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RADIOACTIVE SEMIVOLATILES IN NUCLEAR FUEL REPROCESSING

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Idaho National Laboratory

Idaho Falls, Idaho 83415

http://www.inl.gov

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Radioactive Semivolatiles in Nuclear Fuel Reprocessing

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy

R. T. Jubin, D. M. Strachan*, G. Ilas,
B. B. Spencer, and N. R. Soelberg†
Oak Ridge National Laboratory,
*Pacific Northwest National Laboratory
(Retired) and †Idaho National
Laboratory

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SUMMARY

In nuclear fuel reprocessing, various radioactive elements enter the gas phase from the unit operations found in the reprocessing facility. In previous reports, the pathways and required removal of four radionuclides known to be volatile, ^{14}C, ^{3}H, ^{129}I, and ^{85}Kr, were discussed. Other less volatile isotopes can also report to the off-gas streams in a reprocessing facility. In this report, an effort is made to determine which, if any, of 24 semivolatile radionuclides could be released from a reprocessing plant and, if so, what would be the likely quantities released. As part of this study of semivolatile elements, the amount of each generated during fission is included as part of the assessment for the purpose of controlling their emission. Also included in this study is an assessment of the cooling time (time out of reactor) before the fuel is processed. This aspect is particularly relevant to the short-lived isotopes, especially for cooling times approaching 10 years.

The objective of this study was to determine if semivolatile radionuclides need to be included in a list of gas-phase radionuclides for possible removal to meet Environmental Protection Agency (EPA) and Nuclear Regulatory Commission (NRC) regulations. A list of potential elements was developed based on a literature search and knowledge of the chemical processes in typical aqueous processing of nuclear fuels. A long list of possible radionuclides present in irradiated fuel was generated and then trimmed by considering isotope half-life and calculating the dose from each to a maximum exposed individual using the US EPA airborne radiological dispersion and risk assessment code CAP88 (Rosnick 1992). Control of the elements included on the shorter list needs to be considered because they require high decontamination factors to meet a reasonable fraction of the regulated release. Each of these elements is discussed with respect to what is known in the literature about its behavior in a reprocessing facility.

A UO_2-based fuel processed through an aqueous-based reprocessing system with a tributyl phosphate–based solvent extraction chemistry was used in this evaluation. None of the elements form sufficiently volatile compounds, in the context of the reprocessing facility, to be of regulatory concern from an emission standpoint based on volatility alone and with current or proposed use of scrubbers and particulate filtration technology.

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ACRONYMS

CCIM	cold crucible induction melter
CEA	Commissariat à l'énergie atomique
CETE	coupled end-to-end
CFR	Code of Federal Regulations
Ci	curies
DF	decontamination factor
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
DUPIC	Direct Use of spent PWR fuel In CANDU
DWPF	Defense Waste Processing Facility
GW	gigawatt (10^9 W)
GWd	gigawatt-days
GWy	gigawatt-year
GWd/t	gigawatt-day per tonne (metric ton)
HEPA	High Efficiency Particulate Air
HLW	high-level waste
HWIM	hot-wall induction melter
HWRM	hot-wall resistance melter
IAEA	International Atomic Energy Agency
ICM	in-canister melter
IDMS	Integrated DWPF Melter System
IHM	initial heavy metal (mass of fuel before irradiation)
INL	Idaho National Laboratory
JHMM	Joule-heated metal melter
KAERI	Korean Atomic Energy Research Institute
LEU	low-enriched uranium (enrichment with respect to ^{235}U)
LFCM	Liquid-fed ceramic melter
MEI	maximum exposed individual

mRem	millirem
MW	megawatt (10^6 W)
MWd	megawatt-days
NRC	U.S. Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
PWR	pressurized water reactor
scfm	standard cubic feet per minute
t	tonne (metric ton or 1000 kg)
TBP	tributyl phosphate
UNF	used nuclear fuel
WSEP	Waste Solidification Engineering Prototypes

RADIOACTIVE SEMIVOLATILES IN NUCLEAR FUEL REPROCESSING

1. INTRODUCTION

In nuclear fuel reprocessing, various radioactive elements enter the gas phase across the range of unit operations found in the reprocessing facility. Jubin et al. (2012a, 2012b) reported on the pathways and required removal of four radionuclides known to be volatile, ^{14}C, ^{3}H, ^{129}I, and ^{85}Kr. Other less volatile isotopes such as Cs, Cd, Ru, Sb, Tc, and Te can also report to the off-gas streams in a reprocessing facility, as described by Klein (1991).

A study has been performed to determine if radionuclides present in used fuel, which are or can form compounds known to be semivolatile during used fuel reprocessing, need to be captured along with volatile radionuclides in reprocessing facility off-gas systems, to ensure compliance to Environmental Protection Agency (EPA) and Nuclear Regulatory Commission (NRC) regulations. This is a follow-on study to the volatile radionuclide evaluations reported by Jubin et al. (2012a, 2012b).

1.1 Approach

This study was performed in several steps.

- A list of possible isotopes was generated with the ORIGEN and SCALE codes (Gauld et al. 2011, ORNL 2009).
- A list of possible semivolatile compounds containing these isotopes was developed based on a literature search and knowledge of the chemical processes in typical aqueous processing of nuclear fuels, assuming initially that all elements (isotopes) that can form volatile species through chemical reaction do form those volatile species. Electrochemical used fuel reprocessing was not included in the scope of this study.
- This long list of possible radionuclides was shortened by considering only isotopes with half-lives greater than 91 days, since isotopes with half-lives shorter than 91 days would decay to negligible levels (by a factor of 9.5×10^{-7}) if used fuel is not reprocessed for at least 5 years after removal from the reactor.
- This list of isotopes was further trimmed by calculating the dose from each to a maximum exposed individual (MEI) with the US EPA airborne radiological dispersion and risk assessment code CAP-88 (Rosnick 1992) to yield a shorter list. Control of the elements on this list needs to be considered because they could require high decontamination factors (DFs, the ratio of the uncontrolled and controlled emission) to meet a reasonable fraction of the regulated release.
- Each of these isotopes was then discussed with respect to what is known in the literature about their behavior in a reprocessing facility.

The isotopes of interest are shown in Table 1-1. Of these, cesium has been treated successfully for many years. Removal of technetium has also been studied as part of the development of nuclear waste treatment facilities such as West Valley, the Savannah River Plant, and Hanford.

While ^{130}Te and ^{115}In are significant naturally occurring isotopes, about 34% and 96%, respectively, of the naturally occurring elements, their release to the environment during the processing of UNF requires potential controls since they are generated as fission products. As part of this study of semivolatile elements, the amount of each generated during fission is included in order to assess the need for emission control. Also considered in this study is cooling time (time out of reactor) before the fuel is processed.

Table 1-1. Potentially semivolatile isotopes with half-lives greater than 91 days considered in this study

Isotope	Half-Life	Isotope	Half-Life
^{110m}Ag	249.8 days	^{184m}Re	165 days
^{195}Au	186.1 days	^{187}Re	4.1×10^{10} years
^{207}Bi	32.2 years	^{101}Rh	3.3 years
^{208}Bi	3.68×10^{5} years	^{102}Rh	2.9 years
^{210m}Bi	3.0×10^{6} years	^{102m}Rh	207 days
^{109}Cd	462 days	^{106}Ru	1.02 years
^{113}Cd	9×10^{15} years	^{125}Sb	2.76 years
^{113m}Cd	14.1 years	^{75}Se	120 days
^{134}Cs	2.065 years	^{79}Se	6.5×10^{4} years
^{135}Cs	2.3×10^{6} years	^{113}Sn	115.1 days
^{137}Cs	30.17 years	^{119m}Sn	293 days
^{68}Ge	270.8 days	^{121m}Sn	55 years
^{115}In	4.4×10^{14} years	^{123}Sn	129.2 days
^{40}K	1.25×10^{9} years	^{97}Tc	2.6×10^{6} years
^{22}Na	2.60 years	^{98}Tc	4.2×10^{6} years
^{202}Pb	5.3×10^{4} years	^{99}Tc	2.13×10^{5} years
^{205}Pb	1.5×10^{7} years	^{121m}Te	154 days
^{107}Pd	6.5×10^{6} years	^{123}Te	1.3×10^{13} years
^{208}Po	2.898 years	^{123m}Te	120 days
^{209}Po	102 years	^{127m}Te	109 days
^{210}Po	138.4 days	^{130}Te	2.5×10^{21} years
^{190}Pt	6×10^{11} years	^{204}Tl	3.78 years
^{83}Rb	86.2 days	^{65}Zn	243.8 days
^{87}Rb	4.8×10^{10} years		

This aspect is important for the short-lived isotopes shown in the list, especially for cooling times approaching 10 years.

1.2 Semivolatile Definition

Jubin et al. (2012a, 2012b) reported on recognizable volatile elements forming known volatile or gaseous species associated with the reprocessing of nuclear fuels. They exist as gases at ambient conditions, or they have very high vapor pressures so that they readily volatilize. There is, however, another group of elements with reaction products that, if formed, would be expected to be at least somewhat volatile, or semivolatile, under certain conditions and need to be removed from the off-gas streams. The term *semivolatile* does not appear to be concisely defined in the literature. The EPA defines a semivolatile organic compound as "an organic compound which has a boiling point higher than water and which may vaporize when exposed to temperatures above room temperature" but fails to provide a specific stand-alone definition of the descriptor "semivolatile" (http://www.epa.gov/reg3hwmd/bf-lr/regional/analytical

/semi-volatile.htm). Even a quick search of the literature and Wikipedia did not result in a concise definition. In this study, the term *semivolatile* is used to identify inorganic and organometallic species that are gaseous at ambient conditions within a reprocessing facility or have sufficiently high vapor pressures to report to the vapor phase above process liquids. Generally, the metal elements are not volatile and only become volatile when they react with other elements and form compounds that are volatile.

In a recent International Atomic Energy Agency (IAEA) report (IAEA 2014), these radionuclides are given the description “Potentially Volatile.” This list is shorter than the list shown in Table 1-1. Goles et al. (1981) “defined” ^{78}Se, ^{99}Tc, ^{106}Ru, ^{125,126}Sb, ^{125m}Te, and ^{134,135,137}Cs as semivolatile isotopes (elements).

2. EXPECTED INVENTORIES FOR POTENTIAL SEMIVOLATILE ISOTOPES

An ORIGEN calculation was performed to generate radionuclide inventories for the isotopes shown in Table 1-1. The results are for a pressurized water reactor (PWR) containing low-enriched uranium (LEU) fuel that was irradiated to a burnup of 60 GWd/tIHM. The isotopic content, radioactivity, and residual decay heat data were obtained by performing depletion and decay simulations with the ORIGEN code in SCALE (Gauld et al. 2011, ORNL 2009). The burnup-dependent cross section libraries used in the ORIGEN simulations were generated using TRITON (DeHart and Bowman 2011).

Radionuclide inventories, radioactivity, and decay heat data were generated for cooling times after fuel discharge from the reactor of 0 (discharge), 1, 2, 5, 10, 20, 30, 50, 70, and 100 years. Only 5-year cooling was used in this report (Table 3-1). In Table 3-1, some isotope inventories are not reported as they did not appear in the output list from ORIGEN and SCALE.

3. POTENTIAL REQUIRED DECONTAMINATION FACTORS

Not all the isotopes shown in Table 3-1 result in negligible dose consequences. To understand the required DF for each of the semivolatile elements, the maximum dose was calculated by assuming that 100% of each isotope shown in Table 3-1 is released into reprocessing facility off-gas. This is, of course, a very conservative case because the entire mass of each isotope may not evolve to the off-gas. The CAP88 code (Rosnick 1992) version 4 for the personal computer was used to calculate the dose to the MEI. The Idaho site was used as the basis for the meteorological conditions, and the effluent was released through a 100-m tall stack. Other locations could also have been used, but prior studies that compared results from different locations have shown that use of multiple locations was not needed to meet the objectives of this study (Jubin et al. 2012b, Jubin et al. 2012a). The calculation yielded an MEI at 400 m north-northeast from the stack. Each isotope concentration was input to the code to calculate the exposure. Two dose values were calculated: one for the processing of used fuel at a rate of 1 tonne initial heavy metal per year (tIHM/year) and one for a facility in which 1000 tIHM/year were processed. Since the regulation is based on an annual dose, the second value was used to calculate the maximum DF required for each isotope.

The maximum yearly dose put forth in 40 CFR 190 (EPA 2010) is 25 mRem. In their work on the volatile elements of ^{14}C, ^{3}H, ^{129}I, and ^{85}Kr, Jubin et al. (2012a, 2012b) considered two cases—one in which all isotopes contributed to the full 25-mRem/year limit and one in which 2.5 mRem/year (10%) was ascribed to the volatiles. Similarly in this semivolatile study, a smaller fraction of the overall limit was used to calculate the required DF for each radionuclide. The value selected was 0.025 mRem/year (0.1% of the 25-mRem/year regulatory limit). The assumption here was that the major fraction of the allowable emissions would be taken by the alpha emitters and the four volatile isotopes. This represented a very conservative case in that the low dose allocation requires a higher DF.

Table 3-1. Results for the radioactivity in 1 t of UNF with 60-GWd/tIHM burnup from ORIGEN calculations for the list of radionuclides shown in Table 1-1 for a 5-year cooling time. Isotopes with no entry had no output from ORIGEN; not a zero value

Isotope	Curies	Isotope	Curies
^{110m}Ag	0.675	^{184m}Re	
^{195}Au		^{187}Re	
^{207}Bi	1.55×10^{-15}	^{101}Rh	1.68×10^{-4}
^{208}Bi	1.99×10^{-16}	^{102}Rh	0.0240
^{210m}Bi	3.86×10^{-17}	^{102m}Rh	0.672
^{109}Cd	0.0369	^{106}Ru	3.19×10^{4}
^{113}Cd	6.04×10^{-14}	^{125}Sb	4.53×10^{3}
^{113m}Cd	0.348	^{75}Se	1.69×10^{-8}
^{134}Cs	7.53×10^{4}	^{79}Se	0.118
^{135}Cs	0.753	^{113}Sn	3.60×10^{-11}
^{137}Cs	1.68×10^{5}	^{119m}Sn	1.30
^{68}Ge	2.45×10^{-16}	^{121m}Sn	25.9
^{115}In	1.80×10^{-11}	^{123}Sn	0.342
^{40}K	5.69×10^{-7}	^{97}Tc	1.79×10^{-8}
^{22}Na	1.36×10^{-8}	^{98}Tc	1.45×10^{-5}
^{202}Pb		^{99}Tc	22.8
^{205}Pb	1.77×10^{-19}	^{121m}Te	1.95×10^{-6}
^{107}Pd	0.243	^{123}Te	0.00
^{208}Po	2.48×10^{-16}	^{123m}Te	5.60×10^{-4}
^{209}Po	3.00×10^{-14}	^{127m}Te	0.0240
^{210}Po	2.61×10^{-7}	^{130}Te	0.00
^{190}Pt		^{204}Tl	
^{83}Rb	3.35×10^{-9}	^{65}Zn	2.64×10^{-7}
^{87}Rb	3.47×10^{-5}		

Given a 0.025-mRem/year allocation for each of the isotopes shown in Table 3-2, a more manageable list of radionuclides was developed, as shown in Table 3-3. This table includes only those semivolatile isotopes with a calculated DF > 1; isotopes with DFs of 1 or less do not require any control, even using the conservatively low 0.025-mRem/year dose allocation per isotope.

Because the chemistry of an element dictates the method by which a DF is achieved, the list of isotopes in Table 3-3 can be shortened by only considering the largest required DF for any isotope of that element; for example, the cesium DF is dictated by ^{137}Cs or 4.9×10^{9}. There are three elements with required DF values < 10 (< 90% removal): cadmium, palladium, and tellurium. The chemistry of tellurium is similar to that of selenium; it might be argued that DF requirements for these elements and their isotopes should be considered together as should the effects of abatement processes. Palladium is not expected to form volatile species during aqueous processing, that is, no organometallic species or volatile oxides will be generated. Therefore, palladium can be dropped from further consideration. There remain eight elements, especially those with DF values greater than 10^{3}, that need to be discussed in some detail to determine if the required DFs have been demonstrated in past operations or can be demonstrated through a discussion on known chemistry.

Table 3-2. Doses from the isotopes and associated releases shown in Table 3-1

Isotope	Dose, mRem for 1 tIHM/year	Dose, mRem for 10^3 tIHM/year	Isotope	Dose, mRem for 1 tIHM/year	Dose, mRem for 10^3 tIHM/year
^{110m}Ag	0.0592	59.2	^{184m}Re		
^{195}Au			^{187}Re		
^{207}Bi	1.01×10^{-15}	1.01×10^{-12}	^{101}Rh	6.36×10^{-6}	0.00636
^{208}Bi	6.27×10^{-16}	6.27×10^{-13}	^{102}Rh	3.79×10^{-4}	0.379
^{210m}Bi	2.00×10^{-17}	2.00×10^{-14}	^{102m}Rh	0.223	223
^{109}Cd	1.59×10^{-4}	0.159	^{106}Ru	760	7.60×10^{5}
^{113}Cd	2.52×10^{-14}	2.52×10^{-11}	^{125}Sb	239	2.39×10^{5}
^{113m}Cd	0.0512	51.2	^{75}Se	4.84×10^{-10}	4.84×10^{-7}
^{134}Cs	2.39×10^{4}	2.39×10^{7}	^{79}Se	0.0131	13.1
^{135}Cs	0.0541	54.1	^{113}Sn	1.84×10^{-13}	1.84×10^{-10}
^{137}Cs	1.23×10^{5}	1.23×10^{8}	^{119m}Sn	0.00147	1.47
^{68}Ge	1.55×10^{-17}	1.55×10^{-14}	^{121m}Sn	0.190	190
^{115}In	8.13×10^{-13}	8.13×10^{-10}	^{123}Sn	0.00158	1.58
^{40}K	3.11×10^{-7}	3.11×10^{-4}	^{97}Tc	3.13×10^{-10}	3.13×10^{-7}
^{22}Na	3.87×10^{-9}	3.87×10^{-6}	^{98}Tc	3.26×10^{-5}	0.0326
^{202}Pb			^{99}Tc	2.36	2360
^{205}Pb	1.03×10^{-22}	1.03×10^{-19}	^{121m}Te	3.31×10^{-8}	3.31×10^{-5}
^{107}Pd	3.50×10^{-5}	0.035	^{123}Te	0.00	0.00
^{208}Po	2.85×10^{-22}	2.85×10^{-19}	^{123m}Te	2.15×10^{-6}	0.00215
^{209}Po	1.95×10^{-16}	1.95×10^{-13}	^{127m}Te	7.71×10^{-5}	0.0771
^{210}Po	8.61×10^{-8}	8.61×10^{-5}	^{130}Te	0.00	0.00
^{190}Pt			^{204}Tl		
^{83}Rb	3.66×10^{-11}	3.66×10^{-8}	^{65}Zn	1.73×10^{-8}	1.73×10^{-5}
^{87}Rb	2.01×10^{-6}	0.00201			

Table 3-3. Maximum required DFs for the isotopes shown in Table 3-2 for each isotope to yield 0.025 mRem to the MEI. Only isotopes requiring a DF > 1 for the 1000 tIHM/y case are shown

Isotope	Required maximum DF	Isotope	Required maximum DF
^{110m}Ag	2370	^{125}Sb	9.56×10^{6}
^{109}Cd	6.36	^{79}Se	524
^{134}Cs	9.56×10^{8}	^{119m}Sn	58.8
^{135}Cs	2160	^{121m}Sn	**7600**
^{137}Cs	**4.92×10^{9}**	^{123}Sn	63.2
^{107}Pd	1.4	^{98}Tc	1.3
^{102}Rh	15.2	^{99}Tc	**9.44×10^{4}**
^{102m}Rh	**8920**	^{127m}Te	3.08
^{106}Ru	3.04×10^{7}		

4. CHEMISTRY OF THE ELEMENTS POTENTIALLY REQUIRING CONTROL

Of the potentially semivolatile elements for the isotopes shown in Table 3-3, only eight need further consideration because of their high maximum potential DFs: Ag, Cs, Rh, Ru, Sb, Se (includes Te), Sn, and Tc. While selenium and tellurium have different chemistries, the differences are small (Cotton and Wilkinson 1980), especially at these low concentrations. In the following sections, the chemical behavior of each of these elements is discussed in the context of the expected chemistry in a reprocessing facility and the likelihood that each will form volatile species.

4.1 Silver

Silver is formed as a fission product and is present in the silver (Ag)-loaded zeolite used for the removal of iodine from the process off-gas streams. The silver from the Ag-loaded zeolite is expected to have a different pathway through the reprocessing facility than fission product silver, but the two streams might join at the vitrification process. The total fission product ^{110m}Ag produced in 1 year is about 1.5 µg. If the two processes are joined at the vitrification process, the dilution is likely to be on the order of 1 kg inactive silver to 1.5 µg ^{110m}Ag for a dilution factor of 10^9. Consequently, the required maximum DF of 2370 would be achieved by isotopic dilution. Little information is found in the literature on the volatilization of silver from borosilicate glasses. In one article on the dissolution of filaments in glasses, Kessinger et al. (2001) determined that the silver was present at the surface as Ag^0 if the glass is produced under slightly reducing conditions, as is usually the case in the formation of nuclear waste glasses, for processing reasons. Hence, it is expected that silver would be present in the glass in the metallic state and volatilize as such. The vapor pressures are expected to be close to 1 mPa (Kessinger et al. 2001). These low vapor pressures were found for glasses with very high silver contents by waste glass standards, about 7 mol%. The low silver contents in nuclear waste glasses lower the expected vapor pressures by several orders of magnitude, further reducing the likelihood that releases of ^{110m}Ag would exceed the maximum, consistent with the DF of 2370.

Silver is not expected to form volatile organometallic species under reprocessing conditions. Very few volatile compounds involving silver are found in the literature, and those that are require unusual chemistries not found in a reprocessing facility.

The formation of AgH is energetically favored by -240 kJ/mol. However, it is expected to react with the surrounding water, be trapped in NaOH traps, react with O_2 in air (Musil et al. 2012), or be trapped in the iodine traps.

It is concluded that the control of silver beyond what would be provided by abatement technologies typically installed in a reprocessing facility is not needed.

4.2 Cadmium

Cadmium has a potential maximum DF requirement of about 6, assuming all of the ^{109}Cd isotope present in the irradiated fuel is released. Although this is a very conservative assumption, the potential release of cadmium in a reprocessing plant is considered for completeness.

Volatile cadmium species have been found under moderate environmental conditions, such as gases emitted from sewers and landfills (Feldmann and Hirner 1995). Under more aggressive conditions, naturally emitted cadmium is found in the gases from fumaroles, hot springs, and wet lands in Yellowstone National Park (Planer-Friedrich and Merkel 2006) and in other aqueous media (Feng et al. 2003). The behavior of cadmium in glass melts is also known, but little is written about the volatility. In some cases, the volatility cannot be measured because the amount in the feed is relatively low and the releases were below the detection limits (Soelberg et al. 1997). Most information pertaining to the volatility of cadmium is found in the volcanology literature (Norman et al. 2004, Moune et al. 2006, Keller et al. 2008, Jenner and O'Neill 2012, Johnson and Canil 2011, Mather et al. 2012). With the exception of the work by Norman et al (2004) and a few other authors, the volatility is measured by examining the solidified magma and, so, the cadmium losses are somewhat qualitative. The volatility of cadmium appears to increase as the melt becomes more reducing (Khan et al. 2006).

The form of cadmium that volatilizes from a glass or magmatic melt does not appear to be discussed in the literature, but the DF for the glass melt alone would exceed a value of 6 [see Goles et al. (1981) for typical DF values for nuclear glass melts].

Cadmium does appear to form a hydride that is volatile (Valdes-Hevia y Temprano et al. 1993). However, its fate after being generated, presumably during the dissolution of fuel if nascent hydrogen is present, is not well known.

Although there is a significant amount of uncertainty with respect to the generation of volatile cadmium species, the required DF is low. The anticipated ability to achieve an adequate level of decontamination in systems used for abatement of other gaseous and particulate species (caustic scrubbing and HEPA filtration) in combination with the low probability that it is volatilized in significant proportions, lead to the conclusion that no cadmium-specific control is necessary.

4.3 Cesium

The high maximum potential DF for cesium means that only 2×10^{-10} of it can be released. This means that out of the approximately 1.5 kg that enters a 1000-tIHM/year facility only 0.3 µg can be released each year. This is a very high bar. For example, in one hypothetical case, if 0.001% of the cesium is allowed into the off-gas stream at each of the head-end, dissolver, and solvent extraction processes and only 10% of the remaining cesium is allowed into the off-gas at the vitrification step, then a DF at the vitrification off-gas must be on the order of 5×10^5 with DFs at the other off-gas streams of 1×10^6. A 10% split to the off-gas above a glass melter is conservatively high in most cases. Burger and Scheele (2004) showed that the dominant thermodynamically favored species is Cs_2Cl_2 with a very low vapor pressure. In their assessment, cesium is removed with the installed off-gas treatment systems. Furthermore, the limits of detection for isotopes of cesium appear to be a few tenths of a mBq/m^3 in air. The level expected from the required overall facility DF for ^{137}Cs is about 5 Bq/m^3. Therefore, while the maximum potential DF appears to be very high, it can be achieved and verification of the removal can be measured. Thus, the DF values needed to achieve regulatory release of cesium appear to be achievable with HEPA filters alone at the vitrification process. Wet scrubbers and other off-gas treatment are normally included in most nuclear facilities. These provide additional DF for the removal of cesium. Therefore, particulate and aerosol forms of cesium need not be considered further.

Cesium does not form volatile species under the chemistries associated with typical aqueous reprocessing steps, except for waste vitrification. Virtually all of the cesium released to the off-gas streams is as particulates, except at the vitrification process, where it is volatilized as an oxide or possibly molybdate. These are easily condensed to particulates and are removed with scrubbers and HEPA filters. However, very little is reported on the amount of cesium volatilized in any of the other process steps and even less is reported on the amount of cesium removed in scrubbers and HEPA filters relative to the amount entering the various parts of the process.

4.4 Rhodium

Volatile rhodium compounds exist, but the complexity of the organo-Rh compounds suggest that they are unlikely to occur in aqueous dissolution or tritium pretreatment of oxide fuels. The exception might be the formation of volatile rhodium compounds with ß-ketones, for example, acetone or free radicals with a similar chemistry that might be formed from radiolysis of process organics (Berg and Hartlage 1966). Rhodium hydride can form if nascent hydrogen is present, and this might occur if metallic fuel is dissolved in an aqueous acid under conditions where H_2 is formed. Work has been conducted on the formation of metal hydrides for detection in analytical instruments like inductively coupled mass spectroscopy (Moor et al. 2000). These molecules are unlikely to survive transit through an aqueous scrubber or HEPA filter.

If volatile organo-Rh compounds do form, their control is likely needed in the spent organics treatment processes. In this section of the reprocessing facility, the off-gas is treated with an aqueous scrubber and HEPA filtration. Any organo-Rh that might be formed would need to be sufficiently volatile at the highest operating temperature (organic destruction) where air is present to react to form RhO_2. If formed, the RhO_2 particles would be easily removed from the off-gas at DF values exceeding those shown in Table 3-3.

The conclusion is that even if rhodium volatiles might occur in a reprocessing facility they should be easily captured at levels exceeding the maximum DF values shown in Table 3-3. Thus, under most conditions (with the processing of metallic fuel being a possible exception), a dedicated rhodium capture system would not be required.

4.5 Ruthenium

Semivolatile ruthenium compounds do exist under the conditions of an aqueous chemistry-based process. Notably, Ru-nitrosylnitrates $[RuNO(NO_3)_x(NO_2)_y(OH)_{3-x-y}(H_2O)_2, x > 1]$ are known semivolatiles that occur during the nitric acid dissolution of oxide fuels (Brown 1960, Cains and Barnes 1991, Fletcher 1958, Fletcher et al. 1955, Maya 1979, Maya 1981, Natarajan et al. 2013, Singh et al. 2014, Swain et al. 2013, Wallace 1964, Wallace and Propst 1969, Blasius et al. 1981, Blasius et al. 1984, Blasius and Mueller 1984).

Ruthenium forms volatile oxides at vitrification temperatures (Anderson et al. 1994, Bancroft et al. 1961, Cobb and Hrma 1991, Demin et al. 1995, Gong et al. 2009, Gosse et al. 2010, Gruenewald et al. 2008, Jouan 1969, Kelley 1975, Krause and Luckschieter 1991, Ortins De Bettencourt 1969a, 1969b, Weisenburger and Weiss 1980, Wilds 1979) and are readily treated (Lawson et al. 2010, Natarajan et al. 2013, Oh et al. 1997, Shin and Park 2003).

Once the ruthenium is volatilized, the compounds have a propensity to condense on the ductwork between process equipment, for example, between the fuel dissolver and the first scrubber (Backman et al. 2005, Floquet et al. 2008, Sakurai et al. 1985, Swider-Lyons et al. 2005). While this effect adds to the overall DF for ruthenium, it causes an additional problem in that as the quantity of deposited ruthenium increases so also does the heat generation and dose contributions in the ductwork. The equilibrium partial pressure of these volatile compounds also means that ruthenium compounds migrate during the times when the processes are idle.

It appears that the ruthenium is ultimately converted to particulates that are relatively easily removed from the off-gas stream in the normally installed train of scrubbers, condensers, rough filters, and HEPA filters. This is consistent with the observations of Goles et al. (1981), who observed that the ruthenium concentration in the off-gas stream following the main off-gas scrubber and caustic scrubber sampler solution was below the detection limit of the analytical systems used. Ruthenium was observed in particulates collected on a 0.4 µm membrane filter. The mean particle diameter was 0.13 µm.

The HEPA filters have DFs of 10^6 for particulates and the scrubbers and condensers bring the DF to the required 3×10^7. Despite the documented volatile species for ruthenium, these species appear to be manageable with existing off-gas treatment facilities to meet regulatory releases from a reprocessing facility. However, the fact that ruthenium species react and condense on the stainless steel ductwork is a concern for operation of the facility and may necessitate a ruthenium-specific removal technology.

4.6 Antimony

There are two types of volatile antimony compounds of concern in a reprocessing facility. Antimony hydride (stibene, SbH_3) is a gas at ambient conditions with a boiling point of 17°C (Stock and Doht 1902). Stibine was synthesized and characterized by Stock and coworkers (Stock and Bodenstein 1907, Stock and Doht 1901, Stock and Doht 1902, Stock et al. 1907, Stock and Guttmann 1904, Stock and Wrede 1908). Trimethyl and triethyl antimony [$Sb(CH_3)_3$ and $Sb(C_2H_5)_3$] are also gases at ambient conditions. Trimethly antimony is typically found at landfills and composts (Diaz-Bone et al. 2011, Feldmann 2003, Filella 2010, Jenkins 2002, Jenkins 2011, Kosters et al. 2003, Long and Sackman 1955). They do not react readily with water under aerobic and anaerobic conditions (Filella 2010, Jenkins 2002). All three methylated species— monomethyl, dimethyl, and trimethyl antimony— have been observed. Triethyl antimony appears to have a weaker Sb-C bond than trimethyl antimony (Skulan et al. 2006) and has not been reported at landfills and composts.

Stibine decomposes autocatalytically with the decomposition product antimony serving as the catalyst (Stock and Bodenstein 1907, Stock et al. 1907, Stock and Guttmann 1904). It also reacts with air or water. However, the decomposition appears to be slow. Strachan (1978) showed that SbH_3 likely passed through the scrubbers and HEPA filters at the Hanford PUREX facility to the silver reactors where it reacted with AgI or AgCl to most likely form antimony, HCl or HI, and silver (based on current knowledge). It should be noted that metallic uranium fuel was processed at Hanford.

The fact that SbH_3 appeared to be transported though several gas absorbers and HEPA filters in PUREX suggests that it is a volatile of concern, and the methylated and ethylated volatiles might behave similarly. While the results from Strachan (1978) suggest that SbH_3 would be removed in the iodine removal bed, the behavior on the bed has not been investigated. Likewise, $Sb(CH_3)_3$ and $Sb(C_2H_5)_3$, which form in the organic phase or when the aqueous phase is in contact with the organic phase, might be expected to be transported to the iodine removal media before being converted to an immobile phase. The presence of SbH_3 in process off-gases is only expected when metallic fuels are dissolved, since the formation of SbH_3 appears to require the presence of nascent hydrogen.

The high maximum DF from Table 3-3 for ^{125}Sb suggests that further work on the volatile species SbH_3, $Sb(CH_3)_3$, and $Sb(C_2H_5)_3$ is needed to ensure regulatory releases are met for this isotope.

4.7 Selenium and Tellurium

Like antimony, selenium and tellurium form hydride (H_2Se and H_2Te) and dimethyl [$Se(CH_3)_2$] volatile compounds. Additionally, diethyl compounds [$Se(C_2H_5)_2$ and $Te(C_2H_5)_2$] are more readily formed and appear to be thermodynamically stable. The dimethyl-dichalcogen [$Se_2(CH_3)_2$ and $Se_2(C_2H_5)_2$] and diethyl-dichalcogen [$Se_2(C_2H_5)_2$ and $Te_2(C_2H_5)_2$] species also exist (Srivastava et al. 1999, Winkel et al. 2010). All of these are gases at ambient temperatures (Robinson and Scott 1932). Additionally, selenium and tellurium form dimethyl and diethyl haloids [$X_2Se(CH_3)_2$, $X_2Se(C_2H_5)_2$, $X_2Te(CH_3)_2$, and $X_2Te(C_2H_5)_2$ where X = Cl, Br, or I] and sulfur compounds (Chan and Einstein 1972, Srivastava et al. 1999; Vernon 1920a, Vernon 1920b). This complicates the chemistry of selenium and tellurium with respect to the semivolatile species in a reprocessing facility.

Both selenium and tellurium form these volatile species at landfills and composts (Burra et al. 2010, Diaz-Bone et al. 2011, Fatoki 1997, Feldmann 2003, Ollivier et al. 2008), in soils (Blanc and Jones 1979, Zhang and Frankenberger 2002), and marine environments (Ollivier et al. 2008). The selenium volatiles appear to be stable in concentrated HNO_3 (Winkel et al. 2010). Dimethyl diselenide is highly soluble in water and appears to decompose rapidly to $Se(CH_3)_2$ (Zhang and Frankenberger 2002); presumably the same happens to $Te_2(CH_3)_2$. The dimethyl-chalcogen haloids react with silver and, presumably, would react with silver on the iodine removal media. One complicating factor is that there are two forms of the haloids where the ligand arrangement can be cis or trans (Chan and Einstein 1972); each has a different chemistry.

With respect to the chemistry in a reprocessing facility, the conditions are not very favorable for the formation of any of these compounds. However, no effort, at least no reported effort, has been made to determine their presence in parts of the facility other than the vitrification process. Above the glass melt, selenium and tellurium are found in tests with Hanford wastes (Burger and Scheele 2004, Goles et al. 1990, Goles and Schmidt 1992). While SeO_2 is expected to be volatile at melt temperatures, TeO_2 is not (Burger and Scheele 2004); it is likely carried along with the selenium because of the very low concentrations. However, Goles et al. (1981) found that tellurium did volatilize from the glass melt based on a comparison of elemental (isotopic) ratios. Selenium and tellurium remaining with the waste going into the vitrification process should behave similarly to sulfur and be dissolved in the glass matrix. Much effort has been expended in the design of the glass composition to avoid problems with sulfur release from the glass melt. In general, the waste loading or the amount of sulfur in the waste is lowered to avoid second phase formation and sulfur volatilization. Hence, due to the glass formulations designed to retain sulfur, any selenium and tellurium that enter the glass melter would also be retained in the glass matrix.

4.8 Tin

Tin and antimony are expected to have similar chemistries. Mention of SnH_4 is made in context with the volatile antimony, selenium, and cadmium compounds (Filella 2010; Gunn and Green 1961; Valdes-Hevia y Temprano et al. 1993). Just as with antimony compounds, the methyl and ethyl tin compounds are found in the gases from landfills, composts, sewage, and like environments (Bjoern et al. 2011, Challenger 1945, Fatoki 1997, Feldmann 2003, Filella 2010; Kosters et al. 2003, Mitra et al. 2005). Volatile tin compounds are also described in literature in which chemical vapor deposition is investigated.

The presence of radiation and organics means that it is possible for methyl and ethyl free radicals to be formed. Therefore, the presence of organo-tin compounds is possible, but the concentrations depend on the G-value for their formation (the G-value is the number of molecules produced per 100 eV of ionizing radiation absorbed). If formed, these volatile species are expected to pass unabated through HEPA filters and possibly scrubbers but be decomposed on the iodine removal media.

Given the uncertainty that these volatile species will be formed to any great extent and the relatively low DF needed to ensure compliance with the regulations for release of the three tin isotopes, the presence of volatile tin compounds is assumed to be relatively low. It is further assumed that all off-gas streams will be treated for iodine removal and that the associated DF when coupled with the release rate should exceed that shown in Table 3-3.

4.9 Technetium

Technetium is another element with a relatively high maximum DF (Table 3-3). However, there has been much effort expended on controlling this volatile element, especially for glass melters (Bibler et al. 2000, Ebert et al. 1998, Kim and Schweiger 2013, Lukens et al. 2007, McCloy et al. 2012, Saito et al. 2004, Schreiber et al. 2005, Soderquist et al. 2014, Vida 1989). Technetium forms a volatile oxide Tc_2O_7. It does not appear to form volatile organometallic compounds consistent with the typical aqueous processing of nuclear fuel.

Pertechnetic acid ($HTcO_4$) has a substantial vapor pressure of 1.7 mmHg at 25°C and 23.9 mmHg at 75°C, and it is stable in water and acid solutions (Bostick 2010). The potential that it may form and escape the hot dissolver solution may warrant further investigation (i.e., its vapor-liquid equilibria).

4.10 A General Source of Radionuclides in the Off-Gas – Aerosols and Particulates

Herrmann et al. (1980) report that the air used for stirring various solutions is the major source of aerosols found in the vessel off-gas system. They claim that the majority of the off-gas volume in a reprocessing plant is not from reaction gases generated within the process but the air used for stirring, fluid transfer, and pulsing operations. The off-gas ratio for the dissolver off-gas to vessel off-gas to the cell off-gas is reported to be 1:10:100. They point out that aerosols occur in virtually every reprocessing step. These aerosols can entrain fission products such as ^{144}Ce, ^{134}Cs, ^{137}Cs, ^{90}Sr, ^{106}Ru, and ^{124}Sb as well as the transuranic elements.

The analysis by Herrmann, et al. (1980) points to two methods for aerosol generation. The first results from gas bubbles traveling through the liquid and bursting. The resulting aerosol content is approximately 10 mg/m³. The second aerosol source term occurs when the gas flows over the surface of the liquid, such as what occurs in pulsed columns. The aerosol content in these cases is 0.1 to 1.0 mg/m³.

Table 4-1 provides an example of the aerosol loading in the vessel off gas.

Table 4-1. Aerosol contributions to the vessel off-gas from vessels in the first cycle solvent extraction system (Herrmann et al. 1980)

Aerosol source	Air flow, m^3/s	Air aerosol loading, mg/m^3
Stirring air	0.12–0.83	10
Transfer air (e.g., air lifts)	0.04–0.06	10
Pulse air	0.17	0.1
Scavenging air	0.04	0.1–1.0

Studies conducted in Japan by Fujine et al. (1996) with simulated process solutions explored the generation of aerosols due to air sparging from submerged nozzles in slab tanks and the aerosol contribution from fluid transfer operations with airlifts. The tank was also equipped with a condenser on the off-gas line. Three types of simulant solutions were examined:

$NaNO_3 + LiNO_3$ (100 g/L) in water,
$NaNO_3 + LiNO_3$ (350 g/L) in 3 M HNO_3, and
$NaNO_3 + LiNO_3$ in water (100 g/L) with 100 ppm TBP added.

They drew the following conclusions from their experiments.

1. The aerosol concentration in the off-gas from the slab tank was observed to be in the range of < 20 mg/m³ with off-gas flow rates ranging from 2 to 10 m/s and with mixing air rates up to 50 m^3/hr per m^2 of liquid free surface (m^3/hr·m^2).
2. The aerosol concentration in the off-gas stream was roughly proportional to the mixing air flow rate.
3. Aerosol concentrations were < 10 mg/m³ with mixing air rates < 30 m^3/hr·/m^2 for the high concentration salt solution.

4. Trace amounts of TBP, which decrease the liquid surface tension, increased aerosol concentration by a factor of 2 to 5.

5. Aerosol concentrations after the air-liquid separation in the head pot ranged from a few to several hundred mg/m³.

6. Aerosol concentrations increased with increasing temperature. In addition, more particles of a smaller size distribution were also observed at higher temperatures.

7. During evaporation in the slab tank with sweep air and evaporation rates of approximately 10% per hour, aerosol concentrations of < 10 mg/m³ in the off-gas stream from the condenser located on the off-gas line from the slab tank were observed.

Hanson and Kaser (1976) present some useful information on the off-gas composition and flow rates for a projected large-scale high-level waste (HLW) vitrification facility. They indicate that a 1500-tIHM/year reprocessing facility would produce approximately 378 L/tIHM of HLW concentrate from waste stream evaporation. This is 5.67×10^5 L of HLW per year. Assuming an operating time of 300 d/year, the processing rate of this HLW feed to the melter is approximately 80 L/hr. With these rates, the off-gas flow rate from the melter would be approximately 0.083 m^3/s at 350°C. In the case of direct heating of the melter, the approximate composition of this gas stream is 49% N_2, 35% H_2O, 15.2% O_2, 0.1% N_2O, and <0.1 % NO_x, excluding fission products. In addition to these species, small amounts of fission products may be volatilized or entrained as particulate or aerosols. The fission products identified include Ru, I, Cs, Te, and Se. They estimate that approximately 2% of the iodine in the original fuel reports to the HLW.

Johnson et al. (1998) examined the release factor for the 242–A evaporator located at the Hanford site. This evaporator was installed to reduce the volume of waste in the underground tanks and would be expected to have aerosols as the main component in the off-gas. Since 1994 a number of campaigns have been conducted, reducing the volume of waste by millions of liters. During one of the campaigns, the loading of ^{137}Cs on the primary and secondary HEPA filters was measured. By comparing the change in loading on the filter and the quantity of material processed, a release factor of 1.5×10^{-12} for ^{137}Cs was determined. This value is for the evaporator and the demister combined and supports the conclusion that existing off-gas systems have DFs sufficient to meet those required in Table 3-3.

5. ASSESSMENT OF THE IMPACT OF SEMIVOLATILES IN A REPROCESSING FACILITY

In this section, results from reprocessing facilities and research directly connected to reprocessing of fuel are discussed.

5.1 Head-End Experience with Semivolatiles

5.1.1 Air/Oxygen Low-Temperature (480–600°C) Tritium Pretreatment

The objective of the standard tritium pretreatment process is to remove tritium from the fuel prior to dissolution. To do so, the UO_2 in the fuel is reacted with oxygen to form U_3O_8. This results in a restructuring of the crystalline UO_2 accompanied by particle crumbling and the release of most of the ^3H, significant fractions of krypton, xenon, and carbon, and a very small fraction of the iodine. The voloxidation process usually takes place at 480°C to 600°C. Higher temperatures increase the reaction rate and associated release rate of the volatile species.

It is known that iodine is chemically bonded with cesium and possibly other species, preventing it from being completely released in standard voloxidation. The iodine-containing forms are minerals such as cesium iodide and cesium uranates (Cubicciotti and Sanecki 1978). The thermal decomposition of cesium iodide begins around 670°C (Kulikov and Malyshev 1983), and cesium uranates are stable at temperatures greater than 630°C. For example, Cs_2UO_4 is stable under dry air up to around 950°C but will decompose at 630°C ($2Cs_2UO_4 \rightarrow Cs_2U_2O_7 + Cs_2O$) in humid air (Cordfunke et al. 1975, Dharwadkar et al. 1983).

It has been estimated that <0.2% of the ruthenium, antimony, and cesium would be released during standard air oxidation.

An experimental study was conducted to address concerns about ruthenium transfer and deposition occurring in the tritium pretreatment process (formerly known as voloxidation) (Klein 1977). Ruthenium tetraoxide (RuO_4) was prepared and fed to a heated steel vessel where deposition of RuO_2 on the surfaces was observed at temperatures between 475 K and 825 K, with dense depositions occurring at 525 K. Deposits were reported to be very adherent.

The physical chemistry of RuO_4 includes a high vapor pressure: 1.01 mmHg at 0°C, 161.2 mmHg at 100°C, and a theoretical boiling point of 162°C but with decomposition to RuO_2 and O_2 occurring at about 108°C (Penman and Hammer, 1968, HSC Chemistry, Weast 1989). The predominance diagram (calculations performed with HSC Chemistry 5.11) indicates that decomposition occurs at the same temperature whether the atmosphere is air or air containing substantial concentrations of nitrogen dioxide (NO_2), as shown in Figure 5-1. At low oxygen concentrations and high temperatures there is a tendency for the dioxide to decompose to metal, as shown in Figure 5-2. Because ruthenium is a more noble metal than say iron, there could be a tendency for ruthenium oxide to be reduced at the surface of a free metal, leading to deposition, but that has not been modeled and should be investigated.

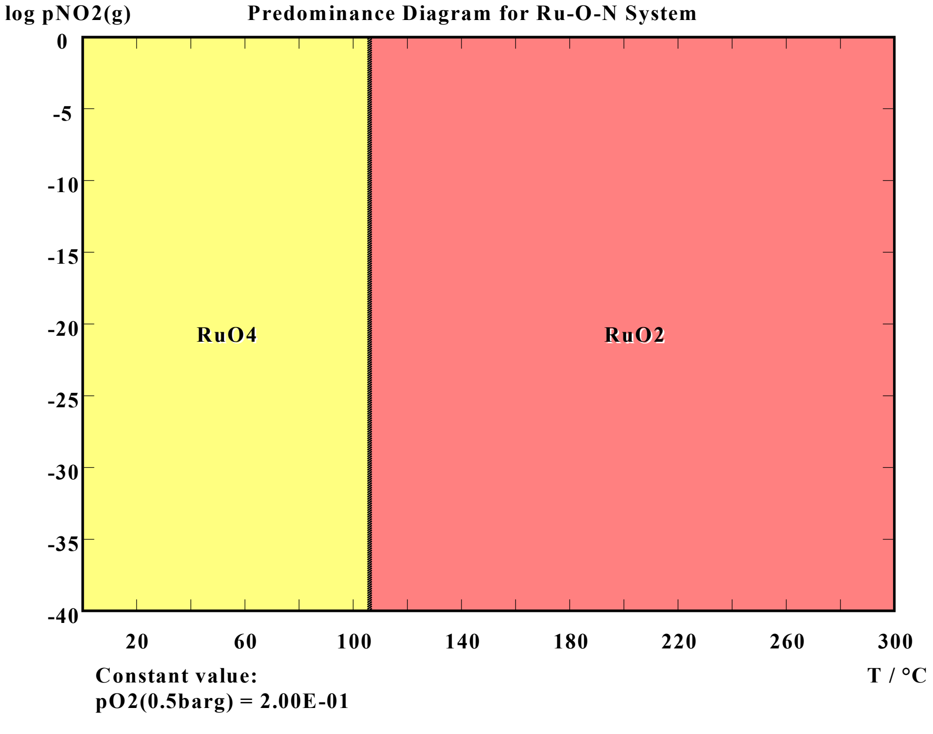

Figure 5-1. Predominance diagram for Ru-O-N system: dioxide and tetraoxide equilibria.

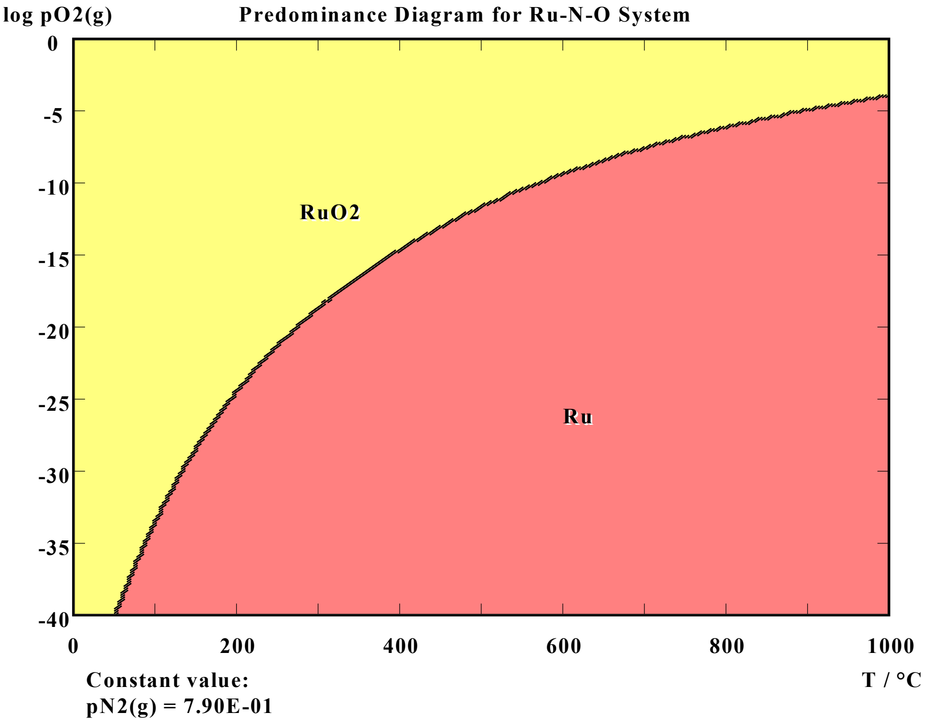

Figure 5-2. Predominance diagram for Ru-O-N system: metal and dioxide equilibria.

Considering both the deposition data and the chemistry, ruthenium may transport as either RuO_2 or RuO_4 and interact with surfaces resulting in deposition. As the deposits are difficult to remove, filtration processes will probably have to utilize one-use media.

During the coupled end-to-end (CETE) tests there was no evidence of semivolatile species reaching the off-gas capture and treatment systems.

5.1.2 Advanced Tritium Pretreatment at Low Temperatures (250–400°C)

Also under consideration for the head end of a reprocessing facility is the use of an advanced tritium pretreatment process.

Scoping studies indicate that alternative oxidants (e.g., ozone and water vapor) may improve release of selected volatile and semivolatile fission products either by further oxidizing the fuel and reducing its particle size or by producing more volatile chemical forms.

The oxidation temperature can also be reduced with NO_2 as the oxidizing gas, with the added benefit that NO_2 can also be used to convert the uranium oxides to uranyl nitrate in a dry process (Collins et al. 2013, 2014). Because ozone decomposes very rapidly at elevated temperatures in the presence of metal surfaces, NO_2 is a preferred oxidant. The use of alternative oxidants also avoids the need for higher temperatures, and it is anticipated that these lower temperatures would also result in a reduction in the release of the semivolatile species.

Very limited data are available on the release of cesium or other semivolatiles under the various pretreatment conditions. Work at ORNL on advanced head-end processes has shown that use of ozone as an oxidant reduces, by about 200°C, the temperature required to volatilize the cesium.

5.1.3 High-Temperature (>900°C) Pretreatment Associated with the Direct Use of Spent PWR Fuel In CANDU (DUPIC) and Accident Conditions

Fission product release studies, performed in support of programs assessing severe fuel damage, provide some data on high-temperature oxidation of fuel in either air or steam. Experiments were performed with fuel samples irradiated up to 33,000 MWd/tIHM in which the sample was first heated to 1100 °C in an argon atmosphere (Iglesias et al. 1986). The heating required about 100 min, and then the oxidant was introduced. Oxidation in air for 100 min resulted in removal of 100% of the ruthenium and cesium. The report indicated that the ruthenium was released only by oxidation of the sample (i.e., none released under the inert atmosphere). The cesium and iodine were released in two steps; first 80%–90% was rapidly released while the sample was oxidizing, and the remainder was slowly released while at 1100°C. The deposition evidence indicated cesium and iodine are released independently from the fuel and not as CsI.

Data in the literature and thermodynamic calculations, as well as recent tests (Westphal et al. 2005), indicate the feasibility of removing additional volatile and semivolatile species from spent fuel by oxidation in air at high temperatures. Treatment of fuel powder with oxygen at 900–950°C followed by vacuum almost completely removed technetium, ruthenium, and rhodium. Further heating under vacuum at 1050–1150°C removed nearly all Cs, Mo, Te, and Se. Tritium, ^{14}C, I, Xe, and Kr were completely removed during the combined process.

In follow-on work, Westphal et al. (2007) reported on the results from a multi-year international collaboration in which the releases from the oxidation of used nuclear fuel (UNF) were examined. As part of this effort, tests were conducted at both the Korean Atomic Energy Research Institute (KAERI) and Idaho National Laboratory (INL). In the tests at INL, BR-3 (breeder reactor) oxide fuel with a burnup of 37 GWd/tIHM that had cooled for 26 years was used. Tests were conducted with the fuel heated with or without oxidative cover gas, in an atmosphere of air or oxygen. The samples were allowed to oxidize at 500°C to 700°C for 1 to 2 hr, followed in some cases with heating to temperatures of up to 1250 °C and decreased pressures. Six elements were monitored: Cs, Mo, Rh, Ru, Tc, and Te.

Results from these tests showed that removal efficiencies increased with temperature. The primary route for removal of these six fission products was by the evaporation of volatile species following the oxidation cycle (Westphal et al. 2005). Results for the volatilization of five of the six fission products at 950°C were reported with and without vacuum. In all cases, vacuum improved the fission product removal, with cesium (50% ambient; 75% vacuum) and technetium (50%; 98%) showing the greatest effects. Molybdenum was the only fission product not removed under ambient pressure at 950°C because of the low vapor pressure of the oxide. About 10% removal for molybdenum was observed under vacuum (Westphal et al. 2005; Westphal et al. 2007).

The effect of the oxidant gas on the removal fractions from the fuel for Cs, Ru, Te, and Tc was studied. The removal fraction for cesium and tellurium decreased with the change in the oxidant from air to O_2 and the removal fraction for technetium and ruthenium increased with the same change. Westphal et al. (2005, 2007) suggested that the technetium and ruthenium results could be attributed to faster oxidation kinetics in O_2 when compared to air, whereas the cesium and tellurium results were thought to be caused by the formation of nonvolatile, complex oxides (Westphal et al. 2005, 2007).

In summary, Westphal et al. (2007) concluded the following.

- Cesium, Mo, Rh, Ru, and Te were shown to be either partially or completely removed during oxidation irradiated UO_2 nuclear fuel.
- Increasing temperature generally increased the removal fraction because of oxide volatility.
- Cesium and molybdenum removal could be enhanced under vacuum.

- The effect of oxidative gas on the removal of fission products increased or decreased the removal, depending on the fission product.
- Fission product removal can be increased by applying oxidant at temperatures greater than 500°C.

5.2 Melter and Waste Operations

Several different melter technologies that have been used in past and existing waste vitrification processes, or could be used in future waste vitrification processes, include the liquid-fed ceramic melter (LFCM), hot-wall induction melter (HWIM), cold crucible induction melter (CCIM), hot-wall resistance melter (HWRM), and in-canister melter (ICM) (Law et al. 2013). Plasma arc melters have also been tested and used for solid waste vitrification but have not been advanced as a viable candidate for liquid/slurry HLW vitrification (Eddy 1995). The majority of partitioning data readily available to the public is for LFCMs, CCIMs, and plasma arc melters.

Volatilization and aerosol entrainment can depend significantly on the melter design, feed material, and operating conditions, as some of the data below show (Soelberg 1997). One of the most significant parameters that can affect volatilization is the melt temperature, although the effects of this dependence can be masked by other operating parameters including the use of bubblers (which can increase both volatilization and aerosol entrainment) and cold cap (which can reduce volatilization by condensing and refluxing volatilized elements back to the glass).

The CCIM technology has been included as the vitrification technology for the Case Study, in part because of its ability to operate at melt temperatures ranging up to 1400°C (Law 2013). Given similar feed conditions, the melting conditions for the CCIM are similar to those for the joule-heated LFCM. At Commissariat à l'énergie atomique (CEA), the CCIM would be used to produce the same glass as has been produced using a HWIM, without the need to increase the operating temperature. Given the same temperature and other melt conditions, the volatilization and aerosol entrainment would be expected to be about the same for the HWIM, CCIM, and HWRM. For cases where a CCIM might be operated to produce a glass-ceramic, which is the direction of continuing research and development, temperatures of 1200 to 1400°C might be needed. In those cases cesium, etc. would be expected to partition more to the gas phase.

5.2.1 Cesium Behavior

Oma and Nelson (1981) discussed the off-gas from a LFCM operating at temperatures as high as 1200°C. Steady-state semivolatiles entering the off-gas system were, in mass%, Cs 13; Ru 0.16; Sb 0.11; and Te 0.44. They also indicated that volatilization accounted for 70 to 90 mass% of the elements leaving the melter; physical entrainment accounted for the remaining 10 to 30 mass%.

Zamecnik et al (1992), in preparation for the startup of the Defense Waste Processing Facility (DWPF), investigated the cesium emissions experimentally using the Integrated DWPF Melter System (IDMS), a pilot-scale test facility. These emissions compared favorably with the design basis for the DWPF. The DWPF design basis and the measured values from the IDMF are shown in Table 5-1. These results indicated that less than 0.0001% of the cesium in the feed to the melter reached the HEPA filters. More than 99.9% was retained in the melter, with the Steam Atomized Scrubber and Condenser and the High-Efficiency Mist Eliminator recovering more than 99% of the cesium that was released from the melter.

Additional information on the off-gas from the DWPF melter is provided by Moeller (1991). He reports that the off-gas rate is approximately 0.19 m^3/s (400 cfm) and contains micrometer-sized particles plus mercury, steam, and non-condensable gases. Cesium-137 and ^{90}Sr are the main radioactive components in the melter feed. Two to three percent of the ^{137}Cs volatilizes and condenses in the off-gas as 0.2–1 µm aerosol particles. Strontium-90 is entrained from the melter, but the fraction entrained was not reported.

Experience at the DWPF suggests that the needed DF for cesium is met under normal operating conditions. The analytical sensitivity is adequate to detect the quantity being released to ensure that regulatory limits are met.

Pilot-scale nonradioactive CCIM tests were performed to generate data on how a CCIM would process DWPF Sludge Batch 4 feed (Soelberg 2009). These tests were operated with the CCIM melt temperature between 1250°C and 1300°C, and resulted in 10% cesium evolution to the melter off-gas (DF = 10), when the total carryover of all solids fed was 0.29% and the carryover of iron (a known very nonvolatile element) was only 0.03%. Cesium, under these test conditions, is about 300 times more volatile than iron.

Table 5-1. Design and measured cesium decontamination factors (Zamecnik et al. 1992)

Process	DWPF design DF	IDMS measured DF
Melter	15	132
Quencher / Off-gas condensate tank	<8.9	2.7
Steam Atomized Scrubber / Condenser	50	28.5
High-Efficiency Mist Eliminator	40	314
Overall before HEPA filters	2.67×10^5	3.19×10^6
HEPA Filter #1	422	1[a]
HEPA Filter #2	24.5	NA
Overall after HEPA filters	2.76×10^9	3.19×10^6

[a] This value was reported as 0.75. However, that means more particles came out of the filter than went in. A value of 1 (no filtering) is assigned.

Goles et al. (1981) report results for the Nuclear Waste Vitrification Project. Results from the analyses of the particulates and the off-gases that pass through a series of scrubbers, condensers, rough filters, and HEPA filters showed less than detectable (< 100 nCi/m^3) emissions at the stack. Particulates were collected separately on a more sensitive filter and measured. Results indicated that about 60% of the particulates were 0.2 μm or smaller. In a later report, essentially the same results were obtained for a ceramic melter (Goles and Sevigny 1983). In the studies conducted by Goles and Sevigny (1983) on the off-gas from liquid-fed joule-heated ceramic melters, they found that particles were responsible for most melter losses. A significant fraction of the particulate mass in the off-gas system was in the form of submicrometer aerosol particles.

Cesium partitioning to the CCIM off-gas in the case study was estimated at 10% (DF = 10) (Law 2013) based on results of extensive measurements on Hanford low-activity waste vitrification using a LFCM at similar operating conditions (Soelberg 2009). Evolution of volatilized and entrained matter to the off-gas downstream of the melter is reduced in this design by recycling a portion of the off-gas wet scrub solution back to the melter, thereby reducing the cesium evolution in the scrubber outlet gas to about 0.01% of the cesium input to the melter (~10^4 combined melter-scrubber DF).

5.2.2 Ruthenium Behavior

At the Idaho Chemical Processing Plant (ICPP) new calcining facility, Christian (1990) reported that 22 to 62% of the ruthenium was volatilized during calcination. The higher value occurred during the burning of the kerosene diluent used in the extraction process. The most likely volatile form was a nitrato or oxyfluoride specie. Silica gel beds were used to retain the ruthenium. A procedure for cleaning the off-gas lines was also described. This involved an initial contact with 4 M HNO_3, followed by 6 M HNO_3 at 80°C or 10 M HNO_3 at 60°C.

Studies in Japan at the Ishikawajima Harima Heavy Industries Co (Kitamura et al. 1993) were conducted with a simulated waste solution. In these studies, the overall performance of an aqueous scrub system was examined. The results showed that a DF of 100 was achievable for a variety of conditions.

Vujisić and Nikolić (1983) discuss the adsorption of gaseous RuO_4 on impregnated Alcoa alumina H151 impregnated charcoal and silica gel. Tests were conducted at 25°C, 60% relative humidity, and a residence time of 0.3 s. In these tests it was shown that silica gel retained between 97.3 and 99.9% of the volatilized ruthenium. They also pointed out that the rapid reduction to RuO_2 and the associated liberation of oxygen may have interfered with the subsequent performance of the sorbent, and recommended that the sorbent be chosen such that the reduction proceeds slowly.

Rimshaw and Case (1981) studied various simulated high-level nitrate waste streams that been denitrated with formic acid. The use of formic acid avoided the production of NO and NO_2 but did produce N_2O. The use of formic acid also significantly reduced the volatilization of RuO_4. Tests conducted on an untreated acidic thorium nitrate waste at temperatures between 250 and 300°C resulted in the volatilization of 26.2 and 27.5% of the ruthenium, respectively. When the same waste was pretreated with 2.0 moles of formic acid per mole of nitrate, the percent volatilized was reduced to 0.07 and 0.15%, respectively.

Hanson and Kaser (1976) report that the ruthenium volatility varies widely and is a function of the process, the product, and the operating conditions. In the case of borosilicate glass production with spray calcination and in-canister melting, less than 2% of the ruthenium should be volatilized based on experience at the Waste Solidification Engineering Prototypes (WSEP) program conducted at Hanford in the late 1960s and early1970s. Cesium losses from volatilization ranged from 0.002 to 0.07% of the cesium in the HLW. In addition to these specific volatile species, it should be expected that particulates would be entrained and contain a mixture of all of the fission products contained in the feed to the melter. They estimate that the particulate fraction is ~0.001 of mass of the feed to the melter.

Table 5-2 provides an estimate of the activity of the major fission products entering the off-gas systems from the filters on the calciner/melter system assuming processing 1500 t of PWR fuel with a burnup of 33,000 MWd/tIHM (Hanson and Kaser 1976). The activity in the feed to the melter is based on time of discharge. The iodine activity in the waste is 2% of iodine in the incoming fuel and the processing rate for the melter is 300 days/year. While the activity, especially for iodine, is very high due to using activity at discharge, the release fractions would remain the same for any age fuel.

Table 5-2. Melter release fractions

Element/isotope	**Activity, Ci/hr**		
	Melter off-gas[a]	**Melter feed**[b,c]	**Fraction released**
Iodine	4.95×10^4	4.95×10^4 [d]	1.00
Ruthenium	7.85×10^3	1.08×10^6	0.0073
Cesium	1.04×10^3	1.64×10^6	0.0006
Particulate	2.43×10^4	3.58×10^7	0.0007

[a] Based on Table II of Hanson and Kaser (1976)
[b] Basis 1500 t of PWR fuel with 33 000 MWd/tIHM burnup at discharge
[c] Melter processing 300 days/year, 24 hr/day
[d] 2% in iodine in discharged fuel

Another interesting comment made by Hanson and Kaser (1976) is that when considering the release limits for the facility, the effluents from the solidification process should only be considered to represent 10% of the allowable limit.

A single-pass melter DF of 67 is used for ruthenium in the case study design (Law 2013). After recycling a portion of the wet scrub solution back to the melter, the combined DF is increased to about 6.4×10^4.

5.2.3 Antimony

Antimony is also a volatile element from glass melters (Beerkens and Van Limpt 1998, Burger and Scheele 2004, Goles et al. 1981). An antimony DF of 5 is used in the case study design (Law 2013). However, the volatilizing species is Sb_2O_5 readily condenses to a particulate and is easily trapped in the scrubbers and HEPA filters (Burger and Scheele 2004), and none was found in the stack gases from the Nuclear Waste Vitrification Project (Goles et al. 1981). Evolution of volatilized and entrained matter to the off-gas downstream of the melter is reduced in the case study design by recycling a portion of the off-gas wet scrub solution back to the melter, thereby reducing the antimony evolution in the scrubber outlet gas so that the combined melter-scrubber DF is about 2.6×10^4.

Not all of the antimony is volatilized during vitrification. The partitioning should result in a combined DF sufficient to remove the antimony below regulatory releases.

5.2.4 Tellurium and Selenium

Goles et al. (1981) found that tellurium did volatilize from the glass melt based on a comparison of elemental (isotopic) ratios. A DF of 5 is used in the case study design (Law 2013) for both tellurium and selenium. After recycling a portion of the wet scrub solution back to the melter, the combined DF is increased to about 5800 for tellurium and 7700 for selenium.

5.2.5 Technetium

Rimshaw and Case (1981) reported that less than 1% of the ^{99}Tc is volatilized during the calcining of either alkaline or acidic nitrate solutions.

Technetium volatilization is expected to occur primarily in the glass melter. Bibler et al. (2000) showed that less than 10% of the cesium and the technetium was lost from the glass during 2.5 years of waste processing at the Savannah River Site DWPF. In tests conducted in a small melter without a cold cap ~30% of the technetium was lost. The much lower technetium losses in the DWPF melter were attributed to the presence of the cold cap in the DWPF melter. For the technetium that is lost to the off-gas system, decontamination factors exceeding that required for technetium (Table 3-3) are typical for HEPA filters [$\approx 10^6$ (IAEA 2014)].

A single-pass melter DF of only 2.5 is used for technetium in the case study design (Law 2013). After recycling a portion of the wet scrub solution back to the melter, the combined DF is increased to about 2.6×10^4.

5.2.6 Comparison of Releases between CCIM and JHMM

Gruber et al. (2011) provide some limited data on the characterization the off-gas from a Joule-heated metal melter (JHMM) and a CCIM. The data were collected over a period of 10 years and are presented in terms of melter DFs based on the feed to the melter compared to the amount of that element found in the off-gas capture /treatment system. Table 5-3 provides a comparison of the system DF.

This table shows that cesium, ruthenium, and tellurium tend to be retained to the same extent by a JHMM or CCIM vitrification system, even though these two technologies differ in a number of process parameters. This included the glass production capacity (25 kg/hr for the JHMM vs. 36 kg/hr for the CCIM), processing temperature (1110°C for the JHMM vs. 1200°C for the CCIM), and bubbling and sweeping rate (4–5 vs 8–10 Nm^3/h) for the JHMM vs CCIM, respectively.

Table 5-3. Melter DFs for selected semi-volatile species (Gruber et. al. 2011)

	JHMM	CCIM
Ruthenium	100	65
Cesium	28	50
Tellurium	65	43

They concluded that the CCIM with a higher molten glass temperature had a contamination control performance comparable to the JHMM and would have no impact on the off-gas treatment system even with the associated higher temperature and gas rate.

The CCIM test for DWPF Sludge Batch 4 waste did not include surrogates for the semivolatile metals other than cesium included in this study (Soelberg 2009). However, partitioning measurements were made for some other elements in the feed known to have semivolatile behavior, including potassium, sulfur, and zinc. Figure 5-1 shows the melter partitioning data for the elements that were in the surrogate feed. The behavior of the potassium, sulfur, and zinc could be generally indicative of some of the potentially semivolatile elements in this study. Figure 5-3 shows the melter partitioning data for the elements that were in the surrogate feed. The DFs for potassium, sulfur, and zinc were 50 (2% to the melter off-gas), 16 (6.3% to the melter off-gas), and 6 (17% to the melter off-gas), respectively.

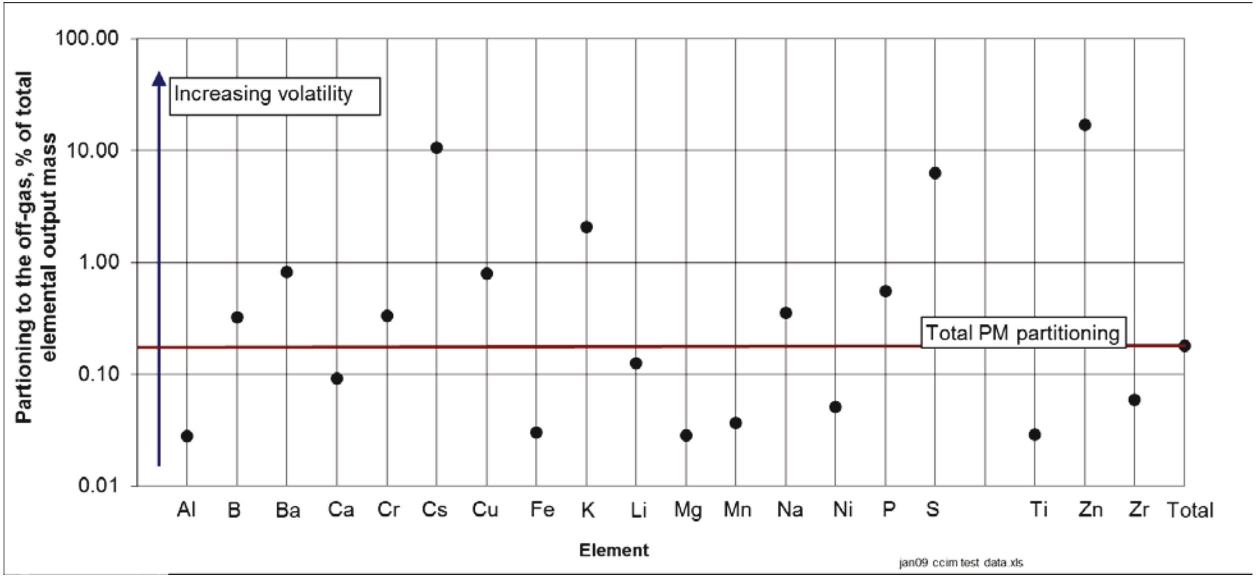

Figure 5-3. Melter partitioning data from a pilot-scale CCIM test for DWPF Sludge Batch 4 surrogate feed (Soelberg 2009).

Off-gas control efficiencies for the metals shown here that can be achieved by a high performance off-gas control system can in some cases be at least as high as can be proven with measurements (Soelberg 2001). When multiple off-gas control technologies are used in series (such as a wet scrubber followed by high-efficiency mist eliminator, reheater, multiple HEPA filtration, and iodine sorbent bed), the overall DFs can reach 10^9 or higher. In some cases, actual measurements for operating systems may not reach such high DFs due to resolution/detection limits of available analytical instruments and methods.

5.3 Storage Tanks

At the CEA, the behavior of Ru in the waste tanks was examined with respect to the consequences of a failure in a high level waste tank. Of concern was the fraction of Ru that could be released in a volatile or aerosol form. Philippe et al. (1990) state that previous studies showed the following:

- *Solution concentrations in nitric acid and nitrates: while the effect of nitrates is less well understood, the volatility of Ru in nitric acid generally becomes high for acid concentrations between 8 and 13 M, with volatile* RuO_4 *being formed by oxidation of the Ru nitrosyl complexes in solution.*

- *The presence of reducing agents: these products inhibit or delay the formation of RuO. They may be formed by radiolysis of the medium (*HNO_2*,* H_2O_2*, etc.), or introduced in the different steps of the process (tributyl phosphate entrained in raffinates, denitration with formic acid).*

- *Solution storage time: the equilibrium of the different chemical species of Ru present in the concentrates is often slow to be established, and depends on the age of the solution. Storage also influences radiolysis in solution (production yield of certain species, degradation rate of organic compounds).*

- *Temperature: during evaporation, the oxidation kinetics of the Ru complexes depends directly on the temperature profile. At higher temperatures, thermal decomposition of the Ru nitrosyl complexes may also cause the formation of volatile* RuO_4*.*

However, it was concluded that the number of parameters involved made it improbable that the behavior of ruthenium could be easily calculated. Thus, Philippe et al. undertook an experimental measurement with actual fission product concentrates to determine the losses as the solution was taken to dryness. Results from this test indicated that ruthenium is only volatilized just as the solution reaches dryness, and the total amount of ruthenium released was approximately 15% at 160°C. The volatilized ruthenium recombined in the presence of H_2O, HNO_3, NO_x and O_2 as ruthenium oxide on the walls of the test apparatus. They also identified three distinct phases for the ruthenium release:

1. the boiling phase – a slight transfer of ruthenium from the tank, occurring by aerosol entrainment,

2. the phase approaching dryness – ruthenium begins to oxidize and volatilization predominates over transfer by aerosol entrainment, and

3. the final dryness or calcine phase – volatilization of RuO_4 that decomposed on the tank walls or reacted with NO_x to form RuO_2.

6. CONCLUSIONS

As a term, “semivolatile” is not clearly defined, so it is not given a specific definition in this document. To compensate for this lack definition, a broad list of the isotopes that could become volatile by reaction with other compounds under certain conditions in the reprocessing plant is considered. This list comes from an ORIGEN code in SCALE (Gauld et al. 2011, ORNL 2009) calculation for UNF with 60 GWd/tIHM burnup and 5 years of cooling. Each radionuclide in this long list is assumed to be the only radionuclide in the off-gas – a conservative case – and is used in an airborne radiological dispersion and risk assessment code CAP-88 (Rosnick 2007) calculation for the resulting dose to the MEI. An assessment of these doses leads to a shorter list of eight isotopes of concern. Each of the elements represented by these isotopes is discussed with respect to its overall volatility and then evaluated as to the likelihood that a volatile compound would be formed and escape through the various off-gas treatments to the stack gases and give rise to a potential regulatory violation. The context for this evaluation is a

UO_2-based fuel processed through an aqueous-based reprocessing system with a TBP-based solvent extraction chemistry. None of these elements form sufficiently volatile compounds in the context of the reprocessing facility to be of regulatory concern from an emission standpoint based on volatility alone and taking into account current or proposed use of scrubbers and particulate filtration technology. Deposition of certain semivolatile compounds on surfaces within the off-gas system is however likely.

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