Initial Assessment of Ruthenium Removal Systems for Tritium Pretreatment Off-Gas

Nuclear Technology Research and Development

Approved for public release. Distribution is unlimited.

Prepared for
U.S. Department of Energy
Material Recovery and Waste Form Development Campaign
B. B. Spencer, M. L. Parks, and S. H. Bruffey

Oak Ridge National Laboratory
31 January 2018
NTRD-MRWFD-2018-000200
ORNL/SPR-2017/576

SUMMARY

The processing of used nuclear fuel releases volatile and semivolatile radionuclides into the off-gas streams associated with the various processing steps. Ongoing efforts to develop methods to control the release of gaseous radionuclides to the environment have identified ruthenium (specifically ^{106}Ru) as one of the semivolatile nuclides requiring a high degree of abatement. The tritium pretreatment process will release a fraction of the ruthenium as volatile ruthenium tetroxide (RuO_4). Scoping tests were conducted to characterize the adsorption/deposition of RuO_4 from dry gas streams by two different substrates: steel wool and silica gel.

A simple test system was assembled to produce RuO_4 through oxidation of powdered ruthenium metal, followed by a temperature-controlled sorption column. Tests were conducted with no sorbent present in the column to obtain baseline data on the evolution of RuO_4 and deposition of ruthenium on the internal surfaces of the column. Silica gel and steel wool were tested as adsorbent media. Gaseous effluent from the column was scrubbed with caustic solution to remove any remaining ruthenium. Ultraviolet/visible spectroscopy (UV/Vis) and inductively coupled plasma–mass spectroscopy analyses were used to measure the amount of ruthenium in the scrub solutions.

The UV/Vis analysis proved to be problematic because of precipitation of ruthenates, ruthenium oxides, and hydrated ruthenium oxides that occurred over time. An effective stabilization agent that does not adversely affect the desired spectra needs to be identified if this method is to be used in the future. There were indications that oxidation of powdered ruthenium metal did not generate a stream with steady concentration of RuO_4, so improved techniques are needed for follow-on experiments designed to infer deposition rate.

Both steel wool and silica gel are able to decrease the effluent Ru concentration by a factor of 10–100 during the 5-hour tests conducted. These tests were conducted using a dilute RuO_4-bearing dry gas stream and the short test duration did not result in sorbent saturation or in an estimation of Ru breakthrough time. RuO_4 desorbs from silica gel at room temperature. As interactions between RuO_4 and silica gel are not irreversible, it cannot function as a disposal media without pretreatment to reduce RuO_4 to a less mobile species. Silica gel may be useful as a RuO_4 sorbent or delay media in some applications. Based on visual observations, steel wool was an effective deposition substrate with no evidence of RuO_4 release. The deposition form should be identified and methods to assay the ruthenium content need to be developed.

This page is intentionally left blank.

CONTENTS

This page is intentionally left blank.

FIGURES

TABLES

This page is intentionally left blank.

ACRONYMS

AgZ	silver exchanged mordenite
Ag^0Z	hydrogen reduced silver exchanged mordenite
DF	decontamination factor
ICP-MS	inductively coupled plasma–mass spectroscopy
TOG	tritium pretreatment off-gas
UV/Vis	ultraviolet/visible (spectroscopy)
VOG	vessel off-gas

This page is intentionally left blank.

INITIAL ASSESSMENT OF RUTHENIUM REMOVAL SYSTEMS FOR TRITIUM PRETREATMENT OFF-GAS

1. INTRODUCTION

The processing of used nuclear fuel to recover materials for reuse or for conversion to geologically stable waste forms results in the release of radioactive volatile and semivolatile nuclides into the off-gas systems of the processing plant. Ongoing efforts to develop methods to control the release of gaseous radionuclides to the environment have identified ruthenium (specifically ^{106}Ru) as one of the semivolatile nuclides requiring a high degree of abatement (Jubin et al. 2014). Ruthenium is a platinum group metal with a high boiling point (4,150°C), but it can be oxidized to the quasi-stable tetroxide, RuO_4, which has a high vapor pressure even at room temperature (10 mm Hg at 25°C, Sakurai et al. 1983). (Note: The vapor pressure also has been related to the equilibrium among RuO_4, O_2, and RuO_2, rather than the pure RuO_4 form. For example, Penman and Hammer (1968) estimate the three-component equilibrium vapor pressure at 6.23×10^{-5} mm Hg at a temperature of 180°C.)

The release of ruthenium within a traditional aqueous reprocessing plant is most likely to occur during fuel dissolution. There is limited data available regarding the distribution of Ru from the dissolver liquid to the dissolver off-gas, but some studies indicate approximately 0.1% of the ruthenium inventory in the fuel can partition to the dissolver off-gas (Voskrenenskaya 2014). An alternative processing method includes a tritium pretreatment (TPT) operation prior to fuel dissolution. TPT oxidizes the UO_2 fuel matrix with an O_2-bearing gas stream to release tritium from the fuel prior to dissolution. This step can decrease the number of tritium separations required in the remainder of the plant, enhance overall recovery of tritium, and decrease the volume of tritiated waste requiring disposal. The amount of ruthenium volatilized during TPT is still unknown, with estimates ranging from 0.1% to 10% of the ruthenium contained within the used nuclear fuel (Klein et al. 1980, Ronneau et al. 1995). Depending on the magnitude of ruthenium release and the time since reactor discharge of the used nuclear fuel, ruthenium abatement may be required on the TPT off-gas stream.

Studies on ruthenium adsorption from the gas phase have primarily been performed in conditions that would simulate a severe reactor accident with gaseous ruthenium release to the environment. The temperature of these accidents is much higher than the operating temperature of TPT, which will impact ruthenium speciation in the gas phase. It is unknown how ruthenium speciation could impact ruthenium adsorption. Further, the TPT process will generate a dry ruthenium-bearing gas stream, whereas in environmental release scenarios the air will have a high moisture content.

Jubin et al. (2017) identified silica gel as a potential adsorbent for removing RuO_4 from humid gas streams. Information on its effectiveness in removing RuO_4 from dry gas streams, as expected in the tritium pretreatment process, was scant. Deposition of the ruthenium on stainless steel surfaces was also identified as a phenomenon that had been exploited to remove RuO_4 from gas streams. Deposition takes place as the tetroxide decomposes to the dioxide and oxygen at the metal surface. Conceptually, metal fibers having a high surface per unit mass of metal may be an effective sequestration agent, but practical engineering data remain unreported (Jubin et al. 2017).

The intent of this report is to document scoping tests characterizing the adsorption of ruthenium from dry gas streams by metal mesh and silica gel. A series of 10 tests were conducted that provided data on the generation of volatile ruthenium species by oxidation of ruthenium metal and the subsequent adsorption by the selected sorbents. Recommendations for follow-up testing are provided.

2. OBJECTIVES AND TEST MATRIX

The primary sorbent scoping tests were meant to evaluate the effectiveness of silica gel as an adsorbent and steel wool as a deposition surface for removing RuO_4 from a dry gas stream. Implicit in these tests was the need for a source of RuO_4. Bulk quantities of RuO_4 were avoided because of the potential of explosion—it is an unstable compound. Consequently, it was necessary to produce RuO_4 as part of the tests and limit its inventory by consumption and decomposition of RuO_4 at the rate of generation. The production rate using simple oxidation was in question, prompting tests to check the production rate of RuO_4. Because RuO_4 deposition, decomposition, or both on the internal surfaces of the process equipment was expected, baseline tests with no adsorbent were conducted at various temperatures to obtain data that could be compared to tests that used an adsorbent.

According to the test plan provided in Jubin et al. (2017) the silica gel was to be tested at 40°C and 150°C, but the initial tests conducted at a sorption temperature of 40°C showed that ruthenium was released from the silica gel after standing at room temperature. From this observation, it was projected that higher temperatures might prevent sorption by silica gel altogether, so tests at higher temperatures were not conducted. Similarly, the steel wool was to be tested at 150°C and 300°C, but because there was no breakthrough at 150°C, the tests at the higher temperature were unnecessary. Table 1 describes the tests performed. The four blank runs (no sorbent) were made to gain a better understanding of how ruthenium metal powder is oxidized and volatilized (two replicate runs at each of the different operating temperatures) and to assess the amount of ruthenium that passed through the test system. To get data on changes in the amount of ruthenium passing the silica gel bed as a function of run time, the bed was left in place for three separate runs (Runs 7–9). For the metal mesh sorbent, two replicates were tested at the same conditions, which was representative of the repeatability of the efficiency of the sorbent bed.

Table 1. Description of completed tests.

Run	Sorbent	Sorbent Temperature (°C)	Comment
1	—	40	Ru evolution baseline
2	Steel wool	150	
3	Silica gel	40	
4	Steel wool	150	Bed in five separate segments
5	—	150	Ruthenium evolution baseline
6	—	150	Ruthenium evolution baseline
7	Silica gel	40	Day 1 of 3-day silica load
8	Silica gel	40	Day 2 of 3-day silica load
9	Silica gel	40	Day 3 of 3-day silica load
10	—	40	Ruthenium evolution baseline

3. MATERIALS AND METHODS

The experimental apparatus consisted of a cylinder of compressed oxygen gas, a mass flow controller to meter the oxygen, two tube furnaces, and a gas scrubber (bubbler). A quartz tube was used in each furnace to contain the test materials and complete the flow path (Figure 1). Each tube had an inside diameter of 1-in. The first furnace was used to heat a small quantity of ruthenium powder to temperatures between

500°C and 700°C. The ruthenium powder was sieved to obtain particles that were >38 µm in diameter to ensure that the gas flow velocity would not blow any of the metal particles through the tube. Approximately 0.5 g of ruthenium was used in each test, and the ruthenium powder was placed in a small quartz boat to aid placement of the ruthenium in the middle of the furnace zone and to aid in recovery of the residual ruthenium. The boat was weighed before and after each test to document the mass of the initial ruthenium charge and the residual ruthenium remaining at end of testing. At the beginning of each run, the ruthenium furnace temperature set point was 400°C, and it was increased to 500°C and then 700°C with the set point changes occurring approximately 15 minutes apart.

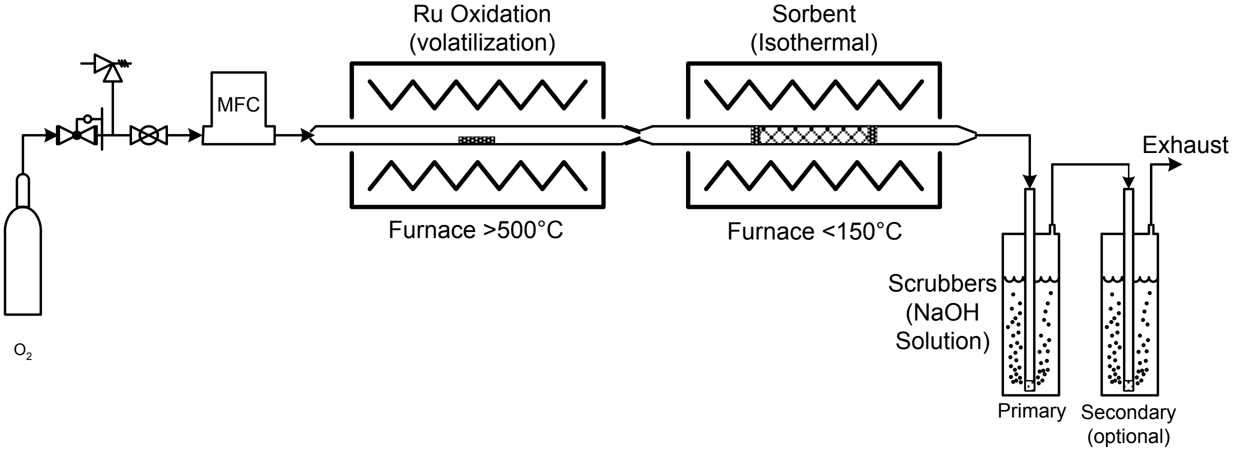

Figure 1. Test system schematic.

The second furnace was used to maintain the sorbent material, or deposition material, at a specific temperature (for brevity, the term "sorbent" may be used to refer to either material). Temperatures were either 40°C or 150°C, depending on the test being performed (40°C for silica gel; 150°C for steel wool). Sorbent was placed in the central zone of the second quartz tube. An amount of sorbent sufficient to produce a bed length of approximately 10 cm was used; blanks with no sorbent were also used. When using the silica gel, which consisted of spherical particles, the trailing end of the bed was confined with a glass frit and glass wool was placed at the leading end of the bed to keep the particles from slumping when the tube was put in the horizontal orientation. The glass wool was not necessary for the steel wool because it was self-supporting. The two tubes were connected by ground glass joints that were located between the two furnaces. The exposed section of the tubes between the furnaces was wrapped with fiberglass insulation to maintain the temperature to 40°C or more.

Pure oxygen was fed to the system from a compressed gas cylinder, using an appropriate pressure reducer. The flow rate was controlled by a Sierra mass flow controller. A flow rate of 0.5 L/min was used in each test. The gas flowed through the system and discharged through a caustic bubbler.

The effluent gas was scrubbed with 1.0 *M* NaOH solution. A standard laboratory bubbler was filled with approximately 250 mL of scrub solution. The effluent gas flowed through a glass frit placed near the bottom the bubbler to disperse the gas stream and enhance absorption of RuO_4 contained in the gas stream. A similar second bubbler was used to ascertain if any ruthenium was passing the first scrubber. Most tests operated for approximately 5 h after the ruthenium volatilization (first) furnace reached >500°C. Every hour a 5 mL sample was drawn from the primary bubbler, and a 5 mL sample was drawn from the secondary bubbler at the end of a test. The scrub solution became an orange color when RuO_4 was absorbed. Color changes were not observed in the second bubbler.

Silica gel and steel wool were the sorbents tested. An engineered form of silica gel desiccant was obtained from Alfa Aesar. The pellets were spherically shaped and the size specification provided by the vendor was -6,+12 mesh (1/16-in. to 1/8-in. diameter). Visually most of the pellets were of the larger 1/8-in. diameter. Steel wool, super fine #0000 was obtained from Rhodes American.

Both the sorbents and scrubber solutions were analyzed. The NaOH samples were analyzed via UV/Vis spectroscopy and ICP-MS. A solution of 0.5% RuO_4 in water (Acros Organics), stabilized with sodium hypochlorite, was obtained and used as a standard. Aliquots of this orange-colored standard solution were diluted in 1 *M* NaOH solution to obtain a range of RuO_4 concentrations from which to obtain UV/Vis absorbance data and thus prepare a calibration chart.

The silica gel was removed in five 2 cm sections and analyzed for ruthenium content by neutron activation analysis at Oak Ridge National Laboratory's High Flux Isotope Reactor. Analysis of the steel wool sorbent is pending and will require either leaching of the material or total dissolution. As stated before, the ruthenium powder was weighed before and after the test. Losses of ruthenium from the solid were calculated under the assumption that the initial powder was pure ruthenium and that the powder remaining in the boat had been oxidized to RuO_2.

4. RESULTS

4.1 Visual Observations

The blank runs, where no sorbent was used, verified that RuO_4 was indeed being produced by oxidation of the metal powder at temperatures over 500°C. The scrubber solution would quickly take on a yellow tint that intensified to a deep orange color as, presumably, RuO_4 continued to accumulate in the solution. Samples were taken at intervals during the run and analyzed by UV/Vis spectroscopy (Section 4.2), but the analysis did not occur immediately following sample collection. It was observed that after standing for 1 day or more, the samples and bulk scrubber solution would become water clear, and small black precipitate particles could be seen. Consequently, the value of UV/Vis measurements for quantitative measurements is questionable, but qualitative information might nonetheless be obtained.

Observation of the powdered ruthenium metal before and after a run indicated a color change from a dark grey to black. The amount of the ruthenium volatilized appeared to be very small (Figure 2). A slight darkening of the quartz tubes was also observed, especially at the ground glass joints where the glass surface is less glossy.

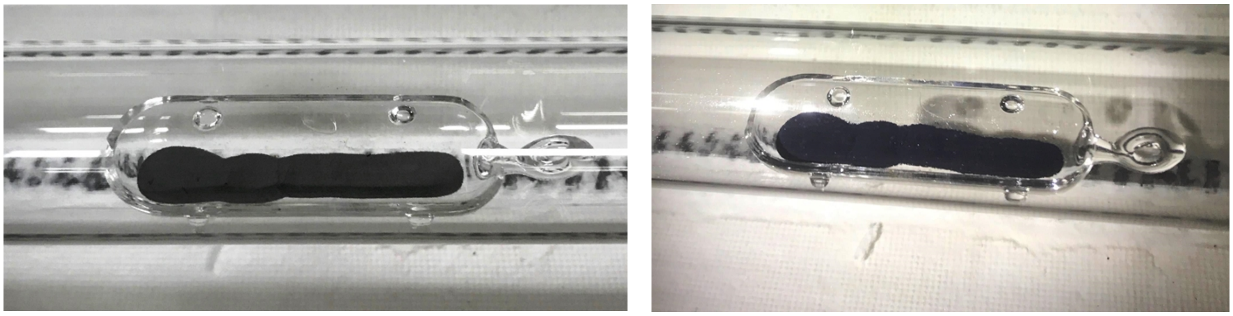

Figure 2. Ruthenium metal powder before (left) and after (right) a run.

In the first run using silica gel sorbent (Run 3), there was a slight color change at the glass frit in the bubbler. This indicated that some RuO_4 was passing the bed. When the run was complete and the furnace had cooled sufficiently to permit opening it for visual inspection, it was observed that the silica gel changed from a white color to a burnt-orange to black, with the intensity of the color greater in the leading portion of the bed (Figure 3). The variations in color in the circumferential coordinate suggest short circuiting of the gas resulting from poor packing of the silica gel in the tube, allowing the gas to pass over the top of the silica bed and into the bubbler with reduced treatment.

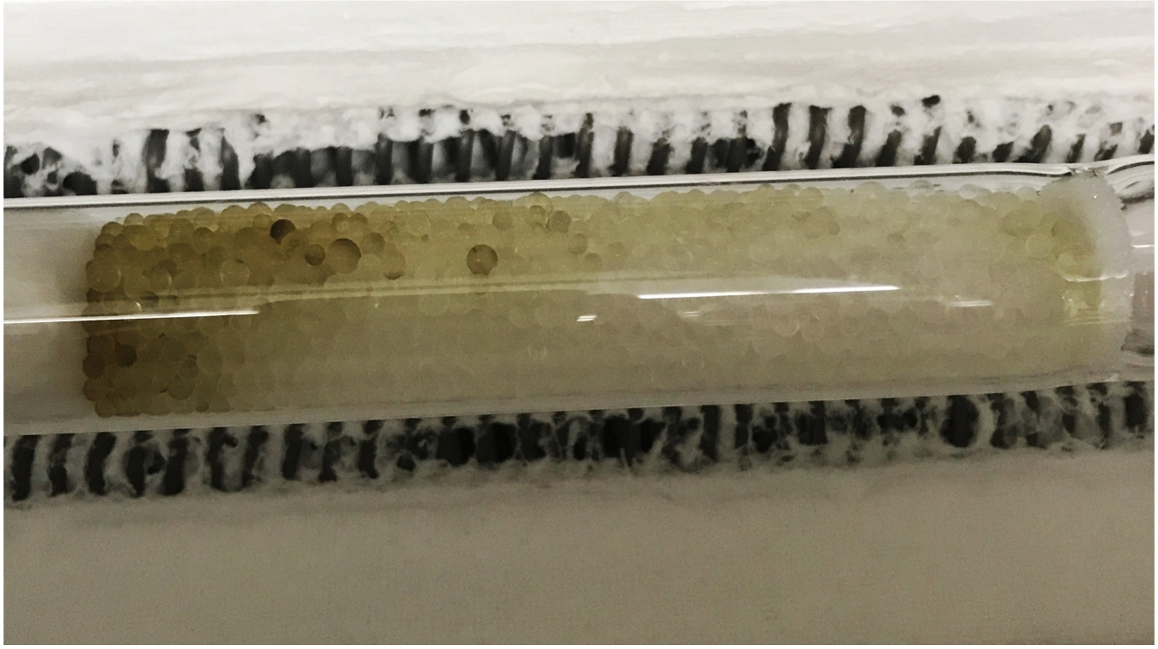

Figure 3. Photo of silica gel bed after exposure to RuO_4-O_2 gas mixture.

In a second test using silica gel, a longer exposure time was implemented in an attempt to saturate the leading portion of the bed with RuO_4. A denser packing of the glass wool at the leading edge of the bed was used to prevent slumping of the bed (the other end of the bed is confined by a glass frit). The test was conducted over 3 consecutive days and comprises Runs 7, 8, and 9 as listed in Table 1. Each day, a fresh supply of ruthenium powder was charged to the oxidation tube, the system heated to operating temperature, and oxygen flow initiated when operating temperature was reached. In addition, fresh scrubber solutions were used each day, and the run time was 5 hours per day. The tests were suspended overnight by shutting off the oxygen flow and shutting down the furnaces. The overall loading of the silica gel was conducted in three 5-hour periods. There was no visual color change in the scrubber solutions, and visual observation of the bed following the 3-day run showed a more uniform circumferential color (no photo is available). The color of the bed ranged from yellowish-black in the front portion of the bed, tapering off toward the end of the silica gel bed. The bed of silica gel was carefully removed in five 2-cm segments and placed in Nalgene bottles. After standing overnight, it was observed that the interior of the bottles blackened, with the most intense color change associated with the sample from the leading end of the bed (Figure 4). This suggests that the RuO_4 desorbed from the silica gel and deposited or decomposed to RuO_2 on the bottle walls. If this is the case, then the RuO_4 does not wholly decompose to RuO_2 on silica gel during the adsorption, and the silica gel may act only as a delay substrate for RuO_4. Nonetheless, samples of the silica gel were irradiated as part of the neutron activation analysis procedure.

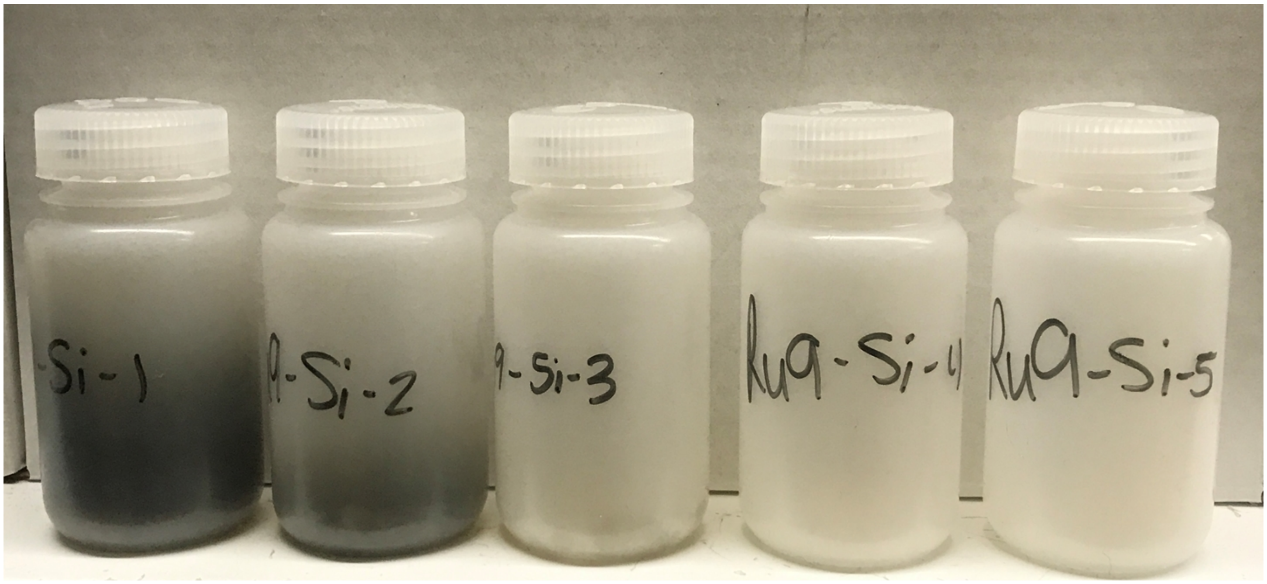

Figure 4. Bottles containing equal-length segments of silica gel from 3-day test.

In the runs using steel wool sorbent, the wool was placed in the quartz tube as five separate slugs to aid removal of the material at the end of the test. Note, the steel wool was packed loosely by hand and pushed into the tube using a small ram-rod, and the implication is that the packing density of the slugs may have varied. There were no open areas that would permit gas to bypass without contacting the steel wool. No color change in the scrubber solutions was visually evident. A short segment of the steel wool at the leading end of the bed changed color from a metal-grey to darker grey. At the conclusion of a test, the slugs of steel wool were recovered and placed in Nalgene bottles. There was no visual indication that RuO_4 was released from the steel wool as happened with the silica gel. The steel wool sorbent was not analyzed for total ruthenium content.

4.2 Ruthenium content of silica gel

The total ruthenium content of each silica gel segment recovered at the conclusion of Runs 3 and 9 is reported in Table 2. A subsample (~0.2 g) of each segment was transferred for neutron activation analysis. From the results and the total mass of the collected segment, the ruthenium loading was calculated, and is shown in Table 2. Sample Ru-9-1 was analyzed in replicate (n = 5) and the ruthenium content of that sample is reported as a range, reflecting the lowest and highest reported values. The range in values is reflective of the variability associated with sampling a non-heterogeneous material.

The segments recovered from Run 3 have lower total Ru content than those recovered from Run 9. This was expected due to difference in test duration (Run 3: 5 h; Run 7–9: 15 h) and the fact that Run 3 included channeling within the sorbent bed such that Ru passed through the bed and was recovered in the caustic scrubber.

Table 2. Ru content of silica gel bed segments.

Sample	Segment Weight (g)	Total Ru content (mg)	Average Ru loading (mg/g)
Ru3 - Si - 1	13.1529	0.39	0.030
Ru3 - Si - 2	6.8596	0.07	0.010
Ru3 - Si - 3	8.4697	0.06	0.007
Ru3 - Si - 4	7.4046	0.04	0.005
Ru3 - Si - 5	8.9757	0.05	0.006
Ru9 - Si - 1	9.4496	1.05–1.43 [a]	0.111–0.151
Ru9 - Si - 2	8.8068	0.75	0.085
Ru9 - Si - 3	9.692	0.13	0.013
Ru9 - Si - 4	7.9372	0.25	0.031
Ru9 - Si - 5	9.7346	0.01	0.001

[a] reflects a range provided by replicate samples

The segments were not subsampled immediately following removal from the tube furnace. Given that visual observation indicated desorption of Ru from silica gel at room temperature, it is likely that the total Ru content of each segment was higher upon initial removal from the bed than is reflected by analysis of the subsample. Future efforts to obtain a RuO_4 saturation value for silica gel should ensure that the material is analyzed quickly or chemically stabilized after sampling to minimize the RuO_4 desorption from the material. Additional tests should also be conducted to determine the amount of Ru retained in the silica gel following a specific period of active purging.

The observed Ru loadings on the silica gel are significantly lower than the 4.3 mg/g reported by Goossens (1991).

4.3 Analysis of Scrubber Solutions by Ultraviolet/Visible Spectroscopy

The gaseous effluent from the sorbent column (or empty tube) passed through a caustic scrubber to remove residual RuO_4 from the stream, as shown in Figure 1. Tests included those without sorbent in the column to obtain baseline information on ruthenium evolution and with sorbent to test the effectiveness of the solid sorbent. A 5-mL sample of solution was withdrawn from the scrubber approximately every hour of each 5-hour test. The samples were analyzed via UV/Vis spectroscopy.

To prepare for analysis of these samples, standards were prepared using a solution of 0.5% RuO_4 in water (Acros Organics). Aliquots of this orange-colored standard solution were diluted in 1 *M* NaOH solution to obtain a range of RuO_4 concentrations. The measured spectra, along with indicated RuO_4 concentrations, are shown in Figure 5.

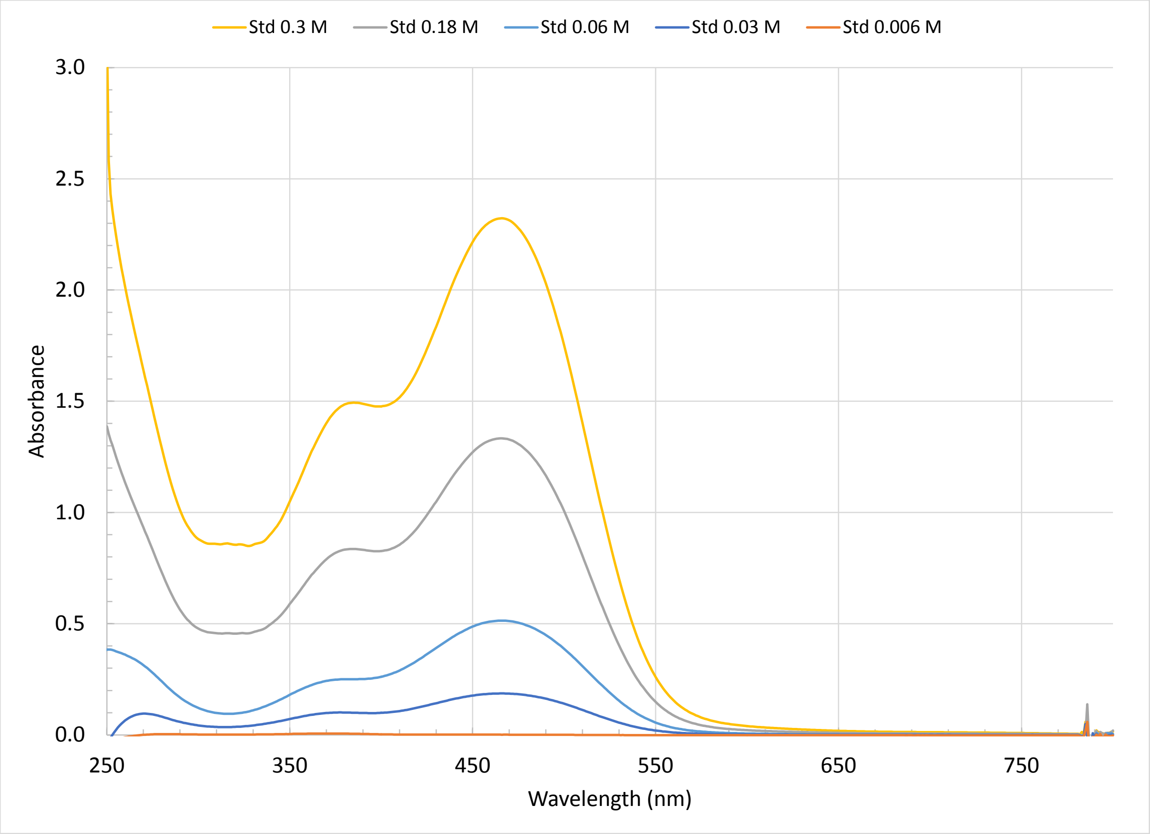

Figure 5. UV/Vis spectra for standard RuO_4 solutions.

Peaks are evident at wavelengths of about 375 nm and 466 nm. This is consistent with the spectral data of Chen et al. (2011), which showed peaks at 373 nm and 468 nm that were correlated to the ruthenate ion, RuO_4^{2-}. Their data also show that peaks at 313 nm and 382 nm are associated with RuO_4 and RuO_4^- ion. Consequently, it is difficult to resolve RuO_4 from RuO_4^-. Chen et al. (2011) also describe the solution color as yellow, green, and orange for RuO_4, RuO_4^-, and RuO_4^{2-}, respectively. Ruthenate ion is consistent with the initially observed color of solutions in the present work. A lower scale is used in Figure 6 to show more detail in the spectra taken using the two lowest concentration standards.

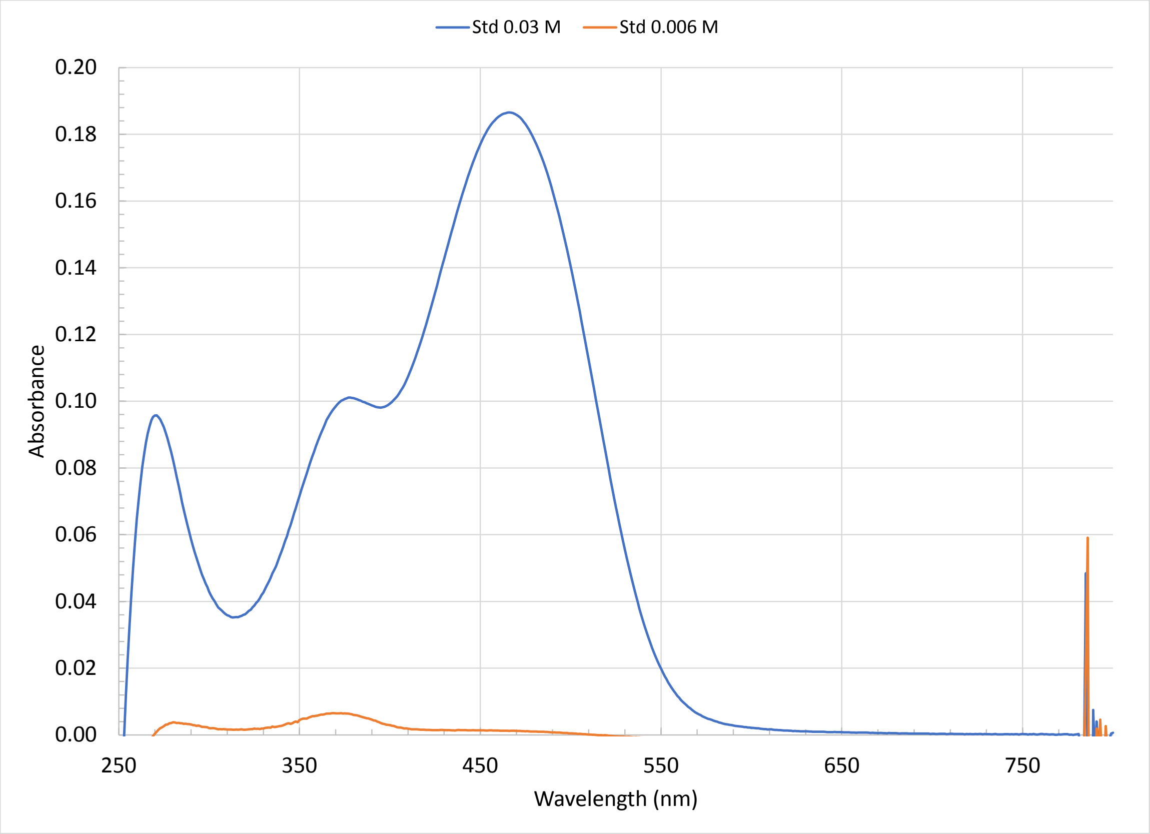

Figure 6. UV/Vis spectra for the two standard RuO_4 solutions of low concentration.

In Run 1 no sorbent was placed in the sorption column. Initially the samples were orange in color. Because of the logistics of analysis, the samples were stored at room temperature for several hours before the spectra was obtained. The spectra are shown in Figure 7, and the spectral peaks are very low compared to those of the standard solutions. The primary peak is just under 400 nm, and there is only a remnant of the peak around 466 nm. This seems to indicate that the ruthenate ion is being reduced. The sample concentration should have been increasing with time because the scrubber solution should have been accumulating RuO_4. The lowest peak should have been associated with Ru1-1 (1-hour sample) and the highest with Ru1-5 (5-hour sample). There is a general trend toward the reverse order, except that Ru1-3 has a higher peak than Ru1-2. Visual reexamination of the samples revealed a very fine black precipitate that could have been either sodium ruthenate ($NaRuO_4$), ruthenium dioxide (RuO_2), or hydrated ruthenium oxide [$RuO(OH)_2$]. Because the precipitate is produced at an unknown rate, it is not possible to quantify the amount of ruthenium present in the scrubber solution by the current UV-Vis analysis method. It was considered that the sequential reduction of RuO_4^{2-} could have caused some RuO_4 to evolve as a gas from the solution when the decomposition sequence passed through that form of ruthenium. However, the secondary scrubber used in most tests never showed a color change, which suggests such an evolution did not take place.

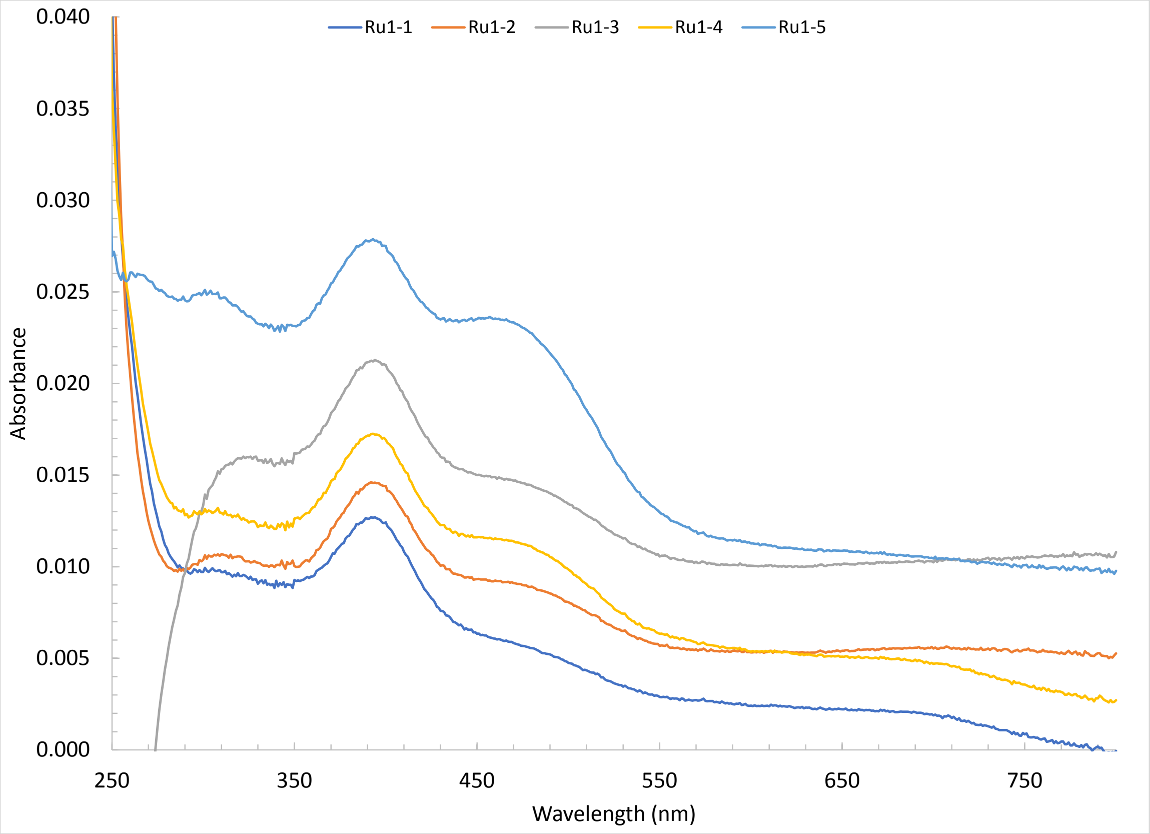

Figure 7. UV/Vis spectra for samples from Run 1 using no sorbent in column.

In Run 2 steel wool was used as the sorbent. The hourly samples denoted by Ru2-n-a (where n is the approximate run time in hours) and the backup scrubber samples denoted by Ru2-m-b (where m = 1 is the sample at the first hour and m = 2 is the last sample of the run, usually fifth hour) had measured spectra as shown in Figure 8. The measured absorbances are very small, and the peaks are in the shorter wavelength range (310–340 nm). The peak heights do not correlate with expected increases in ruthenium concentration.

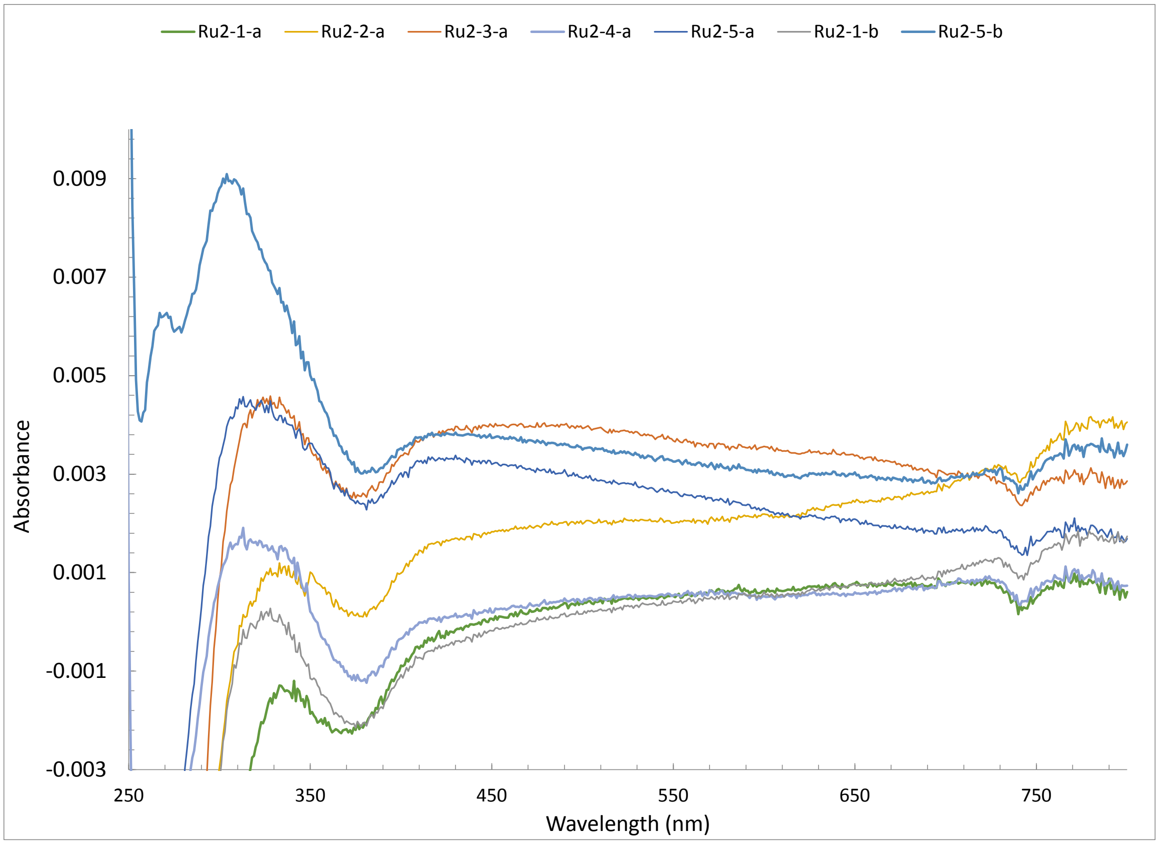

Figure 8. UV/Vis spectra for samples from Run 2 using steel wool sorbent in column.

Overall, the UV/Vis data cannot be used to quantify RuO_4 in the scrubber solutions. There is evidence that RuO_4 may have deposited on the interior surfaces of the equipment and connecting tubing, and the RuO_4 precipitated from solution as either $NaRuO_4$, RuO_2, or $RuO(OH)_2$. With additional work, including selection of a stabilization agent and adsorption spectra of the stabilization agent as a function of concentration, UV/Vis may be improved as a quantification tool.

4.4 ICP-MS and Gravimetric Analysis

All the small samples taken from the scrubbers at specific time increments during each run and the final scrubber solutions (usually the remaining >200 mL) were saved in case further analysis was desired. Samples were selected from these saved solutions for ICP-MS analysis of the ruthenium concentration. Table 3 lists the samples by identifier, the results of the analysis, and a very brief note describing the sample. In this table, samples starting with S are the standards prepared to calibrate the spectra. Those sample identifiers starting with R or Ru are associated with runs 1–10, as indicated by the one or two digits immediately following the letters. Table 1 may be referenced for the associated run conditions.

Table 3. Results of ICP-MS analysis of sample solutions.

Sample ID	**ICP-MS Result**		**Notes**
	Concn. (µg/mL)	**Uncert. (µg/mL)**	
S-RO4-H	144.000	14.4000	Standard solution, 300 µg/mL
S-RO4-M	24.200	2.4200	Standard solution, 60 µg/mL
S-RO4-L	0.499	0.0499	Standard solution, 6 µg/mL
R1-FS	0.312	0.0312	Centrifuged final solution; analyzed supernatant
Ru1-1	0.571	0.0571	5 mL sample recovered from sample bottle and cuvette
Ru1-3	—	—	Sample lost
Ru1-5	1.750	0.1750	5 mL sample recovered from sample bottle and cuvette
R2-FS	0.003	0.0003	Final primary scrubber solution, steel wool sorbent
R3-FS	0.070	0.0070	Final primary scrubber solution, silica gel sorbent
R4-FS	0.006	0.0013	Metal mesh sorbent; final primary bubbler
R5-FS	0.195	0.0195	Centrifuged final solution; analyzed supernatant
R6-FS	0.056	0.0056	Centrifuged final solution; analyzed supernatant
Ru6-1-a	0.554	0.0554	5 mL sample recovered from sample bottle and cuvette
Ru6-3-a	1.050	0.1050	5 mL sample recovered from sample bottle and cuvette
Ru6-5-a	1.240	0.1240	5 mL sample recovered from sample bottle and cuvette
R7-FS	0.014	0.0029	2nd silica gel test, day 1 final scrubber solution
R8-FS	0.006	0.0012	2nd silica gel test, day 2 final scrubber solution
R9-FS	0.007	0.0014	2nd silica gel test, day 3 final scrubber solution
R10-FS	0.133	0.0133	Centrifuged final solution; analyzed supernatant
Ru10-1-a	0.318	0.0318	5 mL sample recovered from sample bottle and cuvette
Ru10-3-a	1.710	0.1710	5 mL sample recovered from sample bottle and cuvette
Ru10-5-a	2.520	0.2520	5 mL sample recovered from sample bottle and cuvette
Ru10-1-z	0.165	0.0165	4 mL sample recovered from cuvette
Ru10-3-z	0.171	0.0171	4 mL sample recovered from cuvette
Ru10-5-z	0.769	0.0769	4 mL sample recovered from cuvette

The following list summarizes the ICP-MS results:

- Standard solutions used to obtain calibration of the UV/Vis spectra are samples S-RO4-x. Analysis showed much lower concentrations than calculated values based on dilution of the purchased standard solution in caustic. ICP-MS indicated the concentration of ruthenium at about half that expected in the two higher concentration standards, whereas the low concentration standard was about 8% of what was expected. It is speculated that the high dilution, which was necessary to achieve the low concentration standard, reduced the stabilization agent concentration to such a level that it was no longer effective.
- Final scrubber solutions are represented by Rx-FS. Samples R1-FS, R5-FS, R6-FS, and R10-FS are the final primary scrubber solutions (>200 mL) resulting from runs with no sorbent in the column (i.e., the blanks). Because black precipitate could be seen in these samples, ethanol was added as a mild reduction agent to precipitate any remaining soluble ruthenium. According to Backman et al. (2004) this should precipitate ruthenates or perruthenates formed from RuO_4 in caustic solution to insoluble RuO_2 or hydrated ruthenium oxide, $RuO(OH)_2$ (or $RuO_2 \cdot H_2O$). The solutions were centrifuged to recover the precipitates, and the supernatant was sampled and analyzed with results shown in Table 4. The remaining concentration of ruthenium in solution is very low.
- For samples R1-FS, R5-FS, R6-FS, and R10-FS, there are companion samples, for example Ru1-1 and Ru6-1-a, which are the small 5 mL samples taken at timed intervals over the run. The last timed sample in the series is the same solution as the final scrubber solution, except the timed samples were not treated with a reduction agent, and they were not centrifuged. The concentrations of ruthenium in these samples increase with time (Table 2), as would be expected as the ruthenium continues to accumulate over the course of the run. However, the concentrations are very small and could be biased downward because of ruthenium precipitates that may have adhered to the walls of the sample bottle. In Run 10, the "-z" samples were from the second scrubber, and the measured concentrations are smaller than in the primary "-a" samples.
- All other final scrubber solutions—specifically Ru2-FS, Ru3-FS, Ru4-FS, Ru7-FS, Ru8-FS, and Ru9-FS—came from runs in which the column was charged with a sorbent. Precipitates could not be seen in these samples. There was no treatment of the sample before analysis (i.e., no reductant added, no centrifugation). Concentrations in these final scrubber solutions were very low as shown in Table 3. Comparison with blank runs would appear to indicate that both sorbents were able to decrease the effluent ruthenium concentration by a factor of 10–100 over the test duration.

Table 4 summarizes a comparison of the amounts of ruthenium (as metal) found in the scrubber solutions of the blank runs. The product of the volume of the final scrubber solution and the untreated sample concentration gives the amount found in solution before treatment with the reductant (see second column). The concentration in the supernatant from the reductant-treated solution similarly allows calculation of the amount remaining in the supernatant solution after treatment (third column). The values show that the ethanol was very effective in precipitating the ruthenium. The precipitates from the treated final scrubber solution were recovered by centrifugation and decanting of the supernatant. The recovered solids were washed with distilled water, centrifuged to remove the bulk of the water, and allowed to dry in open vessels at room temperature. The mass of the recovered solids is given in Table 4 (fourth column). Assuming the solids to be $RuO(OH)_2$, the amount of ruthenium metal was calculated (fifth column). These data show that most of the ruthenium present in the scrubber solution precipitated before addition of the reductant. This is consistent with visual observations and the low concentrations of ruthenium found in the samples obtained during each run.

Table 4. Amounts of ruthenium found in selected solutions with ICP-MS and in separated precipitates.

Sample	**ICP, last timed sample -5[a] (µg)**	**ICP, -FS[b] (µg)**	**Washed and dried precipitate[c] (µg)**	**Metal equivalent[d] (µg)**
R1	393.75	70.20	11,500	7,693
R5	n/m	n/m	4,300	2,877
R6	282.72	n/m	3,300	2,208
R10	554.4	29.26	—	-lost-

[a] The 5 mL sample pulled at the end of the run for UV/Vis.

[b] Final complete scrubber solution supernatant after precipitation of ruthenium species.

[c] Precipitate recovered from the final complete scrubber solution by centrifugation and decantation of supernatant. The solids were then washed with water and dried at room temperature.

[d] Equivalent amount of ruthenium metal in the precipitate assuming solids were $RuO(OH)_2$.

The weight of ruthenium metal charged to the high temperature furnace (the source for RuO_4), and the weight of the remaining ruthenium was also measured. Because the gas used to oxidize the ruthenium metal powder was bottled dry oxygen, the remaining solids were assumed to be RuO_2. The calculated amount of ruthenium metal volatilized as RuO_4 is shown in Table 5, and the calculated amounts are much greater than the amounts shown in Table 4 for Runs 1, 5, 6, and 10. This may be an artifact of incomplete oxidation of the ruthenium because an oxide layer may inhibit oxidation of the metal deeper in the particle or deeper in the heap of powder. Another explanation is that the RuO_4 deposited on the internal surfaces of the quartz tubing before the gas stream reached the scrubbers. Detailed analysis of the remaining powder might help close the material balance; however, the rate of volatilization of RuO_4 over time would remain in question.

Table 5. Estimate amount of ruthenium metal volatilized in feed furnace.

Run	**Ru in oxidation furnace**		**Ru volatilized equivalent to Ru metal (mg)†**	**Compare to Table 3 (mg)**
	Start Ru (g)	**End RuO_2(g)***		
1	0.6030	0.6666	96.7	0.007693
2	0.6261	0.6983	95.7	
3	0.5509	0.6443	61.5	
4	0.5230	0.6112	58.8	
5	0.5282	0.6231	54.9	0.002877
6	0.5604	0.6539	63.7	0.002208
7	0.5616	0.6582	61.7	
8	0.5114	0.5821	69.3	
9	0.5674	0.6358	84.5	
10	0.5185			

* Assumed that all ruthenium metal powder in source boat was oxidized to RuO_2.

† Upper limit to amount of ruthenium metal volatilized; there is potential that not all the metal was converted to oxide.

5. CONCLUSIONS

Scoping tests were conducted to characterize the adsorption and deposition of RuO_4 from dry gas streams using two different substrates, steel wool and silica gel. Dry gas streams are representative of TPT off-gases, which have been studied to a lesser degree than humid gas streams from the dissolution process. Visual observations of the sorbent and scrubber solutions downstream of the absorption columns were very useful. Ruthenium deposits on the silica gel and color changes to the gel were very apparent, but the deposit desorbs from the gel at room temperature. Very slight color changes to the steel wool were discerned on contact with RuO_4, and there was no visual evidence that ruthenium species evolved from it over time. In tests without sorbent present, changes in the color of the solution in the first gas scrubber downstream of the sorption column indicated the presence of RuO_4, but the color faded with time of storage, ultimately resulting in a water-clear solution. No color changes were observed in the second caustic scrubber, indicating that limited or no RuO_4 passed the first scrubber.

The following conclusions and recommendations for follow-on studies are given:

- Based on ICP-MS analysis of the scrubber solutions, both steel wool and silica gel are able to decrease the effluent Ru concentration by a factor of 10–100 when compared to similar tests of 5-hour duration conducted without the sorbent in the treatment column. These tests were conducted using a dilute RuO_4-bearing dry gas stream and the short test duration did not result in sorbent saturation or in an estimation of Ru breakthrough time.
- RuO_4 desorbs from silica gel at room temperature. As interactions between RuO_4 and silica gel are not irreversible, the silica gel cannot function as a disposal media without further treatment to reduce RuO_4 to a less mobile species. Silica gel may be useful as a RuO_4 sorbent or delay media in some applications. The amount of Ru retained on the silica gel after active purging has not been determined.
- Based on visual observations, steel wool was an effective deposition substrate with no evidence of RuO_4 release. The deposition form should be identified and methods to assay the ruthenium content need to be developed. (Note the remaining, presumed, ruthenium oxide used in the volatilization furnace, did not dissolve in boiling 5 *M* HCl. Analysis of the steel wool is pending partly because of the need to identify better analysis methods.)
- Improved methods to generate a stream with steady concentration of RuO_4 are needed for follow-on experiments designed to infer deposition rate.
- UV/Vis analysis of RuO_4 in caustic solution is complicated by reduction of the soluble species over time, resulting in precipitation of ruthenates, ruthenium oxides, and hydrated ruthenium oxides. Use of solution stabilization agents is required for this quick and inexpensive analysis technique to be useful, and such agents should not interfere with the spectra important to measuring RuO_4 concentration.

6. REFERENCES

Backman, U., M. Lipponen, A. Auvinen, J. Jokiniemi, and R. Zilliacus, 2004. *Ruthenium Behaviour in Severe Nuclear Accident Conditions-Final Report*, Report No. NKS-100, Nordic Nuclear Safety Research, Finland.

Chen, J-Y., Y-C. Hsieh, L-Y Wang, and P-W. Wu, 2011. “Electroless Deposition of Ru Films via an Oxidattive-Reductive Mechanism,” *J. Electrochem. Soc.*, **158**(8): D463–D468.

Goossens, W. R. A., G. G. Eichholz, and D. W. Tedder, eds. 1991. "Treatment of Gaseous Effluents at Nuclear Facilities," *Radioactive Waste Management Handbook Volume 2*, Harwood Academic Publishers, Newark, NJ.

Jubin, R. T., D. M. Strachan, G. Ilas, B. B. Spencer, and N. R. Soelberg. 2014. *Radioactive Semivolatiles in Nuclear Fuel Reprocessing*, Report No. FCRD-SWF-2014-000601 (ORNL/LTR-2014/354), Oak Ridge National Laboratory, Oak Ridge, TN.

Jubin, R. T., S. H. Bruffey, B. B. Spencer, and D. M. Strachan, 2017. *Evaluation of Ruthenium Capture Methods for Tritium Pretreatment Off-Gas Streams*, Report No. NTRD-MRWFD-2017-000312, ORNL/TM-2017/330, Oak Ridge National Laboratory, Oak Ridge, TN, June 30.

Klein, M., M. De Smet, W. R. A. Goossens, and L. H. Baetsle. 1980. “Filtration and Capture of Semivolatile Nuclides,” pp. 91–100 in *Proceedings of the International Symposium on the Management of Gaseous Wastes from Nuclear Facilities,* International Atomic Energy Agency, Vienna.

Penman, B. D. and R. R. Hammer, 1968. *The Ruthenium Dioxide-Oxygen-Ruthenium Tetroxide Equilibrium*, IN-1013, Idaho Nuclear Corporation.

Ronneau, C., J. Cara, and A. Rimskikorsakov. 1995. “Oxidation-Enhanced Emission of Ruthenium from Nuclear Fuel,” *Journal of Environmental Radioactivity* 26(1): 63–70.

Sakurai, T., A. Takahashi, and G. Fujisawa, 1983. “Interaction of Ruthenium Tetroxide with Stainless Steel,” *J.Nuclear Sci. and Tech.*, **20**(1): 81–83.

Voskresenskaya, Y. A., O. A. Ustinov, and S. A. Yakunin. 2014a. “Ruthenium Capture from the Gas Phase during Reprocessing of Spent Uranium-Plutonium Nitride Fuel from Fast Reactors,” *Atomic Energy* 115(3): 187–190.