, round-off errors are likely to occur.

2.1.2 Volatile Radionuclides in Reprocessing Facility Off-gas Streams

A generic high-level fuel reprocessing flowsheet is shown in Figure 1. This illustrates the mass distribution of the key components from the processing of 1 metric ton (t) of light-water reactor (LWR) UNF with a burnup of 60 GWd/tIHM and 5 years of cooling. Highlighted by the red circles are the masses and activities (Ci) of the volatile components of interest for off-gas processing.

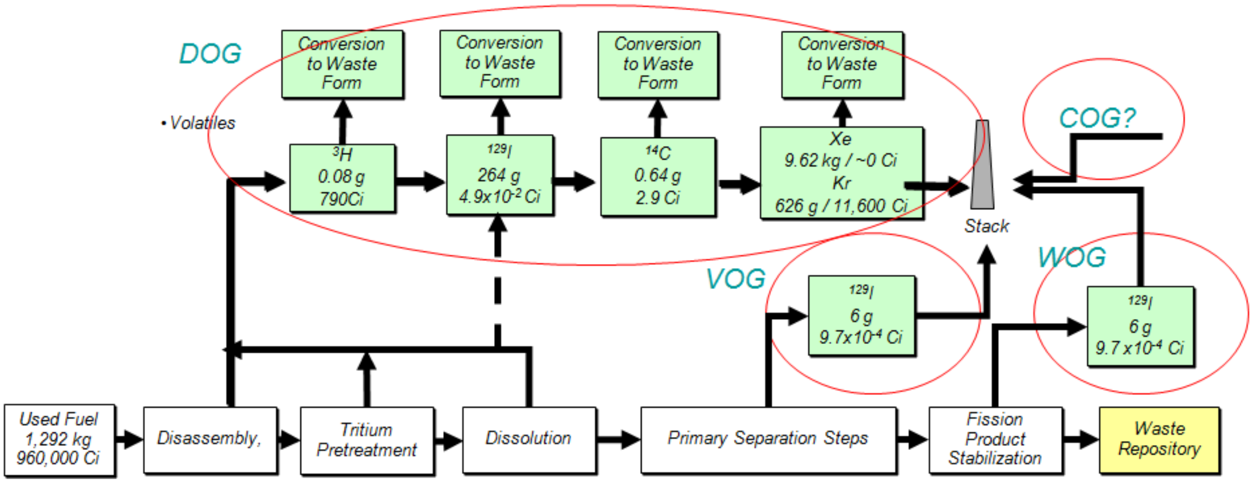

Figure 1. Volatile fission and activation products from the processing 1 t of spent nuclear fuel with a burnup of 60 GWd/tIHM after 5 years of cooling.

Off-gas treatment in a fuel reprocessing facility must address four primary gas streams containing a number of volatile radionuclides. The first stream is the off-gas from the head-end operations that include the shearing of the fuel, an optional tritium pretreatment (TPT) process (Goode and Stacy 1978), and the dissolution of the fuel. This stream is typically referred to as the dissolver off-gas (DOG) in fuel reprocessing flowsheets. The second stream is called the vessel off-gas (VOG) and consists of process equipment off-gas (e.g., the instrument air used in bubblers, air sparge discharge, and in-leakage). The third stream is the cell off-gas (COG) for the process cells that provide radiological confinement in the reprocessing facility. The fourth stream is the waste systems off-gas (WOG) that originates from the operations to produce/solidify waste forms. Each of these streams has unique characteristics and off-gas processing challenges.

In Figure 1 it is assumed that all of the ^{3}H contained in the UNF is released as tritiated water (hydrogen-tritium oxide, H^{3}HO and ditritium oxide, ^3H_2O) into the primary off-gas stream from the TPT process.

Tritium pretreatment is an optional, dry head-end method for removing ^{3}H from irradiated uranium (or mixed oxide) reactor fuel prior to the dissolution step, which is typically an aqueous process but can be an electrochemical molten salt process. The use of TPT avoids introducing ^{3}H into the aqueous streams of the plant where it would accumulate and be extremely difficult to remove. If TPT is not used, then much of the ^{3}H is expected to pass into the dissolver with the chopped fuel, react to form tritiated water in the dissolver, distribute throughout the aqueous separation process streams, and enter liquid waste streams and other off-gas streams. For purposes of this report, the use of TPT is assumed because it provides the bounding-level high estimates for total ^{3}H in off-gas streams.

The off-gas from the TPT process can be combined with the DOG for additional treatment after the ^{3}H is removed. Goode and Stacy (1978) provided data indicating that near-complete (>99%) ^{3}H released from the fuel oxide matrix during TPT is possible. Here the assumption is made that all the ^{3}H resides in the UNF matrix. However, because the fuel cladding may contain ~0–96% of the ^{3}H produced by ternary fission (Robinson and Jubin 2013) and because the cladding does not release ^{3}H during TPT, the ^{3}H concentrations assumed to be in the off-gas (for the present calculations) may be high by a factor of ≥2. The presence of ^{3}H in the cladding waste is acceptable because it is classified as high-level waste for other reasons.

The standard TPT process also releases radiologically significant quantities of other volatile fission and activation products. These include carbon (^{14}C) and krypton (^{85}Kr). For carbon (^{14}C) and krypton (^{85}Kr), the quantities released from the TPT process are assumed to be ~50% of each. The residual ^{14}C and ^{85}Kr are assumed to be released during the dissolution step. Xenon is radiologically insignificant because the longest lived isotope, ^{127}Xe ($t_{1/2}$ = 36.4 d), would have decayed to insignificant levels for the shortest-cooled (t > 1 year) fuel to be processed. Under TPT conditions, release of small fractions of the semivolatiles, such as Ru and Cs, in addition to iodine is also expected. Semivolatile radionuclides are discussed in a separate report (Jubin et al. 2014).

A fuel reprocessing demonstration entitled Coupled End-to-End (CETE) (Jubin et al. 2009b) was conducted at ORNL between FY 2007 and FY 2010 under the DOE/NE Global Nuclear Energy Program (GNEP). The project mission was to provide an integrated test bed for the demonstration of GNEP technologies and included sufficient flexibility to conduct tests on a wide range of flowsheets. As part of this project, the TPT process and an integrated off-gas treatment system were demonstrated to recover and quantify the gases released from the TPT and the aqueous dissolution processes. The goal was to close the volatile radionuclide material balance around the head-end processes and determine any interaction between the various volatile radionuclide capture systems.

In the CETE demonstration, approximately 6 kg of UNF was processed in three separate batches. The first batch of fuel was from the Surry-2 reactor; the second and third batches were from the North Anna reactor. These materials were processed over an extended period of time and several individual processing runs.

Separate gas trapping systems were installed to treat the TPT and DOG streams as these processes occurred in two separate facilities at ORNL. The systems are shown schematically in Figure 2. They were identical in capacity and were very similar in regards to the processes used. The TPT system contained a ^{3}H trap but did not have a NO_x scrubber, whereas the dissolver system had a NO_x scrubber but no ^{3}H trap.

The recovery results for the four volatile radionuclides are summarized below.

<u>Tritium (as tritiated water) recovery</u>

After each TPT experiment, tritiated water traps were recovered and analyzed. Tritiated water was desorbed by heating the Type 3A molecular sieve (3AMS) bed to 125°C in dry flowing air at a rate of 0.25 L/min. The humidity of the exit gas was monitored, and the water containing the ^{3}H was captured in a cold trap operated at -25 °C followed by two ethylene glycol bubbler backup traps. Downstream of the glycol bubblers was a back-up caustic trap to recover any iodine or ^{14}C that was co-absorbed on the beds and subsequently desorbed with the tritiated water from the beds. The ^{3}H concentration was determined by liquid scintillation counting and ^{129}I by gamma spectrometry with a high-purity germanium detector and beryllium window (Table 7). A peak attributed to ^{14}C was detected in the caustic from the traps. A small amount of ^{129}I was recovered from each of the tritiated water traps. Tritium recovery ranged from ~12 to 62% of the total ^{3}H estimated by SCALE to be in the fuel and cladding.

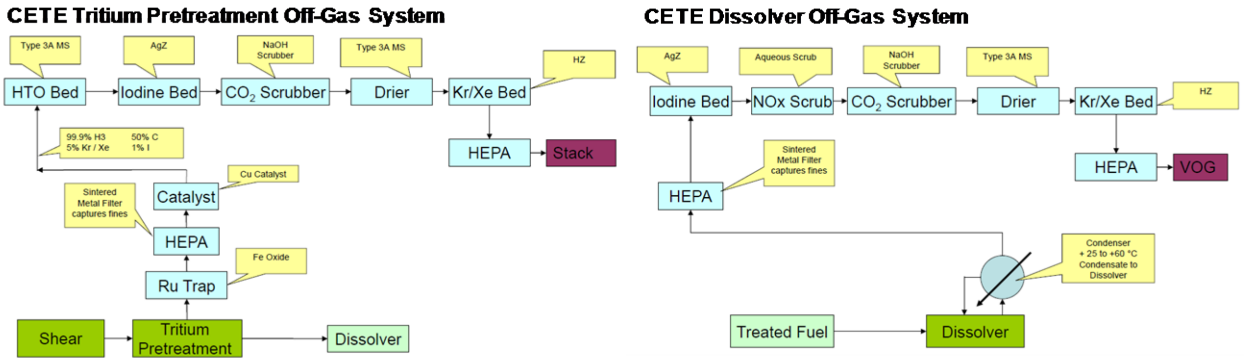

Figure 2. Experimental CETE TPT and DOG systems.

Table 7. Tritium recovery results.

	Total liquid recovered (mL)	Total ^{3}H (Ci)	^{3}H recovery, % of inventory based on SCALE est.	Total ^{14}C (Ci)	Total ^{129}I (nCi)
Fuel Batch 1 – Surry	12.47	0.104	61.9	Detected	13.5
Fuel Batch 2 – North Anna	14.8	0.692	34.3	Detected	161
Fuel Batch 3 – North Anna	2.33	0.225	11.9	Detected	27.3

Iodine recovery

The iodine traps (reduced silver mordenite [AgZ]) were also recovered from the TPT system after each experiment and analyzed. The beds were purged for 24 hr with air at 150°C to remove any physisorbed iodine, which was recovered in a caustic scrubber with a backup glycol scrubber. Any ^{14}C that was co-absorbed on the beds and desorbed along with the ^{3}H and iodine was also trapped in the caustic. Once the beds were purged, five individual bed segments were removed from the trapping column and counted for ^{129}I. A representative sample of each bed was taken to determine the iodine content by chemical analysis.

Analysis of the AgZ indicated that during the TPT operations very little of the iodine inventory was released. All of the iodine recovered was found in the catalyst bed and ^{3}H trap. No iodine was detected in either of the downstream iodine traps (AgZ) or the CO_2 caustic scrubber solution. Iodine releases were estimated to be ~0.04% to ~0.13% of the iodine inventory calculated with the SCALE code for the fuel being processed. These amounts were lower than expected based on published results. Detectable levels of ^{85}Kr were also found on the AgZ.

Carbon (as CO_2) recovery

The CO_2 scrubber solution from each fuel batch was recovered and analyzed. The solution was analyzed for ^3H, iodine, total carbon and ^{14}C content. Analysis of the CO_2 scrubber solutions indicated that the amount of ^{14}C released and recovered from the TPT off-gas was ~ 3 x 10^{-4} Ci/kg of fuel treated on a heavy metal basis.

Krypton recovery

The Kr and Xe were co-absorbed along with significant quantities of N_2 and O_2 on the -80°C hydrogen mordenite (HZ) bed. Upon completion of each TPT experiment or phase, the trap was desorbed in a manner similar to the processes described above for the other traps, and the released gases were analyzed. For the first batch of fuel, 43% of the ^{85}Kr (based on SCALE) was released during TPT; 65% and 53% of the calculated ^{85}Kr inventory was released during TPT for fuel batches 2 and 3, respectively.

After the TPT processing steps were completed, portions of treated UNF from fuel batch 2 and fuel batch 3 were dissolved in separate operations. The resulting off-gas stream was passed through a series of traps and scrubbers to recover the evolved I, C, Kr, and Xe. Table 8 summarizes the ^{85}Kr released during both the TPT process and the fuel dissolution process.

Table 8. Krypton-85 recovery from dissolution and TPT of North Anna fuel.

	Amount of fuel oxide (g)	Initial fuel, SCALE estimate (Ci)	Gamma scan at inlet (Ci)	Gamma scan at trap (Ci)	Trap loading based on desorption gas analysis (Ci)	% Recovered vs SCALE estimate
Fuel Batch 2 – North Anna						
Dissolution	1180	12	3.93	3.49	4.78	39.8
Tritium pretreatment						~65
Fuel Batch 3 – North Anna						
Dissolution	1180	12	7.75	8.06	Not determined	67.0
Tritium Pretreatment						53

Overall recovery

Overall, there was good agreement on the total iodine recovered from two dissolution operations. The total quantities of ^{129}I recovered were 2.66×10^{-5} and 3.02×10^{-5} Ci, respectively, for the first and second batches of fuel. These totals account for about ~50% of the ^{129}I inventory based on the SCALE calculations. The analyses of the iodine beds indicated that 65% to 94% of the ^{129}I released during the 9 hour experiments occurred during the digestion phase of dissolver run.

The total amounts of ^{14}C recovered in the NO_x and CO_2 scrubber solutions were 3.2×10^{-4} and 2.27×10^{-4} Ci, respectively, for the first and second dissolver operations. Note that the 1.18 kg of fuel oxide is the same as 1 kg of IHM, and a nearly equal amount of ^{14}C was released during the TPT process.

2.2 Splits into Various Streams

Figure 1 shows the key components of fuel reprocessing and the volatile components of interest for off-gas processing. The data from the CETE demonstration experiments provided the framework for estimating the masses and volumes of waste form materials. The estimation of the splits of these components into various waste streams is described in the following sections.

Assumptions

In the normal chop-leach process used in existing LWR fuel reprocessing plants (FRPs), most of the ^3H from the fuel matrix would be converted to tritiated water during the dissolution process and would be associated with the dissolver solution. A small fraction of the ^3H inventory would enter the DOG as water vapor, and some would also be found associated with NO_3^- as HNO_3. In the solvent extraction system some would be co-extracted into the tributyl phosphate as HNO_3. The remainder would report to the high-level liquid waste (HLLW) from the first cycle solvent extraction system. If ^3H control is required, it is highly desirable to release and capture the ^3H before the fuel is dissolved, which is typically an aqueous process but can be an electrochemical molten salt process. Once the ^3H reaches the dissolver then all of the liquid streams from the preprocessing facility must be treated as containing ^3H. It has been proposed that ^3H can be removed and captured through the use of an additional head-end process called the TPT process and captured as tritiated water (Hower and Pence 1978; Goode and Stacy 1978; Jubin et al. 2009b; Ferguson et al. 1968, 1969; Inoue and Tsujino 1984; Del Cul et al. 2013; Brown 1976; Bresee et al. 2012).

Iodine may be evolved to some degree during TPT when processing UNF. It is typically evolved in the elemental form, I_2, although some may be present as HI and organic iodides. In aqueous processing flowsheets, most of the iodine, ~94 to ~97%, is expected to be released during acid dissolution. Iodine carried into the molten salt processing of oxide or metal fuels in electrochemical flowsheet is expected to be retained in the molten salt until converted to a waste form.

Carbon-14 is also released to some degree during the TPT of oxide fuels. The remaining fraction is expected to be released during acid dissolution of the fuel as carbon dioxide (CO_2). Carbon-14 carried into the molten salt processing of oxide or metal fuels in the electrochemical flowsheet is expected to be nearly quantitatively retained in the molten salt and not released, but more work is needed to confirm this.

Based on observations from the CETE tests, significant fractions of the Kr and Xe inventories are released during TPT. The balance of the noble gases contained in the fuel is released during acid dissolution. The Kr (all isotopes) would be primarily released in the DOG in the range of 10 to 100 ppm.

In all cases, it is preferable to capture these radionuclides from as concentrated an off-gas stream as possible with as little contamination from additional stable constituents from the air as possible.

Stream compositions

The head-end DOG, TPT off-gas, and VOG compositions shown in Tables 9 to 11 were estimated with results from a large engineering-scale reprocessing integrated equipment test (IET) facility located at ORNL by Birdwell (1990) and reported by Jubin et al. (2009b) with the assumptions described below. Plant capacity and design of equipment can result in significant variations in the off-gas rates and the resulting radionuclide concentrations as well as the amount of nonradioactive constituents contained in the off-gas. The DOG rate for several facilities including the ORNL demonstration facility, IET, the Advanced Fuel Cycle Facility design, the Hot Experimental Facility design, and the Karlsruhe

Reprocessing Plant (WAK) (Ochsenfeld and Schroeder 1975; Ali et al. 1980) facility in Germany when normalized to the throughput were up to a factor of 4 different from the ORNL demonstration rates.

Calculations with the SCALE code (ORNL 2009) for LWR fuel, with a burnup of 60 GWd/tIHM and processing after a 5-year decay period following reactor discharge, were performed, and the results are shown in Tables 9 and 10. The results summarized in Table 9 were based on the implementation of TPT technology, while no such assumption was made for the results shown in Table 11. Results from the calculation with the SCALE code (ORNL 2009) for LWR fuel at a burnup of 30 GWd/tIHM and processing after a 30-year decay period following reactor discharge were summarized (Table 11). These estimates assumed an air atmosphere in the hot cell and a limited or controlled level of leakage into the process equipment. The oxidation gas used in the TPT was CO_2-free air. The VOG flow rate varies with the plant design. The VOG flowrate may be 10 times the DOG rates in some plants (Herrmann et al. 1980). For this study, the VOG flow rate was assumed to be 10 times the total DOG flow.

Two observations are made from evaluating the data in these tables. The concentrations of the volatile species are very low (0.1 to ~50 ppmV). In the case of ^{3}H (as tritiated water), the predicted concentration would result in a dew point for the gas stream of $\leq$-50 °C, if air with a much lower dew point was fed to the TPT process.

The volume of air in-leakage dominates (in terms of mass) the masses of several constituents to be recovered. The $^{14}CO_2$ from the fuel accounts for <0.03% of the total CO_2 that must be treated and managed. The balance of the CO_2 arises from the CO_2 in the air from leakage into the off-gas system and in the gas used to sparge the dissolver solution (Jubin et al. 2009a).

The impurities in the cold process chemicals can also result in additional halogen loadings on the capture processes, depending on the particular streams under consideration: For example common impurities in nitric acid include Cl^- and F^-. Data from several nitric acid chemical specification data sheets are presented in Table 12. Complicating the calculation is the fact that these tramp halides also displace the adsorbed iodine.

Table 9. Source terms – high-burnup (60 GWd/tIHM) and short-cooled fuel (5 years) with TPT.

	Total released to off-gas streams (g/tIHM)	^{3}H Pretreatment (g/tIHM)	DOG (g/tIHM)	VOG (g/tIHM)	TPTOG (ppmV)	DOG (ppmV)	VOG (ppmV)
Tritiated Water as HTO (UNF)	0.545	0.545	--	--	0.79	Removed in TPTOG	
Water (UNF)	2.683	2.683			4.20	Removed in TPTOG	
H_2O (process)		7.24	75 205		12	32500	
CO_2 (UNF)	68	34	34		Combined with DOG	9.3	
CO_2 process		---	2206		Combined with DOG	390	
I (UNF)	358	---	347	10.7	Combined with DOG	8.2	0.03
Cl (from HNO_3)	156		156		Combined with DOG	13.4	
Kr (UNF)	626	313	313	--	Combined with DOG	46	
Ar_{air}	60 924				Combined with DOG	9300	
Kr_{air}	15.6				Combined with DOG	1.1	
Xe (UNF)	9616	4808	4808	--	Combined with DOG	450	

Basis: TPTOG rate 270 L/m
100% ^{3}H release in TPT to TPTOG
DOG rate 1000 L/m
TPTOG combined with DOG after ^{3}H removal
VOG rate 10,000 L/m
Gas to TPT has -60°C dew point
Air cell at 15°C dew point
DOG cooled to 25°C leaving dissolver
50% Kr/Xe release in TPT to TPTOG – balance reports to DOG
50% CO_2 release in TPT to TPTOG – balance reports to DOG
97% of iodine is released from dissolver into DOG – balance reports to VOG
Fuel burnup 60 GWd/tIHM, 5-year cooling prior to processing (Table 5)
Assumed processing rate 100 t fuel processed per year over 200 days based on IET rates

The concentrations of F and Br in HNO_3 are too low to report in this table.
The concentration of Kr in air is about 1 ppmV and Xe about 90 ppbV in air.
Cl will be trapped with I_2 limiting Ag mordenite sorbent bed capacity.

Table 10. Source terms – high-burnup (60 GWd/tIHM) and short-cooled fuel (5 years) with no TPT.

	Total released to off-gas streams (g/tIHM)	DOG (g/tIHM)	VOG (g/tIHM)	DOG (ppmV)	VOG (ppmV)
Tritiated Water as HTO (UNF)	0.545	--	--	Trace	Trace
Water (UNF)	2.683				
H_2O (process)		75 205		32 500	
CO_2 (UNF)	68	68		11.8	
CO_2 process		2206		390	
I (UNF)	358	347	10.7	10.5	0.03
Cl (from HNO_3)	156	156		17.1	
Kr (UNF)	626	626	--	58.1	
Ar_{air}	47 971			9300	
Kr_{air}	15.6			1.1	
Xe (UNF)	9616	9616		570	

Basis: No TPT
DOG rate 1000 L/m
100% ^{3}H combines with nitric acid – additional downstream removal not considered in this scenario
VOG rate 10,000 L/m
Air cell at 15°C dew point
DOG cooled to 25°C leaving dissolver
100% Kr/Xe release during dissolution
100% CO_2 release during dissolution
97% of iodine is released from dissolver into DOG – balance reports to VOG
Fuel burn-up 60 GWd/tIHM with 5-year cooling prior to processing (Table 5)
Assumed processing rate 100 t fuel processed per year over 200 days based on IET rates

The concentrations of F and Br in HNO_3 are too low to report in this table.

The concentration of Kr in air is about 1 ppmV and Xe about 90 ppbV in air.

Cl will be trapped with I_2 limiting Ag mordenite sorbent bed capacity.

Table 11. Source terms – low-burnup (30 GWd/tIHM) and long-cooled fuel (30 years) with TPT.

	Total released to off-gas streams (g/tIHM)	TPTOG (g/tIHM)	DOG (g/tIHM)	VOG (g/tIHM)	TPTOG (ppmV)	DOG (ppmV)	VOG (ppmV)
Tritiated Water as HTO (UNF)	0.065	0.065	--	--	0.094	Removed in TPTOG	
Water (UNF)	1.296	1.296			2.06		
H_2O (process)		7.24	75205		12	32500	
CO_2 (UNF)	34.7	17.4	17.4		Combined with DOG	4.7	
CO_2 process		---	2200		Combined with DOG	390	
I (UNF)	185	---	180	5.6	Combined with DOG	4.3	0.02
Cl (from HNO_3)	156		156		Combined with DOG	13.4	
Kr (UNF)	304	152	152	--	Combined with DOG	22	
Ar_{air}	60924				Combined with DOG	9300	
Kr_{air}	15.6				Combined with DOG	1.1	
Xe (UNF)	4916	2458	2458	--	Combined with DOG	229	

Basis: TPTOG rate 270 L/m
100% ^{3}H release in TPT to TPTOG
DOG rate 1000 L/m
TPTOG combined with DOG after ^{3}H removal
VOG rate 10,000 L/m
Gas to TPT has -60°C dew point
Air cell at 15°C dew point
DOG cooled to 25°C leaving dissolver
50% Kr/Xe release in TPT to TPTOG – balance reports to DOG
50% CO_2 release in TPT to TPTOG – balance reports to DOG
97% of iodine is released from dissolver into DOG – balance reports to VOG
Fuel burnup 30 GWd/tIHM, 30-year cooling prior to processing (Table 4)
Assumed processing rate 100 t fuel processed per year over 200 days based on IET rates

The concentrations of F and Br in HNO_3 are too low to report in this table.
The concentration of Kr in air is about 1 ppmV and Xe about 90 ppbV in air.
Cl will be trapped with I_2 limiting Ag mordenite sorbent bed capacity.

Table 12. The concentration of halogens in different grades of nitric acid.

Vendor	Cl, % (ppm)	F, ppm
No 1 (bulk)	0.002 (20)	Not reported
No 2 (tanker quantities)	0.01 (100)	Not reported
No 3 (reagent grades)	(0.5)	Not reported
No 3 (reagent grades)	(0.08)	1

Nitric acid consumption within a processing plant is dependent on a number of factors, but the most significant is the ability to capture and recycle the acid within the plant. Estimates of the nitric acid requirements vary widely. From the early 1980s design of a small experimental reprocessing facility, the acid consumption was projected to be 68 kg/tHM. Starting with the specification from tanker quantities of nitric acid from vendor #2 (Table 12) would result an additional halogen (Cl) loading of 6.8 g/tHM. In the case of the Spent Fuel Treatment Facility, the acid consumption is estimated to be 800 kg/tHM. For the Advanced Fuel Cycle Facility, the acid usage is estimated to be 3800 kg/tHM. A simple average value is 1560 kg/tHM. From the same vendor #2 (Table 12), the Cl specification would result in Cl releases of ~160 g/tHM. This is on the same order of magnitude as the I_2 in the fuel. In fact, for the low burnup case, the ratio of Cl:I is greater than 3:1. For the high burnup case, this ratio is 1.6:1. This potentially increases the mass of the iodine waste by a factor of 2.5 to 4.

3. APPLICABLE CAPTURE TECHNOLOGIES

A number of separation and capture technologies currently being developed can be broadly applied to the entire category of volatile fission gas products, including ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I. .

3.1 Tritium

As discussed above, ^{3}H is evolved during head-end operations such as the TPT step for oxide fuels prior to treatment by either aqueous or electrochemical methods. If TPT is used, the ^{3}H is oxidized to form tritiated water.

Tritium, as water, may be removed from the off-gas stream with desiccants or molecular sieves. Molecular sieves exhibit high water capacities—10 to 20% based on the dry weight of the sorbent (Brown et al. 1983). Due to the very low dew point of the TPT stream containing only tritiated water, it may be necessary to add additional water to the off-gas to improve the ^{3}H DF for the 3AMS. This was done as part of the CETE demonstration. For the waste form volume calculations performed in Section 3, the water concentration was increased by a factor of 100. Type 3A molecular sieves have been shown to also sorb CO_2 at temperatures significantly below room temperature. There are variations in the performance characteristics of the material obtained from different manufactures as evidenced by differences in the elution temperature for CO_2.

Both iodine and ^{14}C were co-adsorbed on 3AMS in the CETE demonstrations. Previous work at ORNL in the late 1970s also showed significant iodine adsorption on 3AMS (Holland 1979). Co-adsorption is problematic because of the long ^{129}I half-life compared to that of ^{3}H and the impact to potential disposition pathways for ^{3}H if ^{129}I is present. For this reason, current designs for capturing tritiated water and ^{129}I in DOG streams propose that the ^{129}I be done first, to efficiently remove the ^{129}I upstream of the molecular sieve sorbent used for tritiated water capture (Spencer et al. 2013; Spencer et al. 2014; Vienna et al. 2015).

3.2 Carbon-14

State-of-the-art ^{14}C capture is based on a caustic scrub with the resulting alkaline Na/Ca(OH)$_2$/CO$_3$ solution being fed to a follow-on waste stabilization process. This process is described below, along with alternative ^{14}C capture processes.

It should be noted that the total ^{14}C concentration in the waste depends on the ambient CO$_2$ of the gas flow into the TPT process, dissolver, and any process in-leakage. This in-leakage is, in most cases, the limiting factor in terms of waste volume and one that is difficult to estimate. The tramp CO$_2$ in air from in-leakage (nonradioactive C) can dwarf the amount of ^{14}CO$_2$, and increase the ^{14}C waste form mass and volume. For example, 20% oxygen and 80% argon in the TPT process and pure argon or nitrogen cover gas during dissolution could greatly reduce the volume of nonradioactive C that would have to be captured along with the radiogenic ^{14}C. However, the use of CO$_2$-free process and blanket gases may lower the total CO$_2$ concentrations in the DOG stream at the expense of lower ^{14}C DF values. Also, Ar gas mixtures for process or cover gases may increase the ^{85}Kr waste form if the separation of Ar and ^{85}Kr is not efficient.

<u>Caustic scrubbing</u>

Absorption of CO$_2$ in a caustic solution in a packed column to form carbonates is a common industrial process that has been described in detail elsewhere (Bray 1977). While the process has never been applied specifically to ^{14}C recovery in the nuclear fuel cycle, the US Environmental Protection Agency (EPA) indicated in 1977 that it would be the most probable candidate for application at that time (Brown et al. 1983).

The double-alkali process is briefly described in the book edited by Goossens et al. (1991). Carbon dioxide is initially scrubbed from the off-gas stream in aqueous NaOH to form Na$_2$CO$_3$. The resulting solution is then reacted with lime to produce a solid product. The reactions are

$$CO_2 + H_2O \rightarrow H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

and

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \ .$$

Bray (1977) and later Brown et al. (1983) addressed ^{14}C control from a LWR FRP and determined that a column constructed according to the reported design parameters would have a theoretical CO$_2$ recovery of 90 and 99% from a 170 m^3/hr at standard temperature and pressure (STP) air stream containing CO$_2$ at 315 ppmV. The 840-Ci/year reference source term from a 1500-tHM/year LWR fuel reprocessing facility amounts to about 600 g of ^{14}CO$_2$ diluted with 760 kg of nonradioactive CO$_2$, assuming that the dissolver was sparged with a nominal airflow of 170 m^3/hr at STP and the nominal CO$_2$ content of air was approximately 0.03%. Thus, the ^{14}CO$_2$ concentration in the DOG could be as low as 0.3 ppmV. The annual waste product from the scrubber column would be 1.6 t of calcium carbonate containing ~2 kg of Ca^{14}CO$_3$. The mass of this aqueous slurry was 20 t, which, if immobilized in cement at 30 mass %, would generate 65 t of cement waste form or 190 200-L drums of waste product annually. To reduce the impact of nonradioactive CO$_2$, the process could be designed so that CO$_2$ was removed from the air prior to it entering the dissolver sparger at the expense of possibly lowering the ^{14}C DF. Alternately, the sparge gas flow could be minimized or the sparge gas could be replaced with nitrogen.

The Thermal Oxide Reprocessing Plant (THORP) plant at Sellafield, England, has incorporated a ^{14}C removal process within the DOG system to meet stack release limits (Marr 1997; Hudson 1994). Testing in pilot-scale equipment confirmed literature data that most of the ^{14}C was released as CO_2 with 1% as CO. The test results indicated the caustic scrubber would achieve a ^{14}C DF of 70 under these conditions (Hudson 1994). The THORP ^{14}C discharges based on a processing rate of 1200 tHM/year of reference fuel were estimated to be 0.434 TBq/year. The THORP authorized ^{14}C release limit was 0.87 TBq/year. Total ^{14}C inventory arising from the 1200-tHM/year plant was 28.9 TBq/year.

Caustic slurry scrubbing

Limited studies have been carried out with alkaline earth hydroxide slurries in stirred tank reactors to absorb CO_2 (Notz 1980). The DF for $Ba(OH)_2 \cdot 8H_2O$ is about 10 times greater than that for $Ca(OH)_2$, which is about 10 times greater than that for $Mg(OH)_2$. The reaction rates were determined to be liquid-phase controlled and, thus, impacted by the hydrodynamic parameters of the reactor. Processing steps to recover the spent material, dry, and package it in a suitable waste form have not been fully demonstrated (Brown et al. 1983).

Braun (1983) recommended that the CO_2 removal process be located downstream of aerosol removal, iodine removal, catalytic oxidation of hydrocarbons, catalytic reduction of NO_x and oxygen, and water removal. Because CO_2 can accumulate in the Kr separation process, CO_2 removal should be upstream from Kr removal.

Molecular sieve adsorption

Molecular sieves can be used to separate Kr (Lenard-Jones [L-J] kinetic diameter 0.364 nm (Breck 1974)) and CO_2 (L-J kinetic diameter 0.33 nm) from one another (Notz 1980). Zeolites 3A, 4A, and 5A have been studied for off-gas treatment. The 3AMS, which can be used for ^{3}H recovery, has a lattice structure too small to adsorb CO_2 while the 5A molecular sieve can adsorb both CO_2 and Kr. Nonetheless, a 2.5 mass% loading of CO_2 has been observed to reversibly sorb on 3AMS at a temperature of -60 °C and a 5% concentration of CO_2 in the gas phase. Adsorption of CO_2 did not hinder water adsorption at temperatures down to -40 °C, and analyses indicate that CO_2 is sorbed on the particle surface (Rivera et al. 2003). Sorption tests conducted at ORNL with thermal gravimetric analyses indicated, within experimental error, no effect on the sorption of water from a gas stream containing up to 2% V/V CO_2 [unpublished data]. The use of 5A molecular sieves could be coupled with a Kr recovery process or used to effect a Kr from CO_2 separation with a frontal analysis gas-phase chromatographic technique (Notz 1980). The 4A molecular sieve adsorbs Kr at high pressures and moderate temperatures (Brown et al. 1976), but when operated at 100 to 300 kPa and 0°C, the adsorption rate is near zero. Laboratory-scale experiments demonstrate that the 4A molecular sieve removes CO_2 to the level of detection (10 ppm) from a >90% CO_2 stream. The bed was regenerated by heating to 200°C.

A process in which a 4A molecular sieve is used has not been applied to the recovery of ^{14}C in the nuclear fuel cycle, but process flowsheets have been proposed for full-scale application (Brown et al. 1978; DOE 1979). The proposed process involves passing a pretreated gas stream, from which NO_x and water vapor have been removed, through a packed bed of zeolite to adsorb the CO_2. An oxidation step may be required, if other process streams introduce ^{14}C in forms other than CO_2 (Goossens et al. 1991). Either temperature or pressure swing adsorption processes are possible. Air streams containing 330 ppmV CO_2 can be reduced to 3 ppmV CO_2 for a DF of greater than 100. Higher DFs can be obtained at higher CO_2 concentrations. After stripping the CO_2, the adsorber bed would be placed back in service. The adsorption technology would have to be coupled with other technologies, such as caustic scrubbing and cement fixation, to provide a solid waste form.

Fukumatsu et al. (1999) investigated the adsorption of CO_2 on synthetic zeolites and natural mordenites. Both adsorbents have substantial capacity for CO_2, but this capacity is greatly diminished in the presence of water vapor.

Adsorbent bed fixation

Pilot-scale studies have been conducted by researchers at Ontario Hydro (Chew et al. 1983; Goossens et al. 1991) on a gas-solid reaction process to remove ^{14}C according to the following reaction:

$$Ca(OH)_2\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s) + H_2O\ (g\ or\ l)\ .$$

Tests were conducted in a 0.20-m-diameter reaction vessel. A DF of 20 was achieved, and 63% of the reactant was utilized. This development effort focused on CO_2 concentrations of 20 to 50,000 ppmV for application to the moderator cover gas in the Canada Deuterium Uranium (CANDU) nuclear reactors (Chew et al. 1983; Goossens et al. 1991).

A similar process that could also be used to recover and immobilize CO_2 as a carbonate has been developed at the ORNL (Haag 1982, 1983). This process is based on the use of $Ba(OH)_2{\cdot}8H_2O$ according to the reaction

$$Ba(OH)_2{\bullet}8H_2O(s) + CO_2\ (g) \rightarrow BaCO_3 + 9H_2O\ (g\ or\ l)\ .$$

These efforts were directed at air streams containing CO_2 at 330 ppmV. Up to 99% of the bed can be converted to the carbonate, and the CO_2 can be removed to concentrations below 0.1 ppmV (a DF of >3000). The product, $BaCO_3$, possesses both the thermal (up to 1450°C) and chemical stabilities (solubility in water at 20°C of 0.02 g/L) desired for long-term waste disposal. However, while the solubility is low, the dissolution rate is high (Grandjean and Leturcq 2005). Acceptable performance depends on the final repository situation. This process would eliminate the need for handling liquid streams and separating solids from liquids (Notz 1980). Final reactant conversions greater than 99% are also possible. The $BaCO_3$ product is friable and might pose certain operational problems. A prototype unit is described in the book by Goossens et al. (1991). In a recent study, the authors show that some, perhaps as much as 50 mol% $CaCO_3$, may be needed to get adequate product density (Grandjean and Leturcq 2005).

In the reference application to a DOG of 170 m^3/hr at STP containing CO_2 at 315 ppmV, about 32 t/year of $BaCO_3$ waste would be formed (Brown et al. 1983). Engineering details for removing the waste product from the reactor vessel and producing a waste form, such as cement, must be developed.

It is possible to use metal organic frameworks (MOFs) to remove the CO_2 from a particular part of the plant gas-handling system (Keskin et al. 2010; Li et al. 2009; Ma and Zhou 2010; Meek et al. 2011; Mueller et al. 2006; Thallapally et al. 2010). Most MOFs available today adsorb both CO_2 and H_2O (Mueller et al. 2006). Thus, ^3H, as tritiated water, would be taken up on these filter beds. However, CO_2 and H_2O are desorbed from the MOF material at different temperatures. Metal organic framework materials can adsorb up to ~25 mass % CO_2 (Keskin et al. 2010). A future goal of MOF technology development is to make the MOF specific to CO_2 with little or no sorption of H_2O.

3.3 Krypton

The capture of the noble gases can be accomplished either with cryogenic methods or by pressure swing adsorption on a solid matrix (e.g., molecular sieves, MOFs, or porous organic polymers). Generally, to achieve products of high purity, cryogenic distillation is required. Argon, Xe, and Kr are commercially available at 99.999% purity with ~ 1 ppmV cross-contamination, so the separation technology for these inert gases is mature. Fission product, but stable, Xe is present at about 10 times the Kr molar concentration in the off-gas stream. Xenon is a commercially valuable commodity, currently valued at approximately \$10/L, or \$15,000/tHM processed, if sufficiently purified of radioactive contaminants to allow commercial resale. If Xe is not separated from the Kr, the resulting waste volumes increase by a factor of ~10.

The current baseline for removal of ^{85}Kr from the off-gases is a cryogenic process with fractional distillation. This state-of-the-art process and a range of alternative separations processes are described below. They include experimental MOF materials that are being developed with the goal of removing Xe and Kr at much higher temperatures than present capabilities (Liu et al. 2012; Soelberg et al. 2013; Fernandez et al. 2012; Liu et al. 2014a). These MOFs have high capacity (15 mass %) for Xe and Kr and remove Xe and Kr from air at ppm concentrations.

Cryogenic distillation

Cryogenic distillation is a technology to recover rare gases that has been used commercially for many years. This technology has not been optimized for high Kr recovery DFs. The cryogenic process has been under development in Belgium, France, Germany, and Japan. Decontamination factors of 100 to 1000 have been reported (Goossens et al. 1991).

When applied to DOG, the gases must be pretreated to remove interfering constituents to ensure system safety and operability. All gases that would condense at liquid nitrogen temperatures, including NO_x, water vapor, and CO_2, need to be removed to prevent plugging of the equipment. Oxygen must also be removed to avoid the formation and accumulation of ozone from the radiolysis of O_2 by the radiation from the condensed ^{85}Kr. Co-adsorption of hydrocarbons and oxygen from air can also result in a hazardous mixture. Catalytic decomposition of hydrocarbons followed by removal of water vapor and CO_2 with molecular sieves may be necessary. Separations in the distillation process occur because of differences in the boiling points of the gases. Krypton and Xe are then removed from the off-gas stream in a stripping column by dissolution in liquid Ar or N_2. They are subsequently separated in the purification columns, where the solvent is first removed along with most of the impurities and Kr is allowed to boil and separate from Xe. Fractional distillation is greatly simplified when a purified carrier gas, such as Ar or N_2, is used. The benefit of a purified carrier gas has also been discussed as a way to reduce the amount of CO_2 that must be captured and immobilized (see Section 3.2).

Pilot-scale cryogenic units for krypton recovery in the absence of oxygen have been tested with stable Kr in simulated off-gas streams at the Kernforshungszentrum Karlsruhe (KfK, Germany), Commissariat à l'énergie atomique et aux énergies alternatives (CEA, France) and Studiecentrum voor Kernenergie - Centre d'Etude de l'énergie Nucléaire (SCK·CEN, Belgium) nuclear research centers (Hebel and Cottone 1983; IAEA 1980a). Each unit handles gas flows of 20–50 m^3/hr at STP. There are many similarities:

(1) each system has provisions to remove H_2O, NO_x, and CO_2,
(2) each system has a hydrogen recombiner to remove O_2, and
(3) the pretreated gas stream enters a cryogenic column at about -150°C.

Operating pressures, however, vary between the systems (Hebel and Cottone, 1983):

(1) REDUCTION, ADAMO, KRETA - Germany – 0.5 MPa (5 bar),
(2) SCK·CEN - Belgium – 0.8 MPa (8 bar), and
(3) CEA process - France – 1.4 MPa (14 bar).

Xenon solubility and crystallization are functions of column pressure. In the French process, liquid Ar is used in place of liquid N_2 as the solvent. The second columns (second and third in the French process) are operated at lower pressures and higher temperatures to remove the solvent and separate the Kr and Xe by fractional distillation. The three processes provide recovery efficiencies for Kr ranging from 99.5 to 99.99%.

A radioactive pilot plant cryogenic unit for the recovery of ^{85}Kr became active in 1988 at the Power Reactor and Nuclear Fuel Development Corporation (PNC) Tokai FRP in Japan (Leigh 1994). The system capacity is rated at 110 m^3/hr at STP and 330 Ci/hr of ^{85}Kr (Naruki 1985). The combined shear cell off-gas and DOG are pretreated to remove ^{129}I with caustic scrubbing. Oxygen, NO_x, and hydrocarbons are removed with hydrogen recombiner, and H_2O and CO_2 are removed by adsorber beds. To avoid possible crystallization in the cryogenic distillation column, the Xe is adsorbed on silica gel at -160 °C and 0.3 MPa.

A cryogenic system designed to recover ^{85}Kr for beneficial use was operated at the Idaho Chemical Processing Plant (ICPP) for a number of years (Brown et al. 1983; Bendixsen and German 1975; Goossens et al. 1991; Groenier 1985; Hebel and Cottone 1982). The system was designed to treat a DOG flow up to 34–51 m^3/hr (20–30 scfm) (Bendixsen and German 1975). The DOG was pretreated for the removal of H_2, NO_x, N_2O, CO_2, and H_2O. However, unlike the other cryogenic processes described above, O_2 was not removed. While this system was not specifically designed for effluent control from the ICPP, performance data presented by Bendixsen and German (1975) indicate that average recovery efficiencies for Kr were 97% and for Xe were >98% during operations in 1974 . However, due to process startup and upsets, the overall efficiencies for Kr and Xe were only 52% and 63%, respectively, revealing the importance of continuous operation, reliable process equipment, and highly trained operations staff.

Fluorocarbon absorption

Fluorocarbon absorption technology was under development at the Oak Ridge Gaseous Diffusion Plant (ORGDP) and at the KfK (Hebel and Cottone 1983; Henrich 1985; IAEA 1980b; Little 1983; Hebel and Cottone 1982). An organic solvent (CCl_2F_2 called R-12 or Freon) was used to selectively absorb noble gases from air or DOG streams; the noble gases were stripped from the solvent by boiling.

The basis of this recovery process is the solubility difference that exists between the various gas compounds in the organic solvent. The process consists of absorbing the noble gases and several other constituents from the off-gas stream and stripping the gases from the solvent. The solvent selected for the process was R-12 Freon which was used because of its noble gas absorption capacity, noble gas/bulk gas separation factors, and relatively good thermal and radiation stability. Development at ORGDP progressed through three generations of pilot plants (Little 1983) and is described in a series of reports (Eby et al. 1982; Little 1983; Merriman 1980; Stephenson and Eby 1977).

Initial characterization studies were done from 1967 to 1978 (Brown et al. 1983; ERDA 1976; Goossens et al. 1991; Little 1983). Results from these studies indicated that a single column system could be used to effect the needed separation of different gases in the upper, middle, and lower parts of the column. The Kr, Xe, and CO_2 accumulated in the middle or intermediate stripper stage of the column and were drawn off as a product stream. The final stripper operation regenerated the R-12 solvent by removing the remaining dissolved gases. The other constituents, such as I_2, CH_3I, H_2O, and NO_2, remained in the solvent. While not the primary target of this process, DFs in excess of 10,000 were observed for I_2 and CH_3I and over 100 for NO_2 (Stephenson and Eby 1977). Small levels of these impurities can remain in the solvent without interferences; large buildups could be removed by further solvent distillation. Krypton was further purified in a subsystem in which the gases are treated with a 13-X molecular sieve to remove the R-12 and Ag-mordenite to remove the Xe. The regenerated R-12 was reused. Following the removal of the R-12 vapors, the typical product stream would consist of 78% CO_2, 13% Xe, 5.5% N_2, 2.0% Kr, 1.4% O_2, and 0.1% Ar (Stephenson and Eby 1977; Little et al. 1983).

In 1996, the R-12 Freon was banned in the United States and many other countries. Since it is unlikely that R-12 could be used in a FRP, much of the research on Xe and Kr removal would need to be redone if a fluorocarbon-based process was to be considered.

Solid sorbent separation processes

Recovery of Kr from the DOG stream by both activated carbon and zeolites has been studied. One possible system used a bed of synthetic silver mordenite (AgZ) at ambient temperatures to recover Xe. The "Xe-free" gas was then chilled and passed onto a second hydrogen mordenite (HZ) operated at ~-80 °°C where Kr was sorbed. The Kr was recovered and concentrated on a third HZ column by a temperature swing process on the second column at ~60°C. The Kr was recovered from this third column again by a temperature swing to a cold trap (Trevorrow 1983). The Xe bed was regenerated at 200 to 250°C. Results from laboratory tests showed DFs of 400 for Kr and 4000 for Xe (Pence 1981).

Monson (1982) reported that AgZ had the highest Kr adsorption capacity and examined other less expensive zeolites for Kr recovery and non-cryogenic operating temperatures. The Kr capacity of AgZ at ambient temperatures was on the order of 1 mmol/kg and is 10 to 15 times greater than that of HZ.

Munakata et al. (2003) have also examined the use of AgZ and HZ to recover Xe and Kr from a simulated DOG stream. They point out that this approach should have lower operating costs than cryogenic distillation and avoids the possible fire hazard resulting from the accumulation of ozone in the cryogenic systems. It also has the advantage of avoiding the possible explosive reactions and fire from NO_x and activated carbon reactions that have been found in studies of the use of activated carbon for the recovery of Kr/Xe. Krypton loadings on AgZ and HZ of 1 mmol/kg and 0.2 mmol/kg, respectively, were determined by extrapolation of their reported data at a partial pressure of ~5 Pa. Xenon loadings of 200 mmol/kg on AgZ and 15 mmol/kg on HZ were shown at a partial pressure of ~ 55 Pa. Both of these loadings were at 273 K. These isotherm data were obtained using Kr/He or Xe/He gas mixtures. Thus, processing 1 tHM would require a minimum AgZ bed size of ~500 L at a packed density of 0.662×10^3 kg/m^3. Under these conditions, the bed would absorb ~0.3 mol of Kr in addition to the 67.4 mol of Xe (~5% of the Kr).

Ianovski et al. (2002) focused on the use of HZ for noble gas adsorption. They report a significant variation in loading as a function of temperature, making temperature swing adsorption viable. For example, they reported adsorption capacities for Kr on HZ of 0.35 mmol/kg at 273 K and 25 mmol/kg at 198 K both at Kr partial pressures of 10 Pa.

Separation of Kr from DOG by solid-state adsorption was investigated in Germany by Ringel (1990). The laboratory-scale process consisted of adsorption on activated charcoal and separation of the different gas species by purging the charcoal with He. The charcoal selected was MERCK chromatography-grade activated charcoal with a particle size of 0.5 to 0.75 mm, a poured density of 440 kg/m^3, and a specific surface of 1050 m^2/g. Different process adsorption pressures and column temperatures were compared. For hot cell application, a process with gas adsorption at -150 °C and nominal pressure (~100 kPa [1 bar]) was recommended. In this case and for an off-gas flow rate of 100 m^3/hr at STP, the whole column volume for a continuous operating process was about 300 L charcoal and the He purge flow rate was 8 m^3/hr at STP. A Kr DF of ~1000 was achieved.

Industrial-scale demonstration of an adsorptive chromatographic separation of Kr on activated charcoal at low temperatures was conducted at the research center Jülich (Kernforschungszentrum) in Germany (Ringel 1990). In this process, Kr was absorbed at temperatures as low as -160 °C and the charcoal beds regenerated at temperatures of about 120 to 150°C. Krypton DFs of 1600 were obtained and Kr purities in the final product were > 99%. The pilot plant had a throughput of 13 m^3/hr at STP containing Kr at 100 ppmV and Xe at 1000 ppmV. The pilot plant was skid mounted.

A method has been developed for incorporating synthetic AgZ and HZ mordenite powder to produce an engineered form of the sorbents made with polyacrylonitrile (PAN) (Garn et al. 2014b). Bulk densities for the resultant HZ and AgZ engineered sorbents were measured at 0.3×10^3 kg/m^3 and 0.4×10^3 kg/m^3, respectively. The resulting AgZ-PAN and HZ-PAN materials were tested at the bench scale with thermal swing and thermal/pressure swing combination operations. Preliminary test results with HZ-PAN revealed a Kr capacity of 100 mmol/kg at -82 °C at a partial pressure of 15 Pa in He. The Kr capacity for AgZ-PAN under these same conditions was measured at 66 mmol/kg. Xenon capacities at -82 °C could not be measured with a 100 Pa Xe in He because of the experimental design that led to liquefaction of the Xe prior to breakthrough. However, when a test gas mixture of 15 Pa Kr and 100 Pa Xe in He was used, both Kr and Xe capacities on AgZ-PAN could be measured and were reported at 51 and 864 mmol/kg, respectively (Garn et al. 2012). These initial results indicate HZ-PAN may provide better capacity for Kr than Xe and AgZ-PAN better capacity for Xe than Kr.

Capacities for Xe (100 Pa; 1000 ppmV) and Kr (15 Pa; 15 ppmV) in He (100 kPa) on HZ-PAN material at -53°C were 507 mmol/kg and 6 mmol/kg, respectively. Capacities for Xe and Kr on AgZ-PAN under the same conditions were very similar at 506 mmol/kg and 5.7 mmol/kg, respectively [see Table 4 in Garn et al. (2014a)]. Results from room temperature experiments with a Xe partial pressure of ~100 Pa and a Kr partial pressure in air ~15 Pa indicated a Xe capacity of 27 mmol/kg. Although the two sorbents performed very similarly at -53°C, the Kr capacities decrease significantly when the test temperature increased from -82°C to -53°C.

Based on these results, tests with two columns (one with AgZ-PAN and one with HZ-PAN) are being undertaken to effect a separation of Xe from Kr. Experimental results from tests with AgZ-PAN have shown it to have a significant selectivity for Xe over Kr, particularly at room temperature, whereas HZ-PAN has a higher selectivity for Kr than AgZ-PAN; hence, a two-column arrangement would have AgZ-PAN in the first column and HZ-PAN in the second. These columns may be operated at different temperatures.

Metal-organic framework materials are being developed for the removal of Xe and Kr at near room temperature. A nickel dioxobenzenedicarboxylic acid (Ni-DOBDC)-based MOF (Thallapally et al. 2012) and a partially fluorinated MOF with copper (FMOF-Cu) (Fernandez et al. 2012) have shown improved Xe and Kr capacities at room temperature relative to previous materials (Banerjee et al. 2015). Results from adsorption experiments with the Ni-DOBDC showed a Xe adsorption capacity of 4240 mmol/kg at 100 kPa and 25°C (pure Xe gas). However, it only adsorbs 8 mass% Kr (357 mmol/kg) under similar experimental conditions. Silver nanoparticle-loaded Ni-DOBDC (Ag@NiDOBDC) had better Xe uptake capacity (5300 mmol/kg) and selectivity ($Xe/Kr \approx 7$) over the parent framework (Liu et al. 2014b). Under the same conditions (room temperature and 100 kPa), the FMOF-Cu adsorbed 450 mmol/kg and 34 mmol/kg for Xe and Kr, respectively. At -40°C, the FMOF-Cu adsorbed higher Kr (1750 mmol/kg) than Xe (150 mmol/kg) at 100 kPa (Fernandez et al. 2012).

The removal efficiency and capacity of Ni-DOBDC and FMOF-Cu for Kr recovery with two adsorption beds in series at a non-cryogenic temperature (-50°C) have been demonstrated (Liu et al. 2014a). The use of -50°C is strictly an artifact of the experimental setup used in those studies. Independently, these MOFs have been shown to have high capacities and specificities for Xe and Kr at temperatures >0 °C. In these studies a mixture of 400 ppm Xe, 40 ppm Kr (partial pressures of 40 and 4 Pa, respectively) in dry air (similar to the concentrations expected in a reprocessing facility) was passed through the first bed containing Ni-DOBDC. This bed showed preferential capture of Xe and breakthrough of Kr. The outlet gas mixture from bed 1 now containing 40 ppm Kr in Xe free air was then passed through bed 2, also containing Ni-DOBDC, where Kr was removed (0.61 mmol/kg). Similar experiments performed with FMOF-Cu instead of Ni-DOBDC in bed 2 resulted in adsorption capacities 3.7 times higher for Kr (2.26 mmol/kg) than from a mixture containing Xe and Kr. Based on these results, a two-bed system used for a 1000-tHM/y plant would require a 1.9-m^3 MOF column for Xe and a 5.6-m^3 MOF column for Kr (Cabe et al. 2014).

Porous organic cage compounds (CC3) for the separation of Xe and Kr at room temperature are also being studied (Chen et al. 2014). Separate adsorption experiments were carried at 100 kPa and room temperature with Xe and Kr. The Xe isotherm approaches saturation at 100 kPa and 25°C with an adsorption capacity of around 2250 mmol/kg, corresponding to three gas molecules per CC3 cage. Similarly, the adsorption capacity of Kr under identical conditions was found to be 840 mmol/kg. When air containing Xe (400 ppm) and Kr (40 ppm) was passed through this column, the Xe component was retained for more than 15 minutes, even at a flow rate of 0.67 L/s or twice as fast as that used in the studies of Ni-DOBDC(Liu et al. 2012), whereas Kr and the other components (N_2, O_2, and CO_2) broke through the column almost immediately. Under these conditions, CC3 adsorbs twice (11 mmol/kg) as much Xe as the leading Ni-DOBDC (4.8 mmol/kg). Likewise, the Xe/Kr selectivity for CC3 under these conditions is almost three times higher than that for Ni/DOBDC: 20.4 versus 7.3.

Metal-organic framework materials are becoming more available commercially. Although Cabe and coworkers (2014) showed that the cost of the MOFs was not the cost-determining factor for implementing a MOF-based process, decreasing the cost and increasing the availability of MOFs make a MOF-based process that much more cost-effective.

3.4 Iodine

Technologies have been developed for the recovery of gaseous ^{129}I species based on scrubbing with caustic or acidic solutions and chemisorption on silver-coated or silver-impregnated adsorbents. These processes also recover the other halogen elements, i.e., chlorine and bromine. These elements can displace sorbed I. Therefore, in sizing a recovery technology, it is necessary to take into account the fission products ^{127}I and ^{81}Br (stable nuclei) as well as any halogens introduced into the chemicals used for fuel dissolution. This was factored into the subsequent analysis of waste volumes in Section 5.

A relatively simple process of removing I_2 dissolved in caustic aqueous solutions, should they be used to remove I_2, is with the in situ synthesis of mineral analogs of layered (hydrotalcite-like) bismuth-iodine-oxide waste forms (Krumhansl and Nenoff 2011) or iodide or iodate sodalite (Strachan and Babad 1979). Elemental iodine dissolves in NaOH as NaI (I^-) and $NaIO_3$ (IO_3^-). Thus, quite high concentrations can be achieved. These processes do not require advanced separation and isolation of the iodine from the caustic. In the case of the bismuth process, the final product contains 15–20 mass % I; in the case of sodalite, it contains 22 mass % (iodide form) and 20 mass % (iodate form).

Chemisorption

Various types of adsorbents for iodine have been studied and developed over the years. Natural or artificial porous materials, such as zeolite, mordenite, alumina, and silica gels, have been loaded with metals (such as Ag, Cd, Cu, and Pb) or the metal nitrate (e.g., $AgNO_3$) and studied. Commercially available inorganic sorbent materials include silver-exchanged faujasite (AgX), modenite (AgZ), and silver-impregnated silicic acid (i.e., AC-6120 that is no longer commercially available).

The development of AgX and AgZ has been conducted primarily in the United States and has not advanced beyond laboratory tests for ^{129}I recovery. The leading approach to capture radioactive gaseous by-products such as I_2 during nuclear fuel reprocessing involves sorption onto silver-loaded zeolite (AgZ). Silver-loaded zeolite has been studied for radiological I_2 capture for several decades. However, the molecular basis of AgZ performance has been largely unexplored until recently (Haefner and Tranter 2007; IAEA 1987; Kok 2009; Chapman et al. 2011; Krumhansl et al. 2011). Generally, AgZ is believed to benefit from a high Si-to-Al ratio that enhances stability in acidic waste streams and relatively high Ag contents (IAEA 1987; Kok 2009).

A review by Thomas et al. (1978) indicated I_2 loadings on AgX or AgZ ranging from 80 to 200 mg/g could be achieved while maintaining DFs in the range of 100 to 10,000 for I_2. While effective for removing I_2 from gas streams, the AgX substrate decomposed in the presence of NO_x and water vapor. Therefore, a more acid-resistant substrate was desirable for use in the DOG application.

The AgZ sorbent was selected for application in DOG streams because of its high acid resistance. Elemental iodine loadings on AgZ of 170 mg/g (Staples 1976; Thomas et al. 1978) and typical iodine loadings from methyl iodide (CH_3I) were 140 to 180 mg/g in tests with simulated DOG streams (Jubin 1982; Scheele and Burger 1982). Methyl iodide was a stand-in for the various unknown organic iodides that could be present in the DOG. The base material for the adsorbent was a binderless synthetic mordenite produced by Norton Chemical Process Products Corp (Tallmadge, OH). The silver content in the AgZ was ~18 mass %. Commercial production of AgZ ceased many years ago. A similar material became available but was made from a natural mordenite with a binder. Silver loadings were 9.5 to 11 mass %. Loadings of ~90 mg/g (350 mmol/kg) have been reported in thin bed studies at ORNL for freshly reduced Ag^0Z (Jubin et al. 2012b). The lower loadings correspond to the lower silver content. Aging of the material potentially reduced the loading by a factor of two (Jubin et al. 2012a). Recent deep bed studies at Idaho National Laboratory (INL) have shown iodine loadings on the inlet bed of up to 5 mass %, or 50 mg/g (200 mmol/kg), while achieving total bed DFs of 1000 to 10,000 (Soelberg and Watson 2012, 2014). Iodine loadings of 50 mg/g were used here to calculate the mass and volume of AgZ form reported below.

Liquid scrubbers

A variety of liquid scrubbers have been developed for radioiodine control. The principal ones were caustic scrubbing, Iodox, and Mercurex (Hebel and Cottone 1983).

The Iodox technology was developed for application to liquid-metal fast breeder reactor (LMFBR) fuel reprocessing where the spent fuel would have been processed within 180 days of leaving the reactor and would have required high DFs ($>10^4$) to control ^{131}I releases (Birdwell 1990; Goumondy et al. 1981). Decontamination factors up to 10^6 were obtained in cold engineering tests. The method appeared to be about equally efficient for both elemental and organic forms of iodine (as CH_3I). The process used 20–22 M HNO_3 in a bubble cap column to recover the iodine as HI_3O_8. The process required secondary steps to concentrate 13 M HNO_3 to 22 M, recycle and concentrate acid diluted by moisture in the DOG, and concentrate the waste stream to the solid anhydroiodic acid (ERDA 1976). The iodine could also be recovered as $Ba(IO_3)_2$. The postulated iodine-trapping reactions involved were (IAEA 1987)

$$I_2 + 4HNO_3 \leftrightarrow 2I^+ + 2NO_3^- + N_2O_4 + 2\ H_2O$$

and

$$I^+ + 3HNO_3 + NO_3^- \leftrightarrow IO_3^- + H^+ + 2N_2O_4 + H_2O.$$

Organic iodides were converted according to

$$CH_3I + 2HNO_3 \leftrightarrow CH_3NO_3 + ½I_2 + ½N_2O_4 + H_2O.$$

When the iodine waste was concentrated to the solidified form, the ^{129}I and fission product halogen waste volume from an 800-tHM/year FRP would have been about 0.15 m^3/year. The use of cement for immobilizing iodine waste from the Iodox process was investigated (ERDA 1976). Up to 9 mass % of iodine could be incorporated as $Ba(IO_3)_2$. About 1.5 m^3 of cement was required to immobilize 0.15 m^3 of fission product halogens.

The Mercurex process was also developed for the treatment of the DOG evolved during the processing of very short cooled fuels where very high DFs are required ($>10^5$) (Goumondy et al. 1981). A mercuric nitrate–nitric acid solution in a packed or bubble cap column is used to recover the iodine as HgI_2 or $(HgIO_3)_2$. Mercurex was used at Dounreay, Great Britain, and was considered for use in the Nuclear Fuel Services at West Valley, New York, and at the Allied-General Nuclear Services plant at Barnwell, South Carolina (Hebel and Cottone 1982).

In the Mercurex process, gaseous iodine was absorbed in a $Hg(NO_3)_2$–HNO_3 solution to form mercury iodate and iodide complexes. Unger et al. (1970) reported that at low nitric acid concentrations, the DF for organic iodides was low. Nakhutin et al. (1980) reported that iodine trapping was improved by increasing the nitric acid concentration, while increasing the temperature from 50 to 70°C or decreasing the mercuric nitrate concentration was detrimental. Elemental iodine and CH_3I DFs of 1000 to 5000 and 100, respectively, were obtained at 50°C. Decontamination factors of 500 for CH_3I in a 1.7-m packed column were demonstrated in Belgium (Goosssen and Baetsté 1980; IAEA 1980a). At acid concentrations in the range of 12–14 M, DFs $>10^5$ were reported (IAEA 1987).

The reactions involved are (IAEA 1987; Trevorrow 1983)

$$6I_2 + 6Hg(NO_3)_2 + 6H_2O \leftrightarrow 5HgI_2 + Hg(IO_3)_2 + 12HNO_3$$

and

$$CH_3I + 0.5Hg(NO_3)_2 \leftrightarrow 0.5HgI_2 + CH_3NO_3$$

or

$$CH_3I + 0.5Hg(NO_3)_2 + H_2 \leftrightarrow 0.5HgI_2 + CH_3OH + HNO_3\ .$$

As written, the mercuric-iodine salts precipitate. However, in practice, the CH_3I formed stable soluble complexes.

Mercurex was applied at an industrial scale at the Dounreay FRP with a reported DF of 150 (Hebel and Cottone 1982). Two scrubbers in series were installed in the Allied-General Nuclear Services Barnwell FRP. The claimed DFs were 10–75 (IAEA 1987). However, this plant was never placed in service.

Mercurex was also proposed for the Nuclear Fuel Services West Valley FRP when increasing its capacity to a planned DF of 32. The iodine-laden liquid waste stream from a Mercurex process was estimated to be about 4.3 m^3 of mercury-containing liquid waste per year from an 800 tHM reprocessing plant (Goosssen and Baetsté 1980; IAEA 1980a).

Aerogels

Aerogels are being considered for the removal of iodine compounds from the off-gas of the reprocessing plant. Aerogels are a class of materials that have high cross-linking of the SiO_2 matrix, thereby generating a material with high specific surface areas (>1200 m^2/g) and high porosity (Reynes et al. 2001; Woignier et al. 2000; Woignier et al. 1998). Two aerogel materials are being considered: Ag-functionalized silica aerogels (Ag^0-aerogel) and chalcogels.

As with AgZ, aerogels can act as precursors to the final glass matrix in which the waste is actually immobilized (Woignier et al. 2000). The porous network of silica aerogel has been used as a host matrix for nuclear wastes (Reynes et al. 2001). Silica aerogels are made with sol-gel processing from a silica precursor followed by supercritical drying in CO_2. However, drying at ambient pressures can be used as an alternative and more practical approach to maintain the solid network (Brinker and Scherer 1990; Land et al. 2001; Parvathy et al. 2005). The silica aerogels are available commercially in granular or monolithic forms. The Ag^0-aerogel considered here was synthesized using a three-step process (Matyáš et al. 2011): (1) functionalization of pore surfaces of silica aerogel granules with propylthiol monolayer, (2) installation of Ag^+ on the thiol monolayer interface by treatment with $AgNO_3$ solution, and (3) reduction of Ag+ under flowing 2.7% H_2 to produce Ag^0 nanoparticles. The produced Ag^0-aerogel is in the form of granules larger than 0.85 mm with a surface area of ~150 m^2/g, pore volume of ~0.5 mL/g, and bulk density of ~500 kg/m^3. The material is relatively friable. Iodine capacities of Ag^0-aerogel up to 480 mg/g were measured with DFs over 10,000 for laboratory tests with simulated DOG gas streams (Matyáš et al. 2011; Soelberg and Watson 2012). Subsequent to the sorption of I_2 onto the Ag-aerogel, desorption of the material in flowing air without I_2 showed that the loaded Ag-aerogel contained very small amounts (<1%) of physisorbed I_2. In addition, silver-functionalized silica aerogel retained high selectivity and sorption capacity for iodine even after a long-term exposure to dry/humid air and dry air containing 2% NO_2. Aging of this material in dry or humid air over a period of 6 months resulted in a decrease in iodine sorption capacity of 22 relative % (Bruffey et al. 2012; Bruffey et al. 2013). Aging for 4 months in dry air containing 2% NO_2 decreased iodine sorption capacity by 15 relative % (Jubin et al. 2014).

As received, silica aerogel has a bulk density of approximately 20–100 kg/m^3; after functionalizing and loading with I_2, the density can be as high as 4×10^3 kg/m^3. For this study an iodine loading of 35 mass % will be used and a final density of 3.3×10^3 kg/m^3.

The second aerogel is called chalcogel. Chalcogels are aerogels made from S-, Se-, or Te-bearing starting materials that are caused to crosslink in the presence of certain metal ions, such as Pt and Cu (Kanatzidis and Bag 2008). These aerogels also have very high surface areas and porosities, but they do not need to be functionalized. In the case of the chalcogel, the iodine compounds are soluble in the matrix of the material. Because of this, the chalcogel waste loadings are quite high: 100 to 200 mass % relative to the starting material and 50 to 75 mass % I_2 in the final product (Riley et al. 2011). Chalcogels are in an early stage of development and are not available commercially.

Metal-organic frameworks

Metal-organic framework (MOF) structures are viewed by many as the next-generation porous materials with promising applications in many areas (Lee et al. 2009; Long and Yaghi 2009). Gas sorption is the main focus of many MOF studies (Férey et al. 2011; Zhao et al. 2008) because of their high adsorptive capacity associated with very large surface areas and porosity (Furukawa et al. 2010; Koh et al. 2009). At the same time, studies of gas separation are also becoming more widespread given that MOF structures are highly tunable towards specific applications (Li et al. 2009).

The MOFs ZIF-8 and HKUST-1 were selected from a broad library of MOF materials with potential to remove molecular I_2 because of their suitable pore aperture, large specific surface area, and high chemical and thermal stability.

Recent efforts to convert the powder form of ZIF-8 into an engineered form more suitable for use in nuclear fuel reprocessing applications show promise (Sava et al. 2012). Nitrogen sorption isotherms show that there is no change in the porosity upon conversion to extruded pellets. The I_2 sorption behavior of the pellets matched the results of the powdered material. Iodine loadings of up to 55 mass % in static tests have been observed for ZIF-8 (Sava et al. 2011). In these static loading tests, the iodine concentration in the gas phase was $\sim 1.4 \times 10^4$ ppmV. However, a sample of ZIF-8 was tested for iodine separation in flowing gas stream in a thin bed configuration (Jubin 2012) and iodine concentrations of ~30 ppmV. Three tests were performed with between 2.6 and 3.4 mass % iodine uptake. For this study, a loading of 3 to 50 mass % will be used.

Scoping studies with Cu-BTC (HKUST-1) a large-pore MOF with accessible metal centers for direct I_2-Cu interactions showed loading of I_2 (up to 64 mass %) in static tests even in the presence of water vapor (Sava et al. 2013). This material class is being heavily studied worldwide for fuel gases, such as H_2, CO_2, and CH_4 storage, but remains in the early development stage for iodine species. However, it has not yet been tested for iodine uptake in a dynamic (flowing) system.

The as-received density of ZIF-8 is 0.35×10^3 kg/m^3 and HKUST-1 0.89×10^3 kg/m^3. Fully loaded with I_2, (from the static tests) these materials have densities of 0.77×10^3 kg/m^3 and 2.4×10^3 kg/m^3, respectively. For this study a density of 1.5×10^3 kg/m^3 is used.

Irradiation experiments were carried out to obtain preliminary information on the radiation stability of these MOF materials. Iodine-loaded specimens of ZIF-8 were exposed to 2590 Gy (2.59×10^5 Rad) of ^{60}Co radiation. No reduction in crystallinity was evident at this exposure. Self-irradiation studies have yet to be performed.

4. WASTE FORMS

A number of waste form technologies are currently being developed for the immobilization of the volatile radionuclides for storage or disposal. However, the waste form may need to be tailored for specific isotopes to ensure regulatory requirements can be met.

One waste form that has potential for the immobilization of all four volatile radionuclides is silicon carbide (SiC). It is discussed in general in this section and called out in each of the subsections to follow. Because of the low diffusivities for fission products in and superior physical and chemical stability of SiC, it is a candidate for immobilization of C, Kr, I, and Xe (and perhaps other fission products).

Silicon carbide possesses physical and chemical properties that make it a promising material for many uses, not only for advanced electronic devices (Raynaud 2001) but also for structural components in fusion reactors (Fenici et al. 1998; Nogami et al. 2009; Zhao et al. 2007; Wong et al. 2007; Katoh et al. 2007), as a barrier for fission product diffusion in gas-cooled fission reactors (Kim et al. 2000), and as an inert matrix for the transmutation of plutonium and other transuranics (Verrall et al. 1999; Krstić et al. 1996). The high thermal conductivity of SiC also enhances homogeneous heat distribution that facilitates the dissipation of radiodecay heat. Unlike traditional semiconductor materials, thermal diffusion of dopants in SiC requires extremely high temperatures because of the extremely low diffusivities for impurities in SiC. This low diffusivity for impurities is one of the reasons SiC is used as the fission product barrier in tri-structural-isotropic (TRISO) nuclear fuel. Its use for this application has been demonstrated at temperatures over 2000°C (Schenk and Nabielek 1991; Schenk et al. 1990; Nabielek et al. 1990). Thermal release of He generated in neutron-irradiated SiC does not occur until temperatures above 1400 °C (Sasaki et al. 1991; Sasaki et al. 1989). Because of its low chemical reactivity, SiC is also proposed as cladding for advanced LWRs (Filippov et al. 2007a,b; Filippov et al. 2006). A recent discovery of pitting corrosion in β-SiC at 300˚C, however, indicates that it may be susceptible to low-temperature corrosion involving volatile SiOH (Henager Jr et al. 2008). Although pits in SiC were observed in this study, no measurable mass loss occurred for exposure times up to 4000 hr. While oxidation of SiC occurs at elevated temperatures, such oxide films generally form a barrier to further oxidation and should be negligible under repository conditions (Opila 2003). Silicon carbide also occurs in nature as the extremely rare mineral moissanite (Bauer et al. 1963; Di Pierro et al. 2003). Silicon carbide crystals of interstellar origin have been found in primitive meteorites (Alexander et al. 1990). These natural occurrences support its physical and chemical stability.

Since industrial-scale fabrication of SiC monoliths with physical vapor deposition methods is a well-established technology (Abe et al. 2008; Jiangang et al. 2006; Saddow et al. 2001; Moon et al. 2001; Sugiyama et al. 1998), there is little, if any, technology development needed to produce dense, pure SiC. While there are many polymorphs of SiC, the cubic 3C structure is preferred for nuclear and structural applications, such as ceramic composite fibers and matrices and fine-grained coatings for TRISO nuclear fuel particles. Much of our knowledge of diffusivities of nuclear isotopes in SiC comes from studies of TRISO fuel particles (Peterson and Dunzik-Gougar 2006; Schenk et al. 1984; Smith 1979; Fukuda and Iwamoto 1978, 1976, 1975).

In the following subsections, waste forms for each of the four volatile radionuclides are discussed.

4.1 Tritium Waste Forms

Two conversion paths are possible for the tritiated water captured on molecular sieves. In one path, the molecular sieves are regenerated for reuse with temperature swing regeneration of the beds and dry nitrogen as the purge gas. The tritiated water is then condensed to a liquid from the purge gas. The recovered tritiated water can then either be reclaimed with further purification as a beneficial by-product or mixed with grout for disposal. The decay product of ^{3}H is ^{3}He, a valuable resource for neutron detection and in short supply (Kouzes et al. 2010). Alternatively, the tritiated water-laden molecular sieves may be disposed of directly before being regenerated. In this case, the tritiated water-laden molecular sieves would be mixed with grout for final disposal.

A reasonable disposal path includes mixing either the loaded molecular sieves and water, or the recovered tritiated water, with grout and placing the grout in stainless steel drums, sealing the drums, and burying the drums. The relatively short half-life of ^{3}H (12.3 years) ensures that it decays to safe levels before the packaging deteriorates. Grouting is a well-developed technology for stabilizing a variety of waste forms. No problems are anticipated for the disposal of a purified ^{3}H-bearing water stream. However, because the molecular sieves also sequester small amounts of iodine (^{129}I) and carbon dioxide (^{14}C), the method should be evaluated for the effect on a grout waste form and options need to be identified or developed to cleanly separate the water from these other species. Spencer et al. (2013) developed a flowsheet for the management of both iodine and ^{3}H in the tritium pretreatment off-gas (TPTOG). The TPTOG is first passed through an iodine absorber, which removes iodine and some of the tritiated water from the TPTOG. This iodine-free stream then passes through the 3AMS bed used to trap the tritiated water. The water sorbed on the iodine trap can then be desorbed by flowing dry air at an elevated temperature prior to iodine waste form fabrication. Continuing in this manner appears to make a clean separation of iodine to AgZ and water to 3AMS (Spencer et al. 2013; Spencer et al. 2014).

Assuming a grout mix containing H_2O at 30 mass % and a grout density of 2.3×10^3 to 3.4×10^3 kg/m^3 (2.3×10^3 kg/m^3 as a conservative value), the resulting grout volume is ~0.01 L/tHM. If the loaded sorbent is grouted directly with an 11 mass % loading of tritiated water and H_2O on the 3AMS and a grout loading of 25 mass %, the resulting waste volume from UNF processing is ~0.1 L/tHM. Although no specific studies have been carried out on the use of SiC for immobilization of ^{3}H, incorporating H_2O into the SiC matrix is identical to incorporating any other gas; the SiC matrix would be laid down on a substrate from an atmosphere containing tritiated water vapor or tritiated hydrogen gas. The low diffusivity of SiC would limit the release of ^{3}H as would the low dissolution rate of the SiC matrix. Specific studies are, however, lacking and needed if SiC is to be developed as a viable waste form for ^{3}H. The total water loading is assumed to be 5 to 10 mass % with a density estimated to be similar to that of pure SiC 3.2×10^3 kg/m^3.

Co-adsorption of $^{14}CO_2$ on the 3AMS has not been evaluated, but this is not currently envisioned to result in any operational or waste management problems, especially in the case of tritiated water desorption. When the filter bed reaches capacity, it can be taken off line and heated to remove first the CO_2 and then the H_2O. These can then be routed separately to an immobilization process.

4.2 ^{14}C Waste Forms

In the current state-of-the-art process scheme, CO_2 is removed from the off-gas stream in a caustic scrubber and precipitated with the addition of Ba, probably as slaked BaO, to precipitate $BaCO_3$.

Limited studies have been conducted on the direct conversion of the $BaCO_3$ into a waste form. Grandjean and Leturcq (2005) have shown that pure $BaCO_3$ does not sinter optimally. They suggest an equimolar mixture of $BaCO_3$ and $CaCO_3$, i.e., $Ba_{0.5}Ca_{0.5}CO_3$. While not achieving full density, the materials do reach about 90% of the theoretical density (3.5×10^3 kg/m^3), which is just sufficient to close off most, if not all, of the surface connected pores (Shaw 1998). Carbon only represents ~8 mass % of this waste form. The actual ^{14}C loading would be much lower because of the large amount of nonradioactive C that is captured along with the ^{14}C and incorporated into the actual waste form. While carbonates have very low solubilities, the dissolution rates are high relative to most silicate mineral phases (Scislewski and Zuddas 2010; Grandjean and Leturcq 2005). Therefore, depending on the disposal method and repository, a mixed $BaCO_3$-$CaCO_3$ solid may not have the durability to limit the release of ^{14}C to the regulatory limit.

Most of the carbon immobilization studies conducted to date have considered calcium or barium carbonate that has been mixed with cement and packaged in steel drums. Results from leach tests conducted by Scheele and Burger (1982) indicate that ~1% of the ^{14}C would be released in 1000 years. Carbonate loadings of 2.5 mol/kg of dry cement (~4400 mol/m^3) were tested. At these loadings, a waste volume of 8.5 L/tHM for processed UNF would be produced for disposal.

Although MOF technology is being investigated for CO_2 removal from coal power plant stack gases (Keskin et al. 2010), it is unlikely that they can be used for immobilization. While the storage density (kg of immobilized isotope per m^3 of storage and assuming a storage density of 25 mass% CO_2) is comparable to grouted barium carbonate, the current cost of the MOF may be too high relative to Ca or Ba carbonates to be considered as a viable waste form. It does not appear that there have been any measurements on the density of a MOF with gas captured in it. However the crystal density of a MOF is in the range of 1.2 to 1.8×10^3 kg/m^3, and the packing density of the MOF is 0.6×10^3 kg/m^3 (particles of

200 μm). Based on this, an estimated packed density of a fully loaded MOF is ~0.8×10^3 kg/m^3. Additionally, they are currently developed to have low heats of adsorption so that they are easily regenerated. For use in the process of carbon sequestration, they are used primarily to remove CO_2 from the stack gases, after which the CO_2 is desorbed and sequestered by some other means. Although an economic analysis has not been performed, it is unlikely that a MOF-based process for removing CO_2 from process off-gas is less expensive or operationally less intensive than caustic scrubbers. For this analysis, a CO_2 loading in a MOF of 10 mass % is used.

As mentioned above, SiC has physical and chemical properties that make it a strong candidate for the immobilization of several radionuclides. As with other gaseous radionuclides, depositing SiC from a vapor in an atmosphere containing $^{14}CO_2$ would result in the incorporation of the ^{14}C into the SiC matrix thereby immobilizing it. While specific studies for the incorporation of CO_2 into SiC have not been carried out, results from the studies with I and Kr suggest that the results would be favorable. The CO_2 loading is assumed to be 5 to 10 mass % with a density estimated to be similar to that of pure SiC of 3.2×10^3 kg/m^3.

4.3 Immobilization of ^{85}Kr and Waste Forms

Several methods to store captured Kr gases have been studied. These range from storage in compressed gas cylinders to ion implantation in a metal matrix.

Hebel and Cottone (1983) point out that containers must adequately address the following conditions: remain intact for ~100 years; resist corrosion due to the in-growth of Rb, which is chemically aggressive; and dissipate the decay heat. Rubidium metal has a low melting point (38.9 °C) and is highly corrosive toward other metals (Pinchback et al. 1981). Thus, as the ^{85}Kr decays to stable Rb, the likelihood of significant corrosion increases. Low-pressure (assumed 0.1 MPa) cylinders are attractive from the standpoint of reducing the risk of large gas releases in the event of corrosion-assisted rupture of a cylinder. However, the trade-off is storage volume. The use of higher pressure (5 MPa or higher) cylinders reduces the volume with a concomitant increase in the probability of leakage or cylinder rupture caused by Rb corrosion. Storage in compressed gas cylinders provides easy recovery of the nonradioactive Kr for subsequent industrial use once the ^{85}Kr has decayed to acceptable levels, but it also increases the hazard of a release of ^{85}Kr.

The decay of ^{85}Kr also results in radio-decay heat generation of 0.0015 W/Ci. While this appears to be relatively small, a single gas cylinder at 5 MPa containing just the Kr from the 60 GWd/tIHM fuel cooled 5 years would generate 230 W. Further aging of the fuel prior to processing and dilution from any Xe in the captured gas that was not separated from the Kr would reduce the decay heating of a gas cylinder assuming the same loading pressure for the cylinder.

Because MOF materials have a high capacity for Kr and Xe, it has been proposed by Mueller and coworkers (2006) that by loading the gas cylinder with an appropriate MOF material the loading capacity for ^{85}Kr-bearing gases could be increased while maintaining the same cylinder pressure. For this study, an increase in capacity of 1.44 times that of non-MOF loaded gas cylinders is assumed. While the stability of a MOF under pressure has been shown (Wang et al. 2009), it is unclear if all MOF materials share this stability, and the long-term effects of radiation are unknown.

As noted above, as the ^{85}Kr decays, the likelihood of corrosion increases. It has been proposed that this risk can be reduced if the Rb decay product can be isolated from the cylinder walls. Wang et al. (2009) showed that Kr is incorporated within the dodecahedral cage of the MOF. Because ^{85}Kr is trapped in the MOF cage, the decay product ^{85}Rb should also be trapped there (Wang et al. 2009) and therefore isolated from the cylinder wall. There are many unknowns for this potential application. Information on the stability of the MOF with respect to radiation and the decay of a neutral Kr atom to the ion Rb^+ has not been developed. If stable with respect to radiation, their ability to contain both the Kr and the decay Rb at the increased temperatures caused by decay heat is still to be demonstrated.

Encapsulation in a metal matrix has been explored in the United States, United Kingdom, and Germany (Whitmell 1985; Taylor 1990; Knecht 1977; Hayashi 1999). The sputtered metal matrix would contain 5-6 atom% Kr. The product is an amorphous glassy deposit. Depending on the process used, loadings of Kr in the metal matrix would be 16-25 L/kg at STP could be achieved.

Studies have shown that Xe and Kr have extremely low mobility in SiC at low temperatures and only become mobile above 1200 ˚C (Fukuda and Iwamoto 1978, 1976, 1975). The low diffusivities for otherwise very mobile atoms, such as He (Sasaki et al. 1991; Sasaki et al. 1989), suggest by extrapolation that Kr should be equally immobile in a SiC matrix. Preliminary estimates for the encapsulation of Kr into a SiC sputtered matrix assume that loading of ~10 mass% can be achieved. The product density is 2.9×10^3 kg/m^3. If Xe and Kr are not separated from each other, this results in the production of 94 kg of waste with a process volume of 0.032 m^3/tHM. If only the Kr is encapsulated, the mass and volumes are reduced to 5.8 kg and 0.002 m^3, respectively.

An alternative process for ^{85}Kr storage is encapsulation in a zeolite matrix. Krypton loadings of 50 m^3 at standard temperature and pressure per cubic meter solid are readily achieved at 100 MPa in zeolite 5A at 700°C. The Kr is encapsulated in the zeolite structure by a sintering process where the pores of the zeolite are sealed. The relatively low thermal conductivity of the zeolite should be considered and may limit the maximum loading of the zeolite (Penzhorn et al. 1980).

In the late 1970s, an R&D effort to study Kr-85 encapsulation into zeolite 5A followed by hot isostatic pressing was performed at the INL by Christensen, et al (1982; 1983). Krypton loadings of 30 to 60 m^3 at standard temperature and pressure per cubic metre solid were achieved. The resulting product was amorphous.

Waste volumes for Kr range from ~150 L/tHM to <1 L/tHM, depending on the stabilization method selected.

4.4 Solid Waste Forms for ^{129}I

The disposition of ^{129}I-bearing wastes is currently assumed to be in a geologic repository as high level waste. A number of possible immobilization forms for iodine have been suggested. However, the disposition pathway for these iodine containing waste forms considering the 1.6×10^7-year half-life of ^{129}I in something other than a high level waste form is yet to be resolved.

The spent, iodine-loaded, Ag- sorbents may constitute a suitable immobilization form that requires minimal processing and packaging. Bulk density of the AgZ is ~850 kg/m^3. This has been proposed for AC6120 (Wilhelm and Furrer 1977) and may also apply to the zeolite waste forms (Burger et al. 1981). Existing requirements for a US geologic repository require that the waste form not be a powder (DOE 1996). This suggests that the Ag-containing materials from iodine removal bed would need to be consolidated.

One possible stabilization package for iodine is based on the incorporation of the iodine-loaded AgZ into a grout matrix. Assuming that the AgZ filter housing was designed as a storage package, the iodine-loaded filter would have end caps welded in place, and the sealed filter package would be placed into a secondary over pack. Such systems have been described by Furrer et al. (1978). Grout could be added to the annular space, but this would add little to the overall containment of the ^{129}I. A second approach would be to remove the iodine-loaded AgZ pellets from the filter housing and mix the loaded pellets with grout. The waste volume calculations presented in Section 5 are based on a solid loading of 25 mass % AgZ in the grout. The AgZ is loaded with iodine at 50 mg/g (200 mmol/kg). The possibility of cement deterioration over time may time limit its effectiveness as a long-term storage material (Scheele et al. 2002). More studies are needed to determine the adequacy of a AgZ-grout waste form for immobilization of ^{129}I.

The recommended conversion step for the Iodox process is to convert the soluble iodic acid into insoluble $Ba(IO_3)_2$ by simple reaction with $Ba(OH)_2$. Excess $Ba(OH)_2$ should be used to ensure complete removal of the iodine; this excess does not affect the cement stability. In Section 5, a grout loading of 10 mass% $Ba(IO_3)_2$ is assumed for this waste form.

Scientists at CEA worked on the development of synthetic lead-vanadate apatite $[Pb_{10}(VO_4)_6I]$ as an iodine waste form (with an iodine loading of 4.4 mass%) (Fillet 2008). Hot isostatic pressing (HIP) of AgI without zeolite has also been investigated (Maddrell and Abraitis 2004).

Direct conversion of AgIzeolites into a final waste form with the HIP process has been developed by a number of researchers. Hot isostatic pressing with iodine-loaded silver zeolite or silver silica gel and metal (Fukumoto 1998) and iodine-loaded silver alumina sorbents in Pb–Fe-phosphate glass (Perera et al. 2004), along with AgI–zeolite to form sodalite (Sheppard et al. 2006) have also been investigated.

Direct HIP processing of AgI-Z has been attempted at ORNL (Jubin and Bruffey 2014; Jubin et al. 2014) on crushed and uncrushed AgI-Z; results indicated no obvious advantage to crushing. Densities in the range of 2.5 to 2.65×10^3 kg/m^3 were achieved. Under the conditions used in these tests, the majority of the resulting materials were fully amorphous. A density of 2.5×10^3 kg/m^3 will be assumed for volume calculations.

A number of studies have also shown that iodine-loaded silver zeolites can be converted to the alumino silicate mineral sodalite in which the iodine is more strongly bound than in the unprocessed zeolite sorbent (Buhl 1996; Maddrell and Abraitis 2004; Sheppard et al. 2006; Strachan and Babad 1979). Iodide and iodate sodalite that do not contain silver have been successfully synthesized by Strachan and Babad (1979) with theoretical I_2 loadings of about 20 mass % for these materials. Leach test results indicate that it may have sufficiently low dissolution rates to limit the release to that required for a long-term waste form. This material could also be made with HIP. However, more work is needed to fully quantify its performance (Maddrell and Abraitis 2004). The density of the iodide and iodate sodalites is about 2.5×10^3 kg/m^3 (Strachan and Babad 1979).

The use of molten borosilicate glass was found to result in excessive iodine loss at the required processing temperature (Hrma 2010). However, low-temperature melting glasses, such as vanadium or lead oxide-containing glasses, limit the volatility of iodine (Perera et al. 2004) but appear to have relatively low durability. Recently, a glass was formed by melting AgI and $Ag_4P_2O_7$ at 500 °C (Fujihara et al. 1999; Noshita et al. 1999; Sakuragi et al. 2008). These glasses can contain up to 30 mass % I. The assumed density of the resulting glass is 5.3×10^3 kg/m^3.

Recently, a Bi-oxide-based glass has been identified that sinters at low temperatures. A Glass Composite Material (GCM) was developed as a waste form to immobilize AgI or AgI-Z (Garino et al. 2011). Initially, GCM was sintered in air at ~ 550°C for 1 hr. In studies with AgI, at least 25 mass % AgI was incorporated into the GCM (14 mass% I_2). Based on the published densities of the Bi-oxide glass (Garino et al. 2014) and the 25 mass % loading of AgI, the estimated density of the AgI-GCM was 5.7×10^3 kg/m^3. In studies with iodine-loaded AgZ containing up to 25 mass % iodine-loaded AgZ (containing ~9 mass% iodine) has been incorporated in the GCM (Nenoff et al. 2014), which correlates to about 2 mass% I_2 in the final product.

To minimize the loss of iodine during the processing of the iodine-loaded AgZ GCM, additional silver flake was added to the starting mixture of powders. For a GCM waste form containing iodine-loaded AgZ (8.7 mass% iodine loading), only 1.1 mass% Ag flake was needed (Garino et al. 2014). The final GCM composition prior to sintering was 19.8 mass% iodine-loaded AgZ, 1.1 mass% Ag, and 79.1 mass% Bi-Si oxide glass. This waste form has an iodine loading of 1.7 mass% and a density of 4.3×10^3 kg/m^3. Garino et al. (2014) also noted that sintering the iodine-loaded AgZ and GCM mixture in inert atmosphere (instead of air) required no additional Ag flake and produced a final GCM without I_2 loss.

The chemical durability of this product has been measured with the single-pass flow-through method under dilute conditions (Nenoff et al. 2012). Iodine was released from GCM at less than 8.8×10^{-6} g/(m^2·d) at 25 °C and pH = 3 and pH = 8. At the test conditions, Bi-Si-Glass dissolved at rates similar to, and possibly lower than, traditional nuclear waste glasses. Temperature had a relatively small effect on the glass dissolution rate; the maximum glass dissolution activation energy was 30 kJ/mol.

In recent work performed at PNNL, two classes of materials have been studied – silver-functionalized silica aerogel and chalcogels. To convert the iodine-loaded Ag-silica aerogel to a waste form, rapid consolidation, a physiochemical feature of aerogels, at moderate temperatures and pressures yields a final waste form consisting of AgI encapsulated in fused silica. Densification with hot isostatic pressing at 1200 °C for 30 min under 207 MPa resulted in a fully dense silica-based waste form of 3.3×10^3 kg/m^3 bulk density containing ~22 mass% of iodine. Iodine was retained in the form of nano- and micro-inclusions of AgI dispersed in the silica matrix(Matyáš and Walters 2015). Iodine retention of >92% has been demonstrated in the hot uniaxial pressed sample (Matyáš et al. 2011). The durability of the waste form is expected to be controlled by the dissolution of the fused silica to expose the AgI particles, and by the solubility of AgI. Fused silica durability has been studied by many researchers and is significantly higher than that of typical borosilicate waste glasses. Densities are expected to be $>3 \times 10^3$ kg/m^3.

The second aerogel is a chalcogel. Waste loadings of 67 mass% have been observed with rapid sorption kinetics (Strachan et al. 2010; Riley et al. 2011). For this study a mass load of 50% will be assumed. This material can be further consolidated to obtain a nearly fully dense material (ca 3×10^3 kg/m^3) with little surface-connected porosity (Strachan et al. 2010). The chalcogel density is $\sim 3 \times 10^3$ kg/m^3, and when fully loaded with iodine the density is about 5×10^3 kg/m^3.

As discussed above, SiC is a well-studied material for a nuclear fuel matrix (Peterson and Dunzik-Gougar 2006; Smith 1979). By depositing SiC from the vapor state in an atmosphere containing the separated iodine compounds, the iodine compounds can be isolated and, thus, immobilized in an inert matrix. Work on the immobilization of iodine compounds has not been initiated, but a presentation was made by Ryan et al (2011) on the use of SiC as an immobilization matrix for I and Kr. Very low thermal diffusivities were found for both I and Kr; SiC is thermodynamically and kinetically very stable with expected very low (lower than borosilicate glass) dissolution rates. Waste loadings for iodine are assumed to be 10–15 mass%. The density of the iodine-loaded SiC is assumed to be 3.4×10^3 kg/m^3.

5. WASTE ESTIMATIONS AND WASTE FORM VOLUMES/MASSES

Waste volumes for each of the four primary volatile radionuclides have been estimated. A limited number of alternate waste forms and waste loading have been considered. Table 13 provides a summary of the final waste form loadings and volumes for each of the radionuclides of interest. Waste loadings have been calculated based on the composition of the final loaded waste form. In all cases, the volume and mass of the waste package have not been included. These assume that all of the volatile species in the fuel have been captured and immobilized. When "tramp" species are included, they are assumed to be incorporated at the same molar concentration as that of the element or isotope that originated in the fuel. So, for example, if the iodine loading on AgZ is 50 mg/g (200 mmol/kg) and there is an equal molar amount of Cl to be incorporated, the resulting effective iodine loading would be 25 mg/g (100 mmol/kg), since the half of the silver is consumed by the Cl. Little or no engineering margins were built into these estimates, and they should be considered minimum volumes.

Table 13. Waste volumes for radioactive gas components and potential waste form problems.

Component	Form	Loading	Volume (m^3/tIHM)				
			Low Burnup Long Cooled[1]		High Burnup Short Cooled[2]		
			Fuel Only	Fuel + Tramp[3]	Fuel Only	Fuel + Tramp	Comments
Tritium	Drum storage of HTO/H_2O	100% (water only)	1.30×10^{-6}	8.54×10^{-6}	2.682×10^{-6}	9.92×10^{-6}	Liquid storage
Tritium	Grouted HTO/H_2O	30 mass% HTO/H_2O	1.88×10^{-6}	1.24×10^{-5}	3.89×10^{-6}	1.44×10^{-5}	Added complexity
Tritium	Grouted HTO/H_2O-loaded sorbent	25 mass% sorbent loaded at 0.11 g/g	2.05×10^{-5}	1.35×10^{-4}	4.24×10^{-5}	1.57×10^{-4}	Sorbent cost, Added solids handling, Volume increase
Tritium	Co-deposited in SiC	5-10 mass% (Assume 5%)	8.10×10^{-6}	5.34×10^{-5}	1.68×10^{-5}	6.20×10^{-5}	This is based on the estimated density of 3.2×10^3 kg/m^3 and waste loading
Iodine	Drum of iodine-loaded AgZ	50 mg/g (assumes other halogens are included in the iodine loading on a mole for mole basis)	~0.00436	~0.0175	~0.00842	~0.0216	Loose particle in package, Loss of Ag
Iodine	Grouted AgZ	50 mg/g—25 mass% sorbent	~0.00645	~0.02595	~0.0124	~0.0319	Solids handling, Loss of Ag
Iodine	Grouted $Ba(IO_3)_2$	10 mass% iodine	~0.000806	~0.00323	~0.00156	~0.00398	Complexity?
Iodine	Glass	1–20 mol% (Assumed density of ~5300 kg/m^3)	~0.000175–~0.00350	~0.000702–~0.0140	~0.000338–~0.00675	~0.000865–~0.0173	Is regeneration of AgZ required? High temperatures may revolatilize iodine

Iodine	Metal Organic Framework	3–50 mass%	2.47×10^{-4}– 4.12×10^{-3}	9.92×10^{-4}– 1.65×10^{-2}	4.77×10^{-4} – 7.96×10^{-3}	1.22×10^{-3}– 2.04×10^{-2}	Radiation stability of the MOF
Iodine	Sodalite	20 mass%	3.71×10^{-4}	1.49×10^{-3}	7.16×10^{-4}	1.83×10^{-3}	
Iodine	Silicon carbide	10–15 mass% (assumed 10%)	5.45×10^{-4}	2.19×10^{-3}	1.05×10^{-3}	2.70×10^{-3}	Waste form has not been demonstrated
Iodine	Glass Composite Matrix (GCM) – Iodine loaded AgZ	25 mass% iodine loaded AgZ	0.00345	0.0138	0.00666	0.0170	Durability and leach resistance testing underway
Iodine	GCM – AgI	25 mass% AgI	2.57×10^{-4}	9.59×10^{-4}	4.62×10^{-4}	3.27×10^{-3}	Durability and leach resistance has not been demonstrated
Iodine	HIP iodine-loaded AgZ	50 mg/g	1.48×10^{-3}	5.95×10^{-3}	2.86×10^{-3}	7.33×10^{-3}	Very limited development
Iodine	Consolidated Silver-functionalized silica aerogel	30 to 45mass% (assumed 35%)	1.60×10^{-4}	6.44×10^{-4}	3.10×10^{-4}	7.93×10^{-4}	Very limited development
Iodine	Consolidated Chalcogels	50–67 mass% (assumed 50%)	7.41×10^{-5}	2.97×10^{-4}	1.43×10^{-4}	3.67×10^{-4}	Very limited development
Krypton	Low-pressure cylinder	0.1 MPa	0.0.802 (1.83 Type 1A cylinders)	0.0.844 (1.93 Type 1A cylinders)	0.165 (3.77 Type1A cylinders)	0.169 (3.86 Type1A cylinders)	Volume
Krypton	High-pressure cylinder	>5 MPa	0.00161 at 5 MPa (51.8 W/cylinder)	0.00169 at 5 MPa (49.3 W/cylinder)	0.00330 at 5 MPa (230 W/cylinder)	0.00338 at 5 MPa (225 W/cylinder)	Corrosion due to Rb, Pressure, Heat dissipation
Krypton	Zeolite	50 m^3/m^3 solid	0.00161	0.00169	0.00330	0.00338	High-temperature/ high-pressure operation

Krypton	Ion implantation	20–25 L/kg metal (Assuming Cu-metal matrix)	0.000450	0.000473	0.000925	0.000948	Complexity, Higher cost
Krypton	Metal Organic Framework	20–50 mass% [Assume 1.44 X capacity increase based on Mueller et al (2006)]	0.00112 at 5 MPa	0.00117 at 5 MPa	0.00229 at 5 MPa	0.00235 at 5 MPa	Radiation stability of the MOF, pressure, heat dissipation
Krypton	Silicon carbide	10–15 mass% (assume 10%)	0.00105 m^3	0.00110 m^3	0.00216	0.00221	Diffusion of Kr from the matrix at high Kr loadings
Carbon	Co-deposited in SiC	5–10 mass% (Assume 5%)	0.000217	0.0142	0.000425	0.0142	This is based on the estimated density of 3.2×10^3 kg/m^3 and waste loading
Carbon	MOF	Up to 25% (Assume 10%)	0.000434	0.0283	0.000850	0.0284	This is based on the estimated density of 0.8×10^3 kg/m^3 and waste loading
Carbon	Calcium or barium carbonate mixed with cement	19% carbonate (4400 mol/m^3)	0.000179	0.0115	0.000351	0.0117	Volume can be substantially reduced if CO_2 is removed from added cell and process gasses

1) 30 GWd/tIHM cooled 30 y
2) 60 GWd/tIHM cooled 5 y
3) “Tramp” contaminants are those carried by the process chemicals, in-leakage, or other sources of chemicals of like chemical nature to the one being immobilized.

6. CONCLUSIONS

Waste volumes for each of the four primary volatile radionuclides (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I) have been estimated. The resulting waste volume for ^{129}I is highly dependent on the final waste form selected and may be increased by a factor of 2.5 to 4 by tramp halogens that are released into the off-gas stream. The volume of tritiated water ($H^{3}HO$ and $^{3}H_2O$) from the fuel is quite small but is increased by a factor of 4 to 7 by water in the air in-leakage in the head-end processes even at very low humidity (-60 °C dew point). The deliberate addition of water into the TPT off-gas has been suggested as a possible requirement to ensure the recovery of the tritiated water. This could increase the waste volume by another factor of 10. The Kr waste volume was calculated assuming pure Kr, i.e., complete separation from the Xe and Ar. If Xe separation is not performed, the volume is increased by factor of ~10. Argon from the air, if not removed, would increase the Kr waste form volume by a factor of up to 425. The volume of carbon waste is dominated by the CO_2 from the air in-leakage from the processing cell. These estimates do not contain any engineering allowance and should be considered as minimum values.

The analysis reported here does not specifically address many of the potential off-gas streams that may arise in some of the proposed modified open-cycle reprocessing and treatment options. Impacts on gaseous emissions and resulting waste streams should be evaluated as these processes are investigated.

A number of the capture matrices are discussed, and while they appear promising, they still require significant R&D to advance from laboratory- or bench-scale tests to a degree suitable for use in commercial facilities. This should include integrated testing to evaluate the impact and significance of co-adsorption and other process interactions.

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