Evaluation of Ruthenium Capture Methods for Tritium Pretreatment Off-Gas Streams

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SUMMARY

In the reprocessing of used nuclear fuel, radioactive elements are released into various plant off-gas streams. While much research and development has focused on the abatement of the volatile nuclides ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I, the potential release of semivolatile isotopes that could also report to the off-gas streams in a reprocessing facility has been examined. Ruthenium (as ^{106}Ru) has been identified as one of the semivolatile nuclides requiring the greatest degree of abatement prior to discharging the plant off-gas to the environment.

A recent engineering evaluation of an integrated off-gas system for the head-end off-gas stream of a reprocessing facility included Ru capture systems for both the dissolver off-gas and the tritium pretreatment system off-gas. The design of a Ru capture system was noted as challenging due to the lack of critical data on both Ru volatilization from specific unit operations and on gaseous Ru removal by solid sorbents in relevant systems. In traditional aqueous reprocessing, the amounts of Ru volatilized during shearing and dissolution are expected to be low. However, to prevent the partitioning of ^{3}H into the aqueous streams within the plant, upfront dry pretreatment steps, known as tritium pretreatment, have been developed to oxidize the fuel prior to dissolution and release the ^{3}H into the plant off-gas. Little is known regarding the amount of gaseous Ru released during these pretreatment steps, but in most cases the quantities of Ru released are assumed to be greater than those released when dissolution is performed directly after fuel shearing. Thermodynamically, Ru is expected to present as RuO_4 within the temperature ranges of tritium pretreatment processes, but this assumption requires verification.

Beyond the questions associated with the Ru source term, the recent engineering evaluation identified outstanding questions related to Ru removal by solid sorbents, including (1) the partitioning of Ru between solid, volatile, and particulate forms; (2) the degree of Ru abatement by other off-gas processes; and (3) the capacity of common sorbents for Ru.

Silica gel is the most extensively studied Ru adsorber, and some studies have reported the capacity of silica gel for Ru in a flowing system. However, much of the reported work on silica gel was performed in a humid environment, which does not translate directly to Ru adsorption from the off-gas of a dry tritium pretreatment process. Some research has been performed on the adsorption of Ru by metal fibers or metal oxides. Many studies have examined the deposition of Ru on stainless steel and can provide insight into the speciation and the loading of Ru as a function of surface area, but practical engineering data on Ru adsorption by metal sorbents remain unreported.

The literature reviews and calculations detailed in this report provided a basis for the design of an experimental system, an analytical method, and a test plan. The difficulties in handling Ru-bearing gas streams, from both safety and practicality perspectives, drove the decision to propose a very simple test system and a proposed test design.

It is intended that the proposed series of testing will provide (1) Ru breakthrough time and Ru loading capacity of metal mesh in a dry stream, (2) Ru breakthrough time and Ru loading capacity of silica gel in a dry stream, and (3) Ru desorption from silica gel as a function of time (mg h^{-1} g^{-1} loaded silica). In addition, some information, such as the length of the mass transfer zone, may be obtained through successful leaching of the sorbent beds. Finally, any experimental data gathered on Ru quantitation by either ultraviolet–visible spectroscopy or neutron activation analysis may augment the literature available on the subject of Ru analysis. Much of the information intended to be collected from this testing will be directly useful in the refinement of Ru abatement system designs such as those included in the engineering evaluation of an integrated off-gas system for the head-end off-gas stream of a reprocessing facility (Jubin et al. 2016).

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ACRONYMS

ATPOG	advanced tritium pretreatment off-gas
DF	decontamination factor
FY	fiscal year
HEPA	high efficiency particulate air
HLW	high level waste
ICP-MS	inductively coupled plasma–mass spectrometry
IHM	initial heavy metal
LLW	low level waste
MEI	maximum exposed individual
ORNL	Oak Ridge National Laboratory
ppmv	parts per million by volume
PWR	pressurized water reactor
TBD	to be determined
TPT	tritium pretreatment
TPTOG	tritium pretreatment off-gas
UNF	used nuclear fuel
UV-Vis	ultraviolet–visible

1.   INTRODUCTION

The reprocessing of used nuclear fuel (UNF) results in the release of radioactive elements into various plant off-gas streams. In previous reports, the in-plant distribution pathways and abatement requirements for four radionuclides known to be volatile (i.e., ^{14}C, ^{3}H, ^{129}I, and ^{85}Kr) have been discussed in detail (Jubin et al. 2012b; Soelberg et al. 2013; Jubin et al. 2011, 2012a; Jubin et al. 2013). A recent report by Jubin et al. (2014) examined the potential release of other less-volatile (semivolatile) isotopes that could also report to the off-gas streams in a reprocessing facility. In that study, an effort was made to determine which, if any, of 24 semivolatile radionuclides could be released from a reprocessing plant and, if so, the likely quantities released. Of these 24 semivolatile radionuclides, ruthenium (Ru), in particular ^{106}Ru, was identified as one of the semivolatile nuclides that could require the greatest degree of abatement prior to discharge of the plant off-gas to the environment. The study was followed by an engineering evaluation of an integrated off-gas system for the head-end off-gas stream of a reprocessing facility (Jubin et al. 2016). This design included Ru capture systems for both the dissolver off-gas and the tritium pretreatment system off-gas (TPTOG).

The design of a Ru capture system proved challenging due to the lack of critical data on both Ru volatilization from specific unit operations and on gaseous Ru removal by solid sorbents in relevant systems. In traditional aqueous reprocessing, the head-end portion of the process includes fuel shearing and subsequent fuel dissolution in nitric acid. The nitric acid solution is known to volatilize some portion of the Ru contained in the fuel meat (likely <0.1%) along with iodine, krypton, and carbon dioxide, into the dissolver off-gas (Voskresenskaya et al. 2014a.) The bulk of the ^{3}H remains in the nitric acid and is distributed throughout the aqueous waste streams within the plant. To prevent the partitioning of ^{3}H into the aqueous streams within the plant, upfront dry pretreatment steps, known as tritium pretreatment (TPT), have been developed to oxidize the fuel prior to dissolution and release the ^{3}H into the plant off-gas (Goode and Stacy 1980, Del Cul et al. 2012). Little is known regarding the amount of gaseous Ru released during these pretreatment steps, but in most cases, it is assumed that the quantities of Ru released are greater than those released when dissolution is performed directly after fuel shearing (Cadieux and Stone 1980, Johnson and Stone 1977, Goode 1973).

Beyond the questions associated with the Ru source term, Jubin et al. (2016) identified a number of data gaps in the course of engineering design that are related to Ru removal by solid sorbents. For example, one of the observations from the engineering evaluation was the surprising lack of consistency in the literature on the use of silica gel to remove volatile Ru and on the gaseous Ru speciation in the off-gas streams. Silica gel was reported by Goossens (1991) to have Ru loadings of 2.6 kg/m³. In contrast, Cains and Yewer (1985) report silica gel as unsuitable for Ru abatement. Other potential sorbents include a bed of metal fibers or metal oxides, but these sorbents have been evaluated only for Ru surface deposition, not for use in abatement beds (Cains and Yewer 1985, Holm et al. 2009, Sakurai et al. 1985).

This report is a summary of a literature review of relevant information for Ru capture from TPT operations. This review was conducted to provide the technical basis for the design of an experimental system and a test plan with which the identified data gaps could be addressed. This report only briefly discusses questions regarding the Ru source term and focuses on Ru capture from gaseous streams. The specific aims of the literature review are to

1) review relevant technical information on the subject of Ru removal from a TPTOG stream (including an expanded review focused on identifying expected Ru species);

2) provide a summary of methods to produce, in a controlled manner, the expected Ru species; and

3) summarize analytical methods that can be used to differentiate the Ru species.

The information provided in the technical review then allows recommendations to be made regarding the design of an experimental plan to evaluate Ru retention capacity, adsorption rate, capture efficiency, and

nature of Ru species not retained for proposed Ru sorbent materials. The initial experimental work is intended to begin in FY 2017.

2.   DATA GAPS

Jubin et al. (2016) identified several specific data gaps that affected the design of the Ru capture system:

- The required Ru decontamination is known to be high, but there is still uncertainty in the specific requirements. An overall Ru plant decontamination factor (DF) of 3.04×10^7 is needed for 5 y cooled 60 GWd/tIHM fuel. A review of the literature supports a DF value of about 1×10^4. The discrepancy arises from some differences in the literature regarding the conversion of volatile RuO_4 to particulate RuO_2 in the gas phase and regarding the capture methods and efficiencies for these volatile and particulate forms of Ru. In addition, the degree of Ru abatement by other off-gas processes (including filters, adsorbers, condensers, wet scrubbers, etc.) is not well known, and any Ru abatement by these processes is likely affected by the equilibria between RuO_4 and RuO_2. Further, the efficiencies of HEPA filters for particulate RuO_2 and of aqueous scrubbers for volatile RuO_4 are uncertain.

- Improved data are needed on the volatilization of Ru during TPT. Data are needed relative to the relationship between quantity of Ru released, gaseous Ru speciation, and operating conditions (e.g., temperature, time, oxygen content).

- Few data exist on the Ru capacity of metal and metal oxides, preventing the consideration of this sorbent material by Jubin et al. (2016).

Other data gaps were embedded in the assumptions used in the engineering design:

- Material balance calculations were based on 10% of the Ru contained in the fuel being volatilized into the off-gas during TPT. However, early work on TPT suggests that very little Ru is volatilized (Cadieux and Stone 1980, Johnson and Stone 1977, Goode 1973), likely <0.1%.

- A back-flushable HEPA filter could be utilized to protect the Ru adsorber from fuel particulates. Klein et al. (1980) indicates that the Ru deposited on a filter must be washed off and cannot be removed with a blow-back. It was assumed that 90% of the Ru would be captured on the back-flushable filter (an effective Ru DF of 10). In general, the HEPA filter DF for particles greater than about 0.3 μm (DOE 2003) can be as high as 3×10^4.

- It was assumed that combining the DF values of successive removal methods (i.e., HEPA filter, scrubbers, Ru solid sorbent bed) would achieve the desired overall DF for Ru removal.

A full evaluation of these data gaps and the test systems that could be used in their resolution was documented by Jubin et al. (2017). This evaluation was performed for each of the main off-gas treatment unit operations and for the overall treatment train. The resulting data requirements are identified in tabular form in Jubin et al. (2017), and a summary of those are shown here (Table 1) for context. It was recognized that significant gaps existed in the source terms arising from TPT operations and from fuel dissolution, but the evaluation limited the scope of the study to the off-gas capture systems themselves. The proposed experimental system and test design provided in Sections 5 and 7 of this report were informed by this analysis and are intended to facilitate proof-of-principle testing that will begin to address these gaps for two types of sorbent for use in standard TPTOG.

Table 1. Data gaps for Ru capture systems

#	Property	Specific requirements	Approach
Metrics for technical performance and physical and chemical characteristics criterion			
1	**Adsorption capacity** *mol/kg sorbent*	Maximum capacity of selected sorbent material as a function of Ru species, temperature, and concentration - Ru species of interest are TBD but may include RuO_4, RuI_4, and $RuBr_4$ - Operating temperature range is 30 to 600 °C - Ru concentration ranging from 1×10^{-7} kg/m^3 to 1×10^{-4} kg/m^3 - Gas velocities ranging from 5 to 100 m/min	Thin bed testing *Test system must be able to hold a thin bed of sorbent at given temperature and expose sorbent to a generated air stream containing water (and any potentially co-adsorbed species) at varying concentrations within the specified concentration range and gas velocity*
2	**Capture/removal rates for primary species** *mol/kg sorbent/h*	Adsorption rate data for selected sorbent as function of Ru species, temperature, and concentration Recommended experimental ranges and Ru species are provided in Gap ID #1	Thin bed testing *(See Gap ID #1)*
3	**Capacity for other species present in gas stream** *mol/kg sorbent*	Maximum capacity for potential co-absorbed species by selected sorbent material as a function of species, temperature, and concentration - Species of interest are H_2O, O_2, N_2, HNO_3, CO_2, I, etc. - H_2O with a dew point of -60 to 90 °C - HNO_3 concentration of 1000 ppm - O_2 concentrations of 20 to ~100% - N_2 concentrations of 0 to 80% - CO_2 concentrations of 440 ppm - I concentrations up to 0.1 kg/m^3 (10,000 ppm)	Thin bed testing *(See Gap ID #1)*

#	Property	Specific requirements	Approach
		- Operating temperature range is 30 to 600 °C	
4	**Capture/removal rate for co-absorbed species** *mol/kg sorbent/h*	Adsorption rate data for selected sorbent as function of co-absorbed species, temperature, and concentration Recommended experimental ranges and potentially co-adsorbing species are provided in Gap ID #3	Thin bed testing *(See Gap ID #1)*
5	**Change in sorbent capacity for Ru in presence of other species present in gas stream** *mol/kg sorbent*	Ru capacity of selected sorbent material for potential adverse effects to Ru capacity in the presence of co-absorbed species function of species, temperature, and concentration Recommended experimental ranges, Ru species, and potentially co-adsorbing species are provided in Gap IDs #1 and #3	Thin bed testing with post-adsorption sorbent analysis *Thin bed testing (see Gap ID #1) using selected sorbent followed by chemical or gamma analysis of sorbent*
6	**Change in Ru capture rate in presence of co-absorbed species** *mol/kg sorbent/h*	Ru adsorption rate data for selected sorbent as function of co-absorbed species, temperature, and concentration Recommended experimental ranges, Ru species, and potentially co-adsorbing species are provided in Gap IDs #1 and #3	Thin bed testing with post-adsorption sorbent analysis *(See Gap ID #5)*
7	**Selectivity** $(X_a/Y_a) / (X_b/Y_b)$ *(unitless)* *Where X_a and X_b are mole fractions of species a and b respectively in the adsorbed phase, and Y_a and Y_b are mole fractions of species a and b in the bulk phase*	Derived from data on co-absorption studies shown above	Thin bed testing with post-adsorption sorbent analysis *(See Gap ID #5)*

#	Property	Specific requirements	Approach
8	**Sorbent particle density** *kg/m³*	Density of individual particles in kg/m³	Direct measurement or from manufacturer
9	**Sorbent bulk density** *kg/m³*	Bulk density of bed of sorbent material in typical loading configuration in kg/m³	Direct measurement or from manufacturer
10	**Specific heat capacity** *J/K/kg*	Specific heat capacity of fresh and loaded sorbent over range of operating conditions (30 to 600 °C)	Direct measurement of fresh sorbent and loaded sorbent.
11	**Thermal conductivity** *W/m/K*	Thermal conductivity of fresh and loaded sorbent over range of operating conditions (30 to 600 °C)	Direct measurement of fresh sorbent and loaded sorbent.
12	**Radiation stability** *% degradation in capacity, adsorption rate, regeneration time, and MTZ over time as a function of radiation exposure*	Total adsorbed dose for Ru sorbents assume one time use, i.e., no regeneration Total Dose requirement is TBD and design dependent Total dose should factor in both external dose and internal dose	Irradiation and thin bed testing *Exposure of the sorbent to both γ and β radiation for a range of total doses. Testing of the sorbent with both thin and deep bed testing to characterize radiation effects.* *(Thin bed testing: See Gap IDs #1 and #5)*
13	**Mechanical stability** *N/mm (load vs particle diameter)* *µg/kg sorbent loss to gas stream*	Determination of the fines generation and mechanical strength of the sorbent material	Direct measurement *Measurements of both particle crush strength and abrasion resistance will be required*
14	**Thermal stability** *% degradation in capacity over time at selected operating temperature*	Determine the extent of capacity loss due to extended exposure to operating temperature. Determine the extent of capacity loss due to thermal cycling and excursions	Extended testing with thin-bed analysis The sorbent should be exposed to the operating temperature for extended periods of time, and should experience thermal cycling to simulate regeneration of the sorbent. The capacity should be measured after thermal exposure by thin bed testing *(See Gap ID #1)*

#	Property	Specific requirements	Approach
15	**Chemical stability** *% degradation in capacity over time as a function of other species present in gas stream*	Determine the extent of capacity loss due to extended exposure to other species present in the off-gas stream	Extended testing with thin-bed analysis *Age sorbents for various lengths of time to elevated levels of each of the non-target species expected. Determine Ru capacity and rates of adsorption. Differences should be attributable to aging and should be a function of exposure time and non-target species exposure*
16	**Reactivity** *Compatibility as determined by standardized compatibility tables*	Confirmation that any compatibility issues can be avoided through selection of materials of construction, appropriate pretreatment of gas stream, operational envelope, etc.	Direct evaluation
17	**Regeneration capacity stability** *Number of cycles and Δ mole/kg sorbent*	No. of cycles before degrading to 80% of capacity for the target element	Extended testing with thin-bed analysis *Long-term, repeated testing of select sorbent over multiple adsorption/ desorption cycles if sorbent is to be regenerated. N/A if single use*
18	**Desorption rate of Ru** *mol/kg sorbent/h*	Desorption rate as a function of desorption temperature and purge stream gas velocity	Thin bed testing *(See Gap ID #1)*
19	**Desorption of co-adsorbed species** *mol co-adsorbed species retained/ m³ sorbent*	Percentage of co-adsorbed species desorbed during selected regeneration conditions Recommended experimental ranges and potentially co-adsorbing species are provided in Gap ID #3	Thin bed testing *(See Gap ID #1)*
20	**Desorption rate of co-adsorbed species** *mol/kg sorbent/h*	Desorption rate as a function of desorption temperature and purge stream gas velocity Recommended experimental ranges and potentially co-adsorbing species are provided in Gap ID #3	Thin bed testing *(See Gap ID #1)*
21	**Purity of Recovered Ru** *mol impurity/kg Ru*	Prescribed by waste treatment operation	ICP-MS of recovered phase
22	**Cooling time**	Hours to cool from	Derived from heat capacity, thermal

#	Property	Specific requirements	Approach
	h	regeneration temperature (TBD °C) to adsorbing temperature (30 °C)	conductivity, and bed design
Metrics for system design and performance criterion			
23	**Pressure drop** *Pa/m vs m² column*	Size columns and sorbent size for <2.5 kPa pressure drop based on expected gas flow rates	Direct measurement or scaled derivation
24	**Decontamination factor (DF)** $[Ru]_{inlet}/[Ru]_{outlet}$ *(unitless)*	DF data as function of sorbent, Ru species, temperature, concentration, time, and bed depth Recommended experimental ranges and Ru species are provided in Gap ID #1	Deep bed testing with online measurement of inlet and effluent Ru concentrations *Test system must be able to hold a deep bed of sorbent at given temperature and expose sorbent to a generated air stream containing water (and any potentially co-adsorbed species) at varying concentrations within the specified concentration range and gas velocity. Both inlet and effluent gas streams must be assessed for Ru concentration*
25	**Length of Mass Transfer Zone** *m*	Length of MTZ as a function of gas velocity, target species concentration, temperature, and presence of co-absorbed species shown to have impact on total capacity or adsorption rate of >10% Recommended experimental ranges and Ru species are provided in Gap ID #1	Deep bed tests with bed depth that captures 1.5 times MTZ. Predictions can be made from thin bed tests and data may also be determined from DF testing using deep beds *(Deep bed testing: Gap ID #24)*

3. RUTHENIUM SOURCE TERM AND CHEMISTRY RELEVANT TO TRITIUM PRETREATMENT AND RUTHENIUM RETENTION

The amounts of Ru isotopes in used PWR fuel having relatively high burnup are shown in Table 2, and the activity of the radioisotopes of Ru are shown in Table 3. After 5 years of cooling, the only remaining radioisotope of Ru is practically ^{106}Ru, with a mass of ~7 g/tIHM and activity of ~23,300 Ci/tIHM. The required decontamination factor (DF) for the removal of ^{106}Ru from the off-gas stream was estimated to be 3.04×10^7 in order to limit the contribution of Ru to the maximum exposed individual (MEI) to 0.025 mRem (Jubin, et al. 2014). The cited study estimated the required DFs for 5 y cooled fuel, but as with ^{85}Kr and ^{3}H, radioactive decay in aged fuel greatly diminishes (or possibly eliminates) the need to control the volatile specie. After 20 y of cooling, the activity of ^{106}Ru is reduced to only ~0.77 Ci/tIHM. A full description of the potential abatement requirements for ^{106}Ru and other potentially volatile species is found in Jubin, et al. (2014).

Table 2. Mass of Ru isotopes in used nuclear fuel (g/tIHM) as a function of cooling time*

Isotope	$t_{1/2}$ (d)	Cooling time (years)			
		0	5	20	30
^{100}Ru	Stable	2.45E+02	2.45E+02	2.45E+02	2.45E+02
^{101}Ru	Stable	1.28E+03	1.28E+03	1.28E+03	1.28E+03
^{102}Ru	Stable	1.32E+03	1.32E+03	1.32E+03	1.32E+03
^{103}Ru	39.24	5.33E+01	5.39E-13	0.00E+00	0.00E+00
^{104}Ru	Stable	8.90E+02	8.90E+02	8.90E+02	8.90E+02
^{105}Ru	0.185	1.89E-01	0.00E+00	0.00E+00	0.00E+00
^{106}Ru	372.6	2.17E+02	6.96E+00	2.31E-04	2.39E-07
^{all}Ru		**4.00E+03**	**3.74E+03**	**3.73E+03**	**3.73E+03**
^{106}Ru/Ru	%	5.42E+00	1.86E-01	6.20E-06	6.40E-09

* PWR fuel having burnup of 55 GWd/MTIHM.

Table 3. Activity of Ru radioisotopes in used nuclear fuel (Ci/tIHM) as a function of cooling time*

Isotope	$t_{1/2}$ (d)	Cooling time (years)			
		0	5	20	30
^{103}Ru	39.24	1.73E+06	1.74E-08	0.00E+00	0.00E+00
^{105}Ru	0.185	1.27E+06	0.00E+00	0.00E+00	0.00E+00
^{106}Ru	372.6	7.25E+05	2.33E+04	7.74E-01	8.00E-04

* PWR fuel having burnup of 55 GWd/MTIHM.

3.1   Tritium Pretreatment Processes and Their Implications for Ru Volatilization from Used Nuclear Fuel

Either O_2 (air) or NO_2 can be used in TPT as the fuel oxidant to release the ^3H contained in the fuel meat into a small volume of gas for subsequent recovery. In standard TPT, the UO_2 in the fuel is reacted with oxygen (as air or pure O_2) to form U_3O_8. This results in the restructuring of crystalline UO_2, accompanied by particle crumbling, and the release of most ^3H; significant fractions of Kr, Xe, and carbon; and less than 10% of the iodine contained within the fuel. This process is conducted at temperatures ranging from 480 to 600 °C. Higher temperatures increase the reaction rate and associated release rate of the volatile species.

Advanced TPT, utilizing NO_2 as the oxidant, can be applied to chopped fuel or combined with chemical decladding. The process converts oxide fuel into a fine powder product that can be U_3O_8, UO_3, or a nitrate depending on processing conditions. Advanced TPT also releases Kr, Xe, and carbon, and may result in a more quantitative iodine release than standard TPT. Advanced TPT is conducted at temperatures less than 400 °C (DelCul et al. 2016).

For standard TPT, it has been estimated that a fraction (0.1% to 10%) of the Ru is released from the fuel as volatile RuO_4 (Klein et al. 1980, Ronneau et al. 1995), of which about 20% to 30% becomes particulate once the gas stream cools, because RuO_4 is thermodynamically unstable with respect to RuO_2 at temperatures below 800 °C (Cains and Barnes 1991, Backman et al. 2005). During the coupled end-to-end testing, there was no evidence of Ru reaching the off-gas capture and treatment systems, but the piping leading to the off-gas systems was not analyzed for Ru deposition, which prevented a determination of total Ru released during standard TPT. Although volatile RuO_4 is not thermodynamically stable, its existence is exploited in the refining of Ru, where aqueous soluble sodium ruthenate (Na_2RuO_4) is treated with chlorine to release $RuO_4(g)$, which is recovered and further processed to prepare purified Ru metal (Lanam and Zysk 1982).

Few data are available to indicate how the use of NO_2, a more powerful oxidant, affects the release of Ru during advanced TPT. Scoping studies have indicated that alternative oxidants (e.g., ozone and water vapor) may improve the 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 (DelCul et al. 2012). Results from calculations performed with the software HSC Chemistry version 9 (Outotec), described below, suggest the oxidation of Ru metal to RuO_2 is unfavorable at low temperatures, but in practice, Ru metal oxidizes at measurable rates at temperatures >450 °C (Lanam and Zysk 1982). Nevertheless, the lower temperature of the advanced pretreatment process could retard Ru release because slower kinetics are expected.

The examination of the source term, based on reaction free energies, was performed using HSC Chemistry. This software can evaluate the thermodynamics of reactions; from that, the reaction free energies for a system at equilibrium and standard conditions are determined. No kinetics can be evaluated with this software. Results verify that production of gaseous RuO_3 or RuO_4 from solid RuO_2 is thermodynamically unfavored at temperatures ranging from 0 to 2000 °C. Calculations indicate that direct conversion of the free metal to RuO_4 in oxygen or NO_2 is favored at temperatures below 900 °C, but a lower energy state is obtained if the oxidation stops at RuO_2.

Further, the reaction of $RuO_4(g)$ with $U_3O_8(s)$ to produce $RuO_2(s)$ and $UO_3(s)$ is thermodynamically favored at all temperatures between 0 and 1000 °C, which covers the likely range of the TPT process. The rate of the reaction is unknown. Therefore, whether any $RuO_4(g)$ emanates from the process depends on the rapidity with which RuO_4 is produced and transported away and with which it reacts with the huge excess of available $U_3O_8(s)$.

3.2 Speciation and Transport of Volatilized Ru

A number of factors may impact the release of Ru from the fuel matrix through oxidation. The first factor to consider is the speciation of Ru in the fuel. A large fraction of the Ru is present in the fuel as an alloy containing Mo, Pd, Rh, and Tc (Kleykamp 1987, 1988) with the remainder dispersed in the UO_2 matrix. The degree of this alloy's reactivity in the presence of oxygen is unknown. There are a number of stable U–Ru intermetallic compounds (e.g., U_2Ru, URu, U_3Ru_4, etc.) and Ru alloys (Rard 1985), but the production of these compounds from UO_2 has not been fully characterized. Calculations with HSC Chemistry show that oxidation of URu_3 to UO_2 and $RuO_4(g)$ is favorable at temperatures above 0 °C to well over 1000 °C. However, there is little expectation that such an intermetallic could form in the fuel because excess oxygen becomes available as the fission process takes place. Additionally, the overall reaction, $URu_3 + 7O_2 = UO_2 + 3RuO_4$, likely proceeds by a multistep mechanism, meaning that several elementary steps are required to convert reactants to products. Further, RuO_4 is a very strong oxidizing agent and gives up oxygen to any intermediate uranium compound that is not fully oxidized.

Thermodynamically stable RuI_3, and Ru–Zr compounds have been shown to exist (Rard 1985). Thus, when considering the mechanism by which Ru is released from the fuel and the consequent speciation in the gas phase, a better understanding of the Ru chemistry in the fuel is needed to calculate the Ru release during TPT. Thermochemical calculations with HSC Chemistry indicate that reactions between RuO_2 (solid or gas) and oxygen-rich compounds (e.g., Cs_2UO_4 and $Cs_2U_2O_7$) would not produce RuO_4.

Readily available data on the interaction of Ru with NO_2 in the gas phase is sparse. Although there are a number of ruthenium nitrosylnitrate compounds $\{[RuNO(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5-x-y-z}]^{3-x-y-z}\}$, these are most likely found in aqueous systems. The most common of the Ru compounds contain the $Ru(NO_3)^{3+}$ group, generally formed in aqueous nitric acid systems (Rard 1985). Igarachi et al. (1982) found that the presence of NO and NO_2 reduces the proportion of RuO_4 in the gas phase, making it more soluble in water, which could suggest the formation of a NO-bearing compound. Mun (2006) suggests the presence of a nitrosylruthenium compound and also that NO_2 can react with RuO_2 to form RuO_4. The compounds $RuO_3(OH)$ and $RuOH$ might also exist.

A second factor that impacts the release of Ru into the gas phase during oxidation is the thermochemical favorability for release. Thermochemical calculations with HSC Chemistry show that oxidation of gaseous ruthenium dioxide $[RuO_2(g)]$ with oxygen to produce $RuO_4(g)$ is favorable at all temperatures between 0 and 2000 °C. Thermodynamic stability is greater when NO_2 is the oxidant. However, the vapor pressure of $RuO_2(s)$ is estimated to be negligible from 100 to 600 °C. Because of the very small concentrations of RuO_2 that could exist in the vapor phase, production of $RuO_4(g)$ by this route would seem to indicate that the vaporization and oxidation of $RuO_2(g)$ is extremely rapid, while the decomposition of $RuO_4(g)$ is, in relative terms, extremely slow. The slow decomposition of $RuO_4(g)$ at ambient temperatures is supported by the fact that RuO_4 is persistent and can be recovered as a solid or liquid (Rard 1985). The tetroxide decomposes at temperatures above 500 °C (Mellor 1936). Oxidation of gaseous RuO_2 may be the process by which RuO_4 is produced in dry nuclear fuel TPT processes, and the extent of conversion is entirely controlled by the kinetics of the mechanism just discussed.

These results are in line with the literature, namely that RuO_4 is the most produced and persistent Ru species in the gas phase at temperatures below 1000 °C, even though the source term and total amount volatilized remain unclear. The RuO_4 is expected to decompose slowly to RuO_2 in the gas phase and on the stainless steel ductwork (Mun et al. 2006, Giordano et al. 2010). The volatile RuO_4 decomposes to particulate RuO_2 that is trapped in the scrubber and on HEPA filters. At air temperatures less than 700°C, the gaseous concentration of RuO_3 is expected to be negligible (Backman et al. 2005).

The third factor that may affect Ru presence in the gas phase is the presence and generation of particulates. It appears that the Ru is converted to a particulate that is relatively easily removed from the off-gas stream in the normally installed train of scrubbers, condensers, rough filters, and HEPA filters

(Goles et al. 1981). However, the distribution of Ru between gas phase species and particulates is unknown.

Finally, it is unknown how the presence of ozone within the TPT system could affect Ru generation and stability in the gas phase. The intense radiation field that accompanies the head-end processing of highly radioactive UNF likely generates a steady state concentration of radiolysis products in the gas stream from the TPT atmosphere. This effect has been noted and partially studied as part of the severe reactor accident program (Mun et al. 2006; Pontillon et al. 2010; Giordano et al. 2010; Backman et al. 2005; Mun et al. 2008a, 2008b; Kajan et al. 2017a, 2017b; Singh et al. 2014). The projected radiolysis products in air are ozone (O_3), oxides of nitrogen (NO_x), and free radicals (O^-, OH^-, etc.) (Mun et al. 2008a). It has been documented that the presence of O_3 in the gas stream, even at very low concentrations, can oxidize RuO_2 to RuO_4 and cause Ru to be transported (Mun et al. 2008a).

Also as part of the severe reactor accident program, the interactions between RuO_4 and silver and iodine were studied (Kajan et al. 2017b, Kajan et al. 2016). The presence of both silver (as metal or as $AgNO_3$) and NO_2 significantly enhanced the transport of Ru as RuO_4 (Kajan et al. 2017b). The presence of RuO_4 oxidized iodine into volatile forms (Kajan et al. 2016). These findings indicate that Ru should be removed before iodine. The discussion above strongly suggests that the presence of radiolysis products in air or the air–NO_2 mixture can cause some RuO_2 to be oxidized to volatile RuO_4 that could reach an iodine sorbent bed and increase the transport of iodine. These results highlight the importance of determining the effects of air radiolysis products on the performance of the Ru sorption system. These types of experiments are outside the scope of the proposed work but may be needed as the Ru removal design advances.

4.   POTENTIAL RUTHENIUM SORBENTS

As Ru distribution between gas phase species and particulates is unknown, the degree of abatement provided by particulate filters is also unknown. HEPA filters have been shown to remove Ru-bearing particulates with a DF of 1×10^3 to 1×10^4 (Mineo et al. 2002), but they may be less effective against volatile Ru species, including RuO_4. Thus, a removal operation for gaseous Ru is intended for placement within the off-gas treatment train to facilitate effective Ru abatement. The most commonly discussed Ru sorbents in the literature include silica gel, metal fibers or metal oxides, and liquid scrubbers. A solid sorbent would be most desirable for this application, and they are discussed in this section. Liquid scrubbing is useful for laboratory scoping tests and is discussed more fully in Section 6.

4.1   Silica Gel

It was recognized fairly early that volatile Ru could be trapped on silica gel at relatively low temperatures (Gill and Wisehart 1954). Later work suggested that a silica gel bed could be operated at moderate temperatures (20 to 200 °C) to remove RuO_4 from moist air (Vujisić and Nikolić 1982, Klein et al. 1980). The consensus from the literature is that lower temperatures (approaching 25 °C) seem to best facilitate Ru adsorption on silica gel.

Silica gel is the most extensively studied Ru adsorber, and some studies have reported the capacity of silica gel for Ru in a flowing system. Ruthenium loadings on silica gel of 2.6 kg/m³ are reported by Goossens (1991). Newby and Barnes (1975) report a Ru loading on silica gel of 4.8 kg/cm³, but this number may reflect their upper analytical limit. Weisenburger and Seifert (1980) reported Ru loadings on silica gel of 3–4 kg/m³ in the presence of steam.

Much of the reported work on silica gel was performed in a humid environment; such an environment does not translate directly to Ru adsorption from the off-gas of a dry TPT process. Nevertheless, two general observations were made from a review of literature. First, the adsorption of Ru on silica gel depends on the amount of water within the feed stream and within the silica bed. Several authors pretreated a silica bed with water prior to adsorption experiments to activate it (Newby and Barnes 1975,

Vujisić and Nikolić 1982). As silica gel has some capacity for water, the presence of water/steam in the feed stream or adsorber bed could decrease the capacity of silica gel for Ru. However, water may promote the reduction of RuO_4 to the less mobile RuO_2 within the bed and decrease any potential migration of physisorbed RuO_4 through the bed (Cains and Yewer 1985, Klein et al. 1980). Still unclear is whether silica gel has useable capacity for Ru in a dry standard TPT off-gas stream and whether it can retain Ru without water present. Klein et al. (1980) indicate that the physisorption of RuO_4 onto silica gel from dry off-gas effectively creates a "delay bed" rather than a true Ru adsorber.

The second observation is that it is unknown how the presence of NO_x, such as would be present in an advanced TPT process, affects the adsorption of Ru on silica gel. Cains and Yewer (1985) reported that NO_x resulted in higher DFs in their experimental system, and the presence of NO_x decreased the amount of Ru released during desorption. Water was present in this test system. Klein et al. (1980) also indicated that NO_x could increase system DF by facilitating RuO_4 reduction to RuO_2. However, this information is contradictory to that of Kepak et al. (1977), who stated that penetration of RuO_4 through a silica gel bed increased substantially when NO_x was present in the feed stream at several volume percent. In the case of the work by Kepak et al. (1977), the temperature of the silica gel beds was 200 °C.

4.2   Metal Fibers, Oxides, and Alloys

Some research has been performed on the adsorption of Ru by metal fibers or metal oxides (Cains and Yewer 1985, Holm et al. 2009, Sakurai et al. 1985), but results suitable as the basis for an engineering design are limited. Calculations performed with HSC Chemistry indicate that at temperatures between 0 and 1000 °C, oxidation of Fe, Ni, or Cr with $RuO_4(g)$ is thermodynamically very favorable. Reaction products are $RuO_2(s)$ and the oxides of Fe, Ni, and Cr. In stainless steel alloys, the activities of these elements are lower than in the pure state, but stainless steel wool would likely be a good medium for reducing RuO_4 while remaining impervious to the NO_x present in the case of advanced TPT. Tests will be necessary to optimize the temperature for reducing and trapping the Ru.

Newby and Barnes (1975) studied the adsorption of Ru from a flowing stream on a bed of ferric oxide. The DF of this system was found to increase with increasing bed temperature. In this work, the bed was held at 400 °C. They report a Ru loading on stainless steel of 136 mg/g, but this number may be an artifact of their upper analytical range.

Many studies examining the deposition of Ru on stainless steel provide insight into the speciation and the loading of Ru as a function of surface area and report if deposition is enhanced through specific experimental conditions (Sakurai et al. 1985, Mun et al. 2006, Mun et al. 2007a, Holm et al. 2009). However, practical engineering data remain unreported.

4.3   Other Potential Sorbents

Two other sorbents that may merit scoping-level testing for this application are alumina and glass. Newby and Barnes (1975) report a DF of 50 within their system with porous glass as the adsorbent. Mun et al. (2007a) and Holm et al. (2009) indicate that Ru loading on glass wool could be similar to that of stainless steel alloys. Holm et al. speculate that the deposition may be a function of surface area, rather than the specific material on which Ru deposits.

Vujisic and Nikolic (1982) considered alumina as a Ru sorbent and report loadings of 5–10 mg/m^3. In Klein et al. (1977) a number of metal coupons were coated with Ru deposits, and the Ru coating on alumina coupons was reported to be extremely resistant to physical abrasion. An alumina sorbent could be operated at high temperature, perhaps the same as the TPT process temperature.

5.   PROPOSED EXPERIMENTAL SYSTEM FOR EVALUATION OF RUTHENIUM SORBENTS

The proposed experimental system consists of three parts: (1) a reliable method of generating the Ru species of interest, (2) an experimental apparatus to reliably test the proposed capture media, and (3) analysis methods suitable for the given application. These are treated in Sections 5 and 6. A test plan for determining key engineering parameters relating to Ru abatement by solid sorbents is described in Section 7.

5.1   Proposed Ru Species Generation Systems

As stated in Section 3.2, the predominant volatile species expected is RuO_4; however, given the thermodynamic instability of this compound, the generation of a RuO_4-bearing gas stream is not straightforward. Many of the RuO_4 generation systems detailed in the literature rely on the evaporation or purging of highly oxidizing Ru-containing solutions. This is not viewed as ideal for this project given that the evaporation step would add some level of steam (water or acid vapor) to the test system. The steam would later have to be removed through a drying step that could significantly alter the Ru content of the simulated off-gas stream. Since either TPT process is carried out at temperatures less than 800 °C, the temperature below which RuO_3 is unstable with respect to RuO_4, only techniques for RuO_4 generation need be considered.

5.1.1   Sparging or evaporation of oxidative solutions

Several solution-based methods to produce metastable $RuO_4(g)$ have been summarized in the literature (e.g., Rard 1985, Mellor 1936), and most rely on the use of chlorine (Cl_2) to coax it from aqueous solution, for example, reaction of Na_2RuO_4 in aqueous solution by sparging with Cl_2. The generation of volatile RuO_3 and RuO_4 from Ru and RuO_2 has been carried out in simple systems consisting simply of a glass container with an acid solution of $RuCl_4$ (Sasahira et al. 1996, Shin and Park 2003, Swider-Lyons et al. 2005, Voskresenskaya et al. 2014b, Vujisić and Nikolić 1982) or RuO_3 (Mun et al. 2007a) to which an oxidizing agent (permanganate, potassium chlorate [$KClO_3$], or similar) is added. Generation of a continuous stream of $RuO_4(g)$ that is dried over $Mg(ClO_4)_2$ can be achieved by continuous addition of an oxidizing agent to an acid solution of RuO_3.

To prepare a RuO_4 generating system for simulation of TPT off-gas treatment systems, water vapor must be removed as neither of the TPT processes contain water. Since RuO_4 is the primary gas in these generating systems, it is dried in a column packed with magnesium perchlorate [$Mg(ClO_4)_2$]. Magnesium perchlorate is used to both dry the gas and, because it is a strong oxidizing agent, keep the Ru as RuO_4 (Mun et al. 2007a).

Both Cains and Yewer (1985) and Klein et al. (1980) generated RuO_4 through evaporation/purging of RuO_4 from a highly oxidizing solution. The system described by Cains and Yewer is shown in Figure 1. In both Cains and Yewer (1985) and Klein et al. (1980), Ru ($RuCl_3$) was slowly fed into the oxidizing solution and, as RuO_4 formed, it was removed in a continuous inert gas purge. In the case of Klein et al. (1980), the solution was KIO_4 in 6N H_2SO_4 solution. They reported that they generated a stable evolution of Ru at 3 to 50 mg/h at a concentration of 50 to 830 mg/m^3 (11 to 184 ppmv).
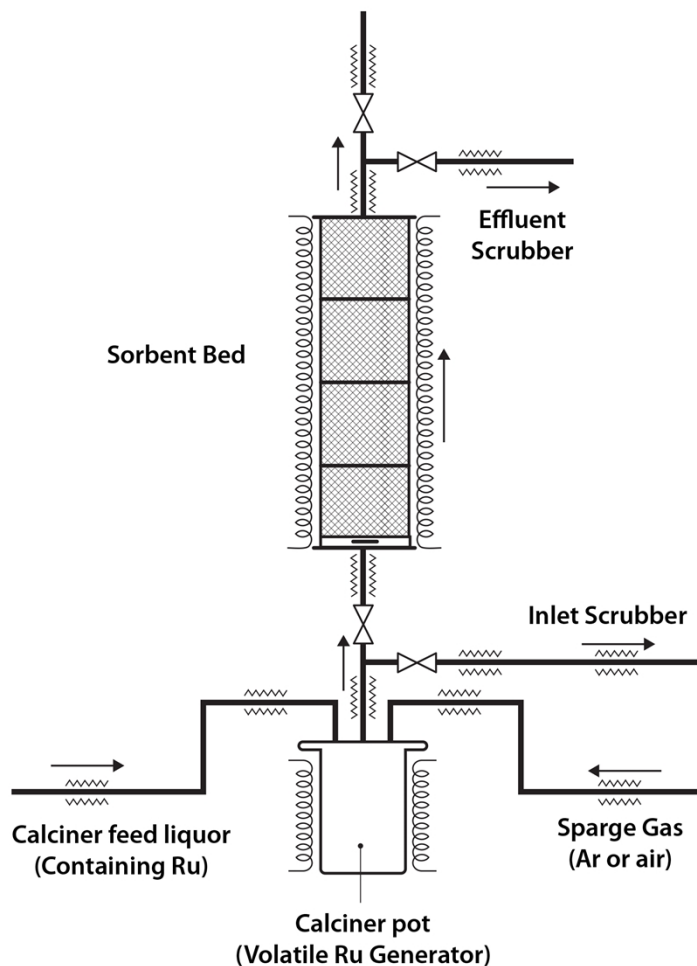
Figure 1. Evaporative/sparging system of the type described by Cains and Yewer (1985).

5.1.2   Sublimation of RuO$_4$ crystals

Methods for preparing solid RuO$_4$ crystals have been reported. Mellor (1936) describes one:

> …recommended preparing the tetroxide of a high degree of purity by distilling at 40° to 50°, in a current of air, an acidified solution of the mass obtained by fusing in a silver crucible a mixture of 1 part of finely divided ruthenium, 2 parts of potassium permanganate, and 20 parts of potassium hydroxide. The tetroxide condenses in a receiver, cooled with ice, in the form of long yellow needles.

This method, although useful for producing an air stream carrying RuO$_4$, contains water vapor and the acid used for the acidification. Amundsen and Stern (1982) report essentially the same RuO$_4$ preparation method as Mellor (1936) but indicate that Cl$_2$ may be used instead of permanganate.

Holm et al. (2009) utilized RuO$_4$ crystals in the chemical vapor deposition of RuO$_4$ onto metal surfaces. The crystals were condensed on the exterior of a chilled sample vial and allowed to sublime into flowing O$_2$ and deposit on metal coupons contained in the test system. This type of test system is shown in Figure 2.
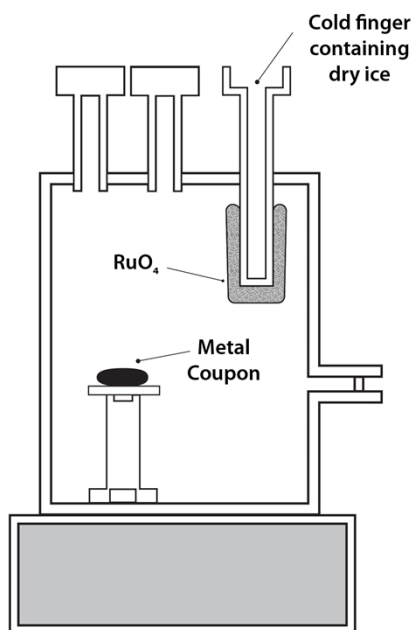
Figure 2. RuO$_4$ crystalline generator of the type described by Holm et al. (2009).

5.1.3   Oxidation of Ru or RuO$_2$ solids

Dry oxidation of Ru solids to generate RuO$_4$(g) is not documented extensively in the literature. Backman et al. (2005) oxidized RuO$_2$ powder with air in a two-zone tubular flow furnace. The temperature of the RuO$_2$-containing zone was varied from 1227 to 1427 °C and the air flow was metered at 5 L/min. A similar concept was employed by Maas and Longo (1979, 1980) in which hydrated RuO$_2$ was volatilized in O$_2$ at 750 °C. This type of experimental system is shown in Figure 3.
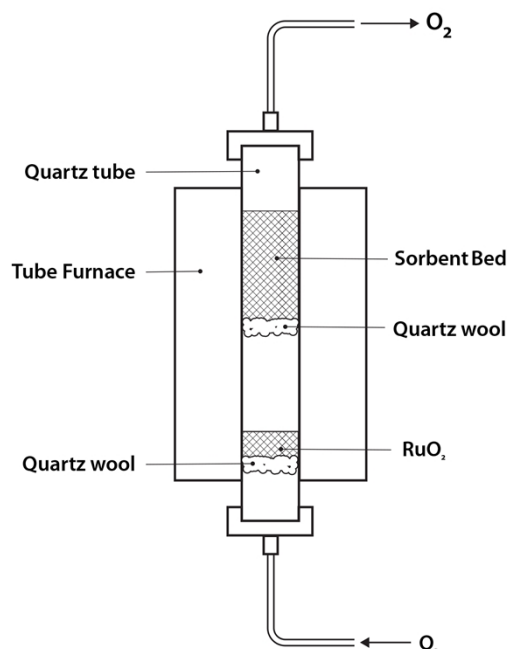
Figure 3. Dry volatilization system of the type described by Maas and Longo (1979).

As discussed in Section 3.1, calculations performed with HSC Chemistry verify that production of gaseous RuO_4 from solid RuO_2 is not thermodynamically favored at temperatures below 2000 °C, which is in conflict with the generation methods described by Backman et al. (2005) and Holm et al. (2009). Calculations indicate that direct conversion of the free metal to RuO_4 in oxygen or NO_2 is favored at temperatures below 900 °C, but a lower energy state is obtained if the oxidation stops at RuO_2.

5.2   Proposed Experimental Apparatus

Work on Ru abatement system designs performed in the engineering evaluation of an integrated off-gas system for the head-end off-gas stream of a reprocessing facility (Jubin et al. 2016) determined that further characterization of both metal- and silica-based sorbents would be advantageous in refining future Ru abatement system designs. The literature reviews and calculations detailed in Sections 3 and 4 provided a basis for the design of an experimental system, an analytical method, and a test plan, which are documented in the remaining sections of this report. The difficulties in handling Ru-bearing gas streams, from both safety and practicality perspectives, drove the decision to propose a very simple test system and test design.

5.2.1   General experimental considerations

Care must be exercised in the handling of $RuO_4(g)$, as it tends to decompose on many surfaces. Those surfaces that appear to have the least tendency to act as a decomposition site for RuO_4 are alumina and Teflon (polytetrafluoroethylene, or PTFE). Although PTFE has been used in experiments (Mun et al. 2007a, 2007b), a glassier form of Teflon, perfluoroalkoxy alkanes (PFA), should be considered. Teflon can be used at temperatures up to about 250 °C. Regardless of the materials of construction, some decomposition of RuO_4 to RuO_2 is expected, and this must be taken into account when assessing the experimental results.

Care must also be taken with respect to the partial pressures of RuO_4, given the potential for explosive decomposition of RuO_4 to RuO_2. Eichler et al. (1992) demonstrated that as the concentrations of Ru decrease, the thermodynamic stabilities of the vapor and solid species change, favoring the stability of

solid RuO_3. They point out that the decomposition temperature for $RuO_3(g)$ could fall below 700 °C. This could lead to enhanced transport of Ru in the silca gel sorption bed. Thus, the test matrix should include a wide range of Ru concentrations of probable species in the TPT off-gas streams.

5.2.2   Proposed test system

Designers of a test system for Ru abatement studies must first determine the method by which the Ru-bearing gas stream will be generated. The evaporative approach described in Section 5.1 is the most extensively documented method for generating gaseous RuO_4; however, this approach adds moisture to the gas stream. One of the large data gaps related to Ru capture by the sorbents reviewed is their performance in a dry stream, such as would be generated by TPT. Therefore, the evaporative method is not ideal for use in the experimental application described here. Although a gas stream could be dried after Ru generation and prior to entering the sorbent test bed, it is likely that Ru would be lost during this drying step and that characterization of the loss would add experimental uncertainty to the results.

The generation of Ru from RuO_4 crystals was also considered, but the mass of RuO_4 crystals required to generate a Ru-bearing gas stream would be larger than can be safely handled without specialized facilities. Solid-phase RuO_4 can decompose explosively at temperatures within the range of interest for this application.

Given the concerns described here, the generation of a Ru-bearing stream from Ru metal exposed to air or oxygen appears to be the easiest method to implement for this application. Figure 4 shows a diagram of the proposed test system. Ruthenium metal is held in a horizontal tube furnace at high temperatures (likely >500 °C) through which O_2 or air will be metered. This configuration is expected to volatilize some of the Ru metal. The test beds are to be connected to the tube furnace such that the Ru-bearing gas stream remains in the heated zone and is immediately passed through the sorbent bed. Upon exiting the sorbent bed, any RuO_4 not absorbed by the sorbent bed is removed in an aqueous scrubber. All materials of construction are quartz, with the temperature of both the tube furnace and the sorbent bed carefully controlled to avoid unexpected Ru deposition within the test system. The mass of the Ru metal is measured before and after each experiment, allowing determination of the expected gas-phase concentration for each experiment.
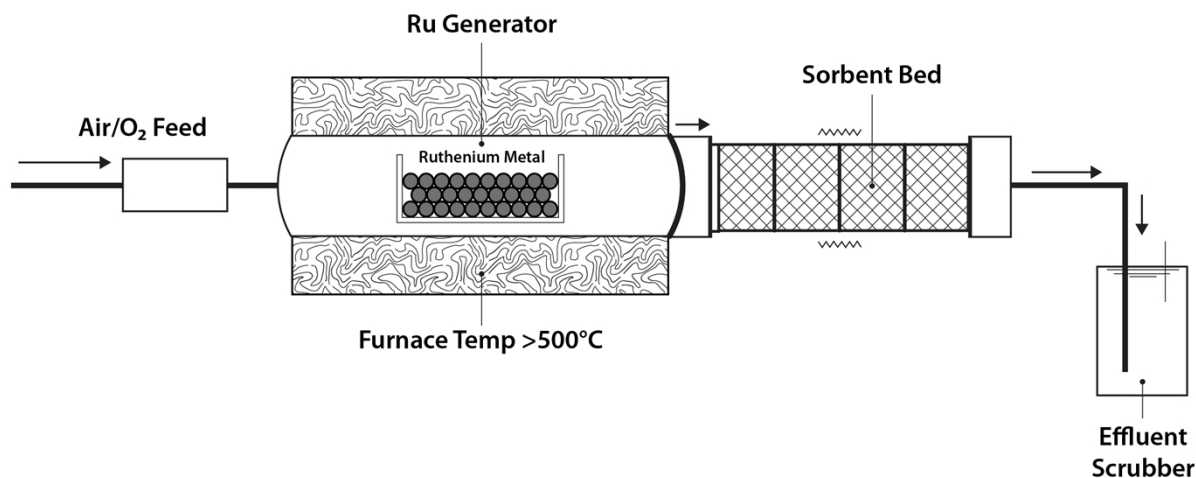

Figure 4. Proposed Ru test system.

6.   PROPOSED ANALYSIS METHODS

The tests proposed here support the use of various analytical techniques. Quantification of the volatilized solid Ru (RuO_4 crystal or RuO_2) is accomplished by measuring the mass of the source (Ru metal or RuO_2) before and after the experiment. The rate at which the Ru is volatilized is calculated from the mass loss and the time of the experiment. It is assumed that mass change due to Ru oxidation during the experiment is negligible in comparison with the amount volatilized.

Ruthenium trapped in the bubbler solution (KOH) has been determined after quantitatively precipitating Ru with the addition of ethyl alcohol to the KOH and centrifuging the precipitated Ru; the precipitated Ru can be dissolved and determined with ICP-MS (Holm et al. 2009, Kajan et al. 2016, Mun et al. 2007b).

The Ru on the Ru sorbent can be characterized with solid-state analyses (SEM) and chemical analyses with dissolution followed with ICP-MS. Neutron activation analyses can also be used.

6.1   Liquid Scrubbers

Wet scrubbing of the off-gas streams has been reported to have DF values of 10 to 10^4 (Klein et al. 1980, Kitamura et al. 1993, Oma and Nelson 1981). For the tests to be performed in this study, a 1 molal KOH solution and two scrubbers in series is recommended. Each of these scrubbers has a DF of about 1000. The Ru captured in the scrubbers can be measured with ICP-MS.

Alternatively, a scrubber solution of NaOH-NaOCl could be used and the perruthenate peak at 385 nm monitored as an online method. Separation and spectrophotometric characterization of the dissolved Ru species is possible (Kuchekar et al. 2015), but analyses of the solutions with ICP-MS is a more developed method.

7.   RECOMMENDATIONS

A proof-of-principle test matrix is proposed here, based on the literature review of Ru gaseous behavior and Ru abatement technologies. This test matrix provides insight into the behavior of Ru in laboratory test systems and generates initial results for Ru deposition on two solid sorbents. The test system, as described in Sections 5 and 6, consists of a tube furnace in which Ru metal is oxidized to RuO_4, a sorbent bed directly adjacent to the tube furnace, and an aqueous scrubber to capture any gaseous RuO_4 passing through the sorbent bed. The test system is constructed of single-use glass parts so that no residual Ru is carried over from one experiment to the next. The glass components may be leached to assess residual Ru. Dissolution of the RuO_2 deposits can be accomplished with a solution of KOH (0.2 molal) and $K_2S_2O_8$ (18.5 mmolal) followed by Ru analyses with ICP-MS. Gill and Wisehart (1954) report that the RuO_2 deposited on silica gel can be quantitatively removed with hot concentrated (12 molal) HCl.

7.1   Characterization of Ru Generation and Deposition within the Test System

Ruthenium is expected to be deposited throughout the test system. To quantify Ru loss to the test system, baseline testing is performed with the fully assembled test system and no emplaced sorbent. A Ru-bearing gas stream is generated by flowing O_2 or air over Ru metal at elevated temperature (likely >500 °C) and sending it through the empty sorbent holder. The amount of Ru recovered from the effluent in the liquid scrubbers (described in Section 6.1) is compared to the amount of volatilized Ru, as measured by mass loss of Ru contained in the generation cell. The difference represents the amount of Ru lost to the test system. As Ru deposition is dependent upon experimental conditions, testing to quantify deposition of Ru within the system should be replicated for each expected sorbent test condition.

The liquid scrubbers are used both to quantify Ru deposition within the test system and to characterize the Ru generation method. After exiting the sorbent holder, the gas stream goes through NaOH-NaOCl bubblers; aliquots of the solutions are taken on a time schedule and submitted for analysis. This testing provides insight into the stability of the Ru concentration in the gas stream.

Although the scrubber solutions are expected to be analyzed by ICP-MS, RuO_4 forms an orange complex in NaOH. The extinction coefficient for this complex is not adequately documented. Beer's Law is used to determine the lower limit of quantitation and if UV-Vis spectroscopy is found to be sufficiently sensitive, it can be used for monitoring the effluent stream in sorbent testing experiments. This could provide nearly real-time estimation of breakthrough times for the sorbents investigated.

7.2   Adsorption of Ru by Metal Sorbent

This test will characterize the adsorption of Ru by stainless steel wool at temperatures of 150 and 300 °C. In the literature, porous stainless steel disks as Ru filters were tested (Klein et al. 1980). Stainless steel in general has been found to catalyze the transformation of RuO_4 to RuO_2 and O_2. In the removal of Ru, a high-surface-area medium, such as stainless steel wool, could provide sufficient surface area at low pressure drop to result in high Ru removal efficiency.

Testing exposes the stainless steel wool to a Ru-bearing stream for up to 48 hours. Periodic sampling of the effluent scrubber allows for estimation of Ru breakthrough time through the sorbent bed. The sorbent bed, after being contacted with Ru, is purged with dry air or O_2 to ensure full removal of any physisorbed Ru within the sorbent bed. It is unlikely that Ru will be desorbed from the sorbent bed, but if so, it is collected in the aqueous scrubber. Following desorption, the bed is removed in sections to allow analysis of Ru loading and estimation of the mass transfer zone depth.

7.3   Adsorption of Ru by Silica Gel

This test is used to characterize the adsorption of Ru by silica gel at a temperature of 150 °C. As stated previously, there is some discrepancy in the literature as to the usefulness of silica gel in Ru abatement, but lower temperatures should facilitate Ru deposition within the sorbent media, with higher temperatures promoting continued volatility and mobility of RuO_4 within the system.

Silica gel can be used as received or after washing and heat treating (drying) at 150 °C. Testing then proceeds similarly to that described in Section 7.2. Ruthenium loading on silica gel can be determined directly from neutron activation analysis, but it can also be dissolved for ICP-MS analysis by either a solution of KOH (0.2 molal) and $K_2S_2O_8$ (18.5 mmolal) or hot concentrated HCl.

7.4   Data Obtained

This series of initial testing is intended to provide (1) Ru breakthrough time and Ru loading capacity of metal mesh in a dry stream, (2) Ru breakthrough time and Ru loading capacity of silica gel in a dry stream, and (3) Ru desorption from silica gel as a function of time (mg Hg^{-1} g^{-1} loaded silica). In addition, information such as the length of the mass transfer zone may be obtained through successful leaching of the sorbent beds. Finally, any experimental data gathered on Ru quantitation by either UV-Vis spectroscopy or neutron activation analysis may augment the literature available on the subject of Ru analysis. Much of the information intended to be collected from this testing will be directly useful in the refinement of Ru abatement system designs such as those included in the engineering evaluation of an integrated off-gas system for the head-end off-gas stream of a reprocessing facility (Jubin et al. 2016).

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