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Tc-99 Decontamination from Heat Treated Gaseous Diffusion Membrane -Phase I, Part B

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EXECUTIVE SUMMARY

Uranium gaseous diffusion cascades represent a significant environmental challenge to dismantle, containerize and dispose as low-level radioactive waste. Baseline technologies rely on manual manipulations involving direct access to technetium-contaminated piping and materials. There is a potential to utilize novel decontamination technologies to remove the technetium and allow for on-site disposal of the very large uranium converters.

Technetium entered these gaseous diffusion cascades as a hexafluoride complex in the same fashion as uranium. Technetium, as the isotope Tc-99, is an impurity that follows uranium in the first cycle of the Plutonium and Uranium Extraction (PUREX) process. The technetium speciation or exact form in the gaseous diffusion cascades is not well defined. Several forms of Tc-99 compounds, mostly the fluorinated technetium compounds with varying degrees of volatility have been speculated by the scientific community to be present in these cascades. Therefore, there may be a possibility of using thermal or leaching desorption, which is independent of the technetium oxidation states, to perform an in-situ removal of the technetium as a volatile species and trap the radionuclide on sorbent traps which could be disposed as low-level waste.

Based on the positive results of the first part of this work[1] the use of steam as a thermal decontamination agent was further explored with a second piece of used barrier material from a different location. This new series of tests included exposing more of the material surface to the flow of high temperature steam through the change in the reactor design, subjecting it to alternating periods of stream and vacuum, as well as determining if a lower temperature steam, i.e., 121°C (250°F) would be effective, too. Along with these methods, one other simpler method involving the leaching of the Tc-99 contaminated barrier material with a 1.0 M aqueous solution of ammonium carbonate, with and without sonication, was evaluated.

The results may indicate that the following conclusions are possible:

- Superheated steam treatment of the barrier material at 232 °C or 121 °C did not reduce the Tc-99 concentrations in the Paducah barrier material to levels comparable to the desired Oak Ridge disposal Waste Acceptance Criteria (WAC) limit of 172 pCi/converter waste.
- The thermal desorption process for uranium isotopes from the barrier material may be independent of the processes or chemistry involved in the thermal desorption of Tc-99
- Leaching with ammonium carbonate solution, with or without sonication, is a more reliable method of consistently obtaining better Tc-99 removal efficiency from the barrier material; one that meets the WAC limit for eventual Tc-99/barrier material disposal
- Leaching with ammonium carbonate may also result in excessive removal and accumulation of isotopes, U-235 in particular, which may lead to criticality problems if neutron poison agents are not incorporated with the ammonium carbonate based lixiviant.

The following recommendations are proposed:

- Ammonium carbonate-based lixiviant or other leaching agents, doped with neutron poison agents to address criticality concerns which may result from the accumulation of uranium isotopes with leaching of the barrier material, should be considered for further studies. This leaching study will also include the evaluation of other Tc-99 target lixiviants, leaching time, ammonium carbonate concentrations, pH, solid/liquid ratio (phase ratio), and temperatures effects on Tc-99 and uranium isotope removal efficiency with and without sonication.

- The use of fluorinating agents, such as environmentally compatible nitrogen trifluoride, which under thermal conditions will convert the technetium compounds in the barrier material into more volatile technetium compounds, should be considered as a means of attaining the desired Oakridge Tc-99 waste disposal WAC limit or even a Tc-99 waste disposal WAC limit lower than the 172 pCi/converter-waste.

- Thermal decontamination of both Tc-99 and uranium isotopes from the Paducah barrier materials should be performed with emphasis on superheated steam treatment at more elevated temperatures; temperatures greater than the boiling temperature of technetium oxides.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CPT	Chemical Processing Technology
DL	Detection Limit
EM	Environmental Management
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
M&TE	Measurement and Testing Equipment
MDA	Minimum Detectable Activity
MDL	Minimum Detection Limit
NA	Not Applicable
P&ID	Piping and Instrument Diagram
PPPO	Portsmouth/Paducah Project Office
PUREX	Plutonium Uranium Extraction
SRNL	Savannah River National Laboratory
TTQAP	Task Technical and Quality Assurance Plan
WAC	Waste Acceptance Criteria

1.0 INTRODUCTION

The Department of Energy's Portsmouth/Paducah Project Office (PPPO) is responsible for the large uranium gaseous diffusion plants that are now shutdown. As the plants operated to enrich uranium, some of the source of uranium included material that had been irradiated in the production reactors at Hanford and Savannah River. The spent fuels were processed using the Plutonium and Uranium Extraction Process (PUREX) to recover the uranium and remove the bulk of the fission product impurities. The first cycle PUREX product stream contained the purified uranium but also contained a small amount of impurities. The most notable one was technetium, in the form of pertechnetate. Following the Paducah flowsheet, the uranium oxide was reacted with anhydrous hydrogen fluoride to produce uranium tetrafluoride. Subsequently, the tetrafluoride reacted with fluorine to produce uranium hexafluoride. Golliher, et al, [2] determined that the technetium was entrained within the uranium in each of these steps. Upon entering the gaseous diffusion cascade, some of the technetium deposited within the barrier material.

It is estimated that more than 500 kilograms[3] of Tc-99 were originally fed to the cascades, with the current Tc-99 inventory in the Paducah cascades at less than 50 kilograms[4]. In addition to the cessation of feeding of Tc-99 contaminated UF_6 to the cascades, most of the Tc-99 had been removed during cascade and maintenance operation activities over the last 30 years of operations. At the Oak Ridge Gaseous Diffusion Plant, the barrier material was manually removed; and if this method is implemented at Paducah, it will be labor intensive and very costly. Therefore, developing and deploying an in-situ decontamination process, one which can reduce the manual labor, and risk of personnel radiological exposure, offers advantages in terms of schedule duration, costs and safety. An on-site disposal cell at Paducah is also being considered, and the waste acceptance criteria (WAC) are under development. The on-site disposal cell at Oak Ridge Tennessee has a Tc-99 WAC[5] limit of 172 pCi/g of waste and is a reference point for this testing. To compare Tc-99 results from this testing in pCi/g of barrier material to the WAC limit of 172 pCi/g of waste material, a correction factor was needed to convert from barrier to a converter. This factor can be obtained from the Paducah Technetium-99 Sampling Results Graph.[6]

Early studies[7] showed some removal of technetium from cascade components in the form of barrier material. Additionally, a statistical design set of experiments[8,9] showed removal of technetium at 30 – 60% at temperatures below 270 °F. The only direct evidence of a volatile technetium species in the cascades was determined by infrared spectroscopy to be in the pertechnetyl fluoride, TcO_3F [10] form. However, there are other Tc-99 compounds with little volatility such as the oxides of technetium (TcO_2 and Tc_2O_7), pertechnetic acid ($HTcO_4$) and the oxyfluorides of technetium (TcO_2F_3 and $TcOF_4$). Therefore, based on these early findings, there is the potential to utilize higher temperatures and perhaps different atmospheres to affect the decontamination, such as thermal desorption under vacuum, flowing air or flowing steam prior to the application of gases like hydrogen fluoride, fluorine or chlorine trifluoride.

The results of the first part of these tests at SRNL [1] demonstrated that the use of just air or vacuum was not effective, but steam did show some promise by obtaining a measurable decontamination of Tc-99, as well as uranium isotopes. However, one concern was the lack of knowledge about whether flow of steam was over the entire surface of the barrier material or just a limited area. The test reactor was a straight tube through which the stream flowed and the barrier material simply sat at undefined location on the bottom of the tube. The steam flowed over and around the specimen but not on the bottom of the specimen or not necessarily through the tubular specimen. In this follow-up tests or extension of previous

SRNL investigation of Tc-99 superheated steam decontamination as cited above, with modifications of the test reactors, the steam is forced through the tubular specimen and then back over the outer surface so that the entire surface would be exposed to the steam flow.

Besides subjecting more of the test specimen's surface area to steam, other variations were tried. For example, using just straight vacuum was not effective in the previous tests, [1] therefore, alternating periods of steam and vacuum treatments of the test specimens was planned to minimize membrane pore blinding due to the presence of steam or moisture in the pores of the barrier material membrane. This will otherwise prevent thermal desorption of embedded Tc-99. The Tc-99 decontamination factor would increase with such alternating steam/vacuum treatment process. Another method investigated was the use of lower temperature steam treatment because it was not known if decontamination with steam could also be attained at a lower temperature. If lower temperature steam was effective, too, it would be easier to implement; therefore, tests were done at 121°C (250°F). Finally, because steam may be difficult to sustain on large and long-term basis, two tests were performed where the test material was simply exposed, at room temperature, to an aqueous solution of 1.0 M ammonium carbonate with and without sonication to demonstrate if leaching with ammonium carbonate would successfully decontaminate the material.

2.0 SCOPE OF PROJECT; PART B OF PHASE I

The objective of Part B of this SRNL follow-up scoping experiment was to demonstrate the following:

- Whether thermal Tc-99 decontamination of the barrier material, with a technology based on flowing superheated steam at constant temperatures of 121°C (250°F) and 232°C (450°F), will result in a significantly larger Tc-99 decontamination factor; meeting a WAC limit of 172 pCi/converter or lower and
- Whether a room temperature leaching of the barrier material in an aqueous media1.0 M ammonium carbonate solution, with and without sonication, will result in a significant removal of Tc-99 from the barrier material.

The preliminary laboratory data could eventually be used for the scale up of a viable technology for Tc-99 decontamination from the barrier material. This report documents the scoping investigations performed at SRNL and the planned test matrix is summarized in Table 1.

Table 1 Overall Test Matrix

Test No.	ADS Sample ID	Test Description (1)
0-A	As Received P 4-1	Baseline Tc-99 concentration for one sample (2). Sample from one end of the length of the original test sample.
0-B	As Received P 4-2	Baseline Tc-99 concentration for second sample (2). Sample from the other end of the length of the original test sample.
0-C	As Received P 4-3	Baseline Tc-99 concentration for third sample (2). Sample from middle section of the length of the original test sample.
1-A	1-Hour Steam-232°C-1	Limited sample exposure - as previous test (3)
1-B	4-Hour Steam-232°C-2	Limited sample exposure - as previous test (3)
2-A	SV-Pulse-4HR-232°C	Full exposure of a sample: Alternating between steam & vacuum conditions.
2-B	SV-Pulse-4HR-232°C	Repeat of Test 2-A with same sample in the reactor (4)
3-A	SV-Pulse-4HR-232°C	Full exposure of a sample: Alternating between steam & vacuum conditions.
3-B	SV-Pulse-4HR-232°C	Repeat Test 3-A with same ample in the reactor (4)
4-A	Leach with Sonication	Solution of 1.0 molar $(NH_4)_2CO_3$ with sonication. The temperature increased from 20.5°C to 51.6°C during the 2-hour test
4-B	Leach without Sonication	Solution of 1.0 molar $(NH_4)_2CO_3$ without sonication at 20.5°C for 2 hours
5-A	8-Hour Steam-121°C-1	Full sample exposure with low steam temperature of 121°C for 8 hours
5-B	8-Hour Steam-121°C-2	Repeat of Test 5-A but with a new sample
6-A	HS-4HR-232°C-1	Repeat of Test 1-B, but with Full sample exposure 232°C
6-B	HS-4HR-232°C-2	Repeat of Test 6-A but with another sample

Notes to table:

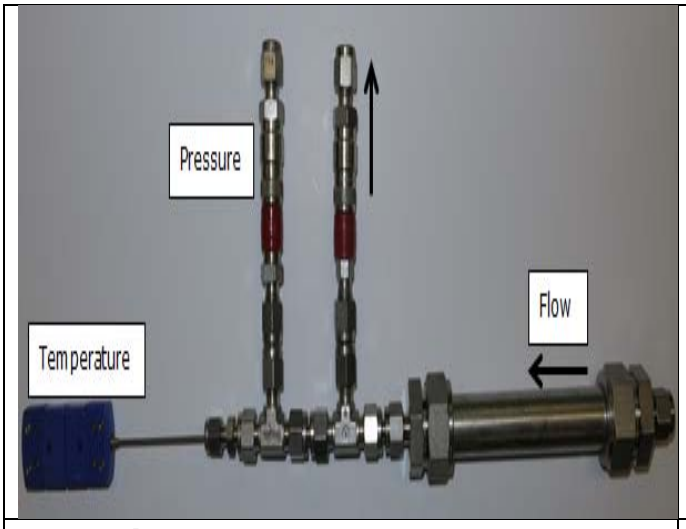
(1) The terms "limited" and "full sample exposure" refer to how a sample was secured in the test reactor. For partial exposure, a sample sat on the bottom of the test reactor where the flowing media, e.g., steam, flowed around, but not necessary through a sample. Full exposure indicates the test flow was directed such that the entire sample surface came in contact with the flowing media.
(2) These were subsamples of material used in subsequent tests 1 through 6.
(3) Previous tests are documented in SRNL-STI-2016-00740, Rev. 0, March 2017.
(4) Tests 2-A/B and 3-A/B were duplicate runs with the same sample used in each run and in the following order: steam-vacuum cycle (A runs) and steam-vacuum cycle (B-runs).

3.0 Experimental Setups/Sample Description and Preparations/Methodology

The experiment was performed in three different setups: Leaching, flowing steam where there was limited exposure of the surface of the test material to superheated steam (repeat of previous test [1]), and flowing steam where there was full exposure of the surface of the test material. The simplest was the leaching test. Here a test specimen was placed in a 150-mL capacity Teflon® vessel containing a 1.0-M solution of ammonium carbonate with and without sonication. These tests started at room temperature, but for sonication the liquid temperature increased from 20.5 °C to 51.6 °C from the process of energy dissipation. The steam setup was comprised of a reactor to contain the test specimen, a heating mantle to heat the reactor, a steam generator, a class 5 Security safe to protect the sample specimen during unattended testing periods, and a radiological hood to protect the workers and environment from the radiological nature of the test materials. All the steam tests were to be performed at a constant reaction temperature of either 121°C (250°F), or 232°C (450°F). The steam tests with limited surface exposure of the test specimen were basically a repeat the previous test campaign [1] to confirm the results. For those tests, a test specimen had no special orientation in the reactor other than it sat on the bottom of the reactor tube. The more complicated steam test is where the specimen was fully exposed to the steam by forcing the steam through the center of the tubular specimen and the back over the outside surface of the test piece. However, the steam system feeding the reactor for either the limited or full exposure test was the same and the piping and instrument diagram (P&ID) for flowing superheated steam shown in Appendix A, Figures 20 and 21. Explanations of some of the key aspects of the test equipment follow.

3.1 Test Reactor

The old reactor device that held the barrier material was a stainless-steel tube as shown in Figure 1 insert A. Figure 1, insert A, shows the old reactor design with the flow from right to left and the two ports to measure temperature and pressure and an exit port. Figure1, insert B, shows the modified reactor (new design) with double by-pass tubing. This metal flange held the sample piece in place inside the reactor insured steam delivery to all sample surfaces both inside and outside the sample. Figure 2 shows the arrangement of possibly two reactors inside the heating mantle which is designed to maintain a temperature of 121°C ± 5 °C or 232 °C ± 5 °C during the test durations. The superheated steam in this phase B of testing was performed using a single reactor for all steam tests.



Insert A: Old test reactor showing the thermocouple, pressure, and flow connections (old reactor design)

Insert B: New test reactor designed to ensure steam flow through all sample surfaces

Figure 1 Test reactor showing the thermocouple, pressure, and flow connections.

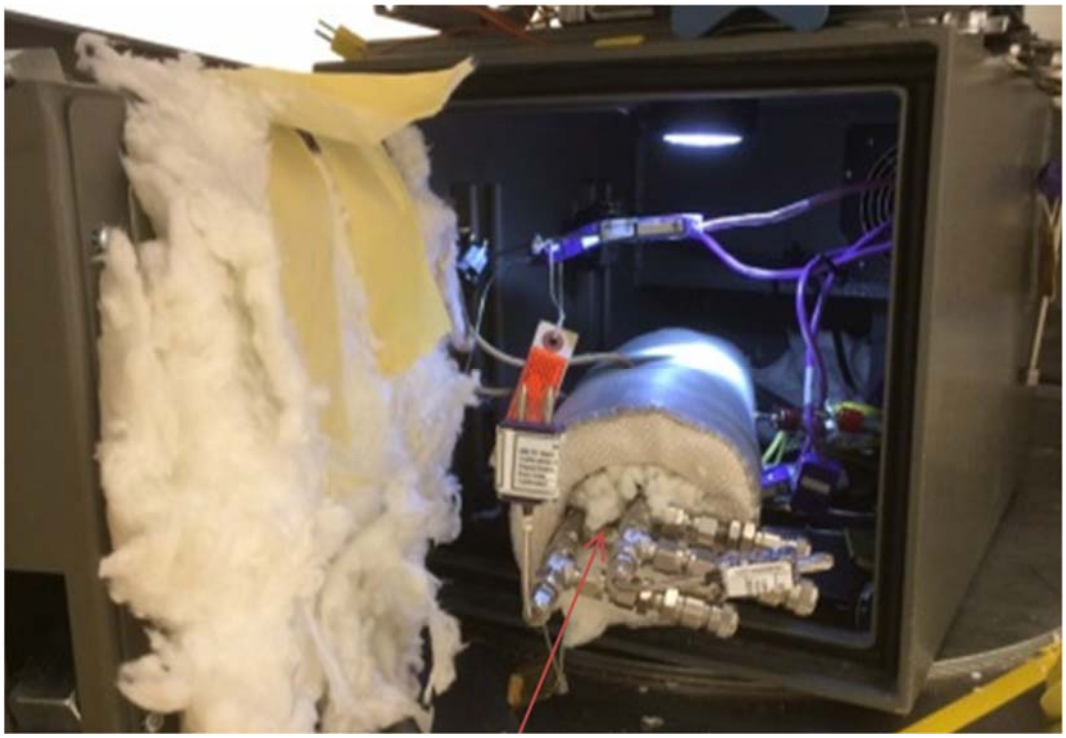


Figure 2 Interior and exterior of the class-5 security safe and the location of the reactor

3.2 Security safe

To ensure classified matter controls were in place, the test material was contained inside a classified repository as shown in Figure 3. This work utilized a repository from Trusted Systems, Inc. and specifically the TSM131V IPS Security Container. The security safe is equipped with two interior exhaust fans to ensure adequate exhausting of hot air from the interior of the security safe during heating operations.

The exterior plumbing on the rear of the safe is shown in Figure 4. Interior wiring, both inside the security safe and directly outside the heating mantle, consists of twisted/shielded thermocouple wires and extension wires with polyvinyl insulation (Newport Electronics EXPP-K-20-TWSH-UL-1000 UL Listed Shielded Extension Grade Thermocouple Wire) and with low noise connectors from Omega. These polyvinyl insulation grade wires and connectors have a maximum temperature rating of 90 °C. The immediate transfer lines, into and out of the security safe and reaction chamber (reactor), which carry the steam to the barrier sample material being heated, were made of 316L SS, followed by an outer reinforcement of 321 SS braided hose. This had a maximum temperature rating of 454 °C. E-type thermocouples were used throughout the set up. The transfer lines from the exit section of the reactors, outside the security safe were made of 1/4th inch stainless steel tubing. All tubing outside the safe were contained within the radioactive hood, except the single tube to the steam generator.

Figure 3 Exterior of the class-5 security safe and the location of the reactor

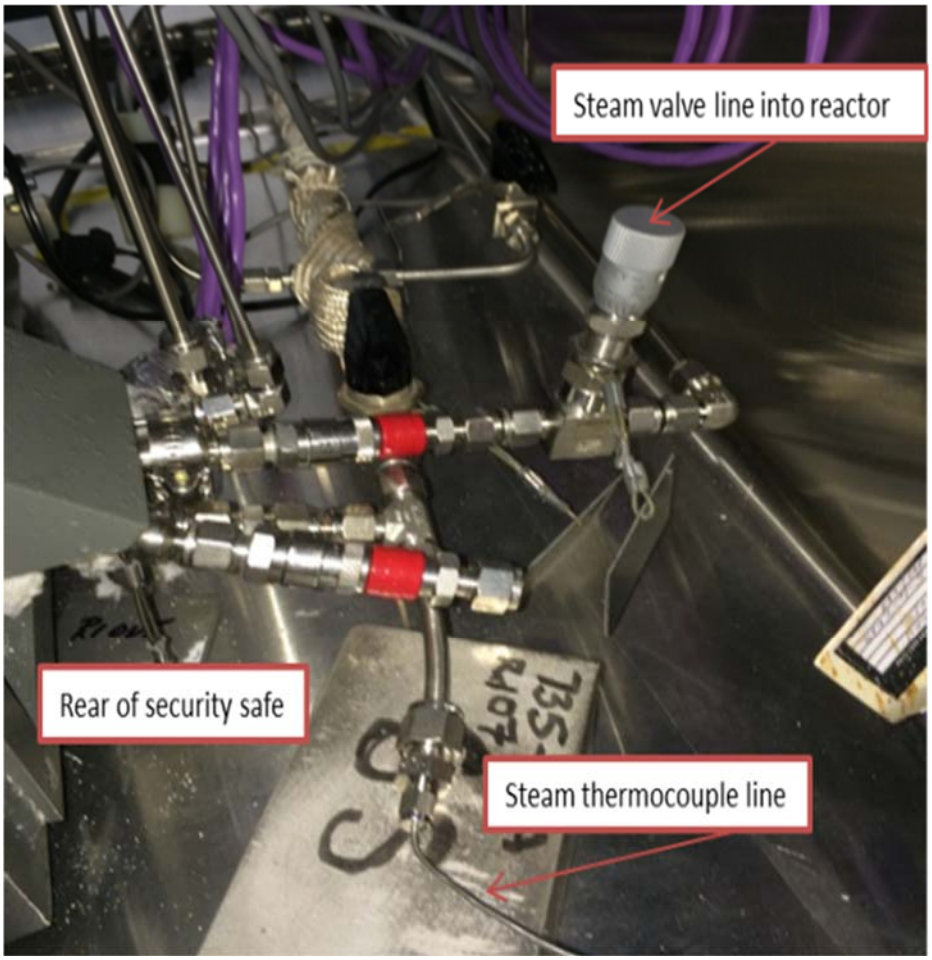


Figure 4 Steam pipe and valves entering and exiting rear of safe without insulation

The interior door of the security safe was covered with insulating glass wool material to prevent the temperature of the security safe door from reaching 30°C (the safe electronic lock temperature requirement condition is 68°C). The maximum temperatures recorded for the security door during the longest test durations of 72 hours were 23 °C and 25 °C for the security safe interior. It is worth noting that both ends of the heating mantle which housed the reactor inside the safe were also insulated with glass wool. The interior security safe exhaust fans were allowed to operate throughout the duration of the test runs.

3.3 Sample Preparations and Analysis

The baseline Tc-99 and uranium isotope concentrations in the Paducah barrier material used in this part B of the investigation were obtained from three different sections of the same barrier material (sample 23327-Mid (Paducah sample identification or P_2 based on SRNL sample identification). These three sample pieces were cut from along the length of the barrier material. Of the three different pieces of sample 23327-Mid used for baseline data, two of the test pieces, each weighing about 0.7 grams, were obtained each from the end section of the barrier material (one piece from one end and the other piece from the other end), while the third piece, also weighing about 0.7 grams, was cut from the middle section of the original material length. The weight of the sample pieces used for all these tests averaged 0.68± 0.03 grams.

Both thermally treated and untreated Paducah barrier materials, after complete digestions, were analyzed for Tc-99 and uranium isotopes by inductively-coupled plasma-mass spectroscopy (ICP-MS). In the digestion and analytical processes, samples of the barrier material were digested in a combination of concentrated nitric and hydrochloric acids (aqua regia) and a few drops of 50% hydrogen peroxide.

3.4 Ammonium Carbonate Leaching Tests

The simplest test was the ammonium carbonate solution leaching test. Ultrasonic cleaning, resulting from acoustic cavitation in sonicated ammonium carbonate solution, was used to enhance the leaching of Tc-99 and uranium compounds present in the Paducah barrier material. In this acoustic treatment of the barrier material, a small tabletop continuous wave (without timer) ultrasonic cleaning device with an input wattage of 22 Watts was used in the leaching of a small piece of the barrier material inside a solution of ammonium carbonate.

A bulk solution of ammonium carbonate was prepared from laboratory grade ammonium carbonate and was used for the leaching experiments. The measured density of the ammonium carbonate solution was 1.034 ± 0.001 g/mL at 20.5 °C. During the leaching tests, the piece of sonicated barrier material was fully immersed in ammonium carbonate solution (lixiviant) inside the sonicator. The orifice of the sonicator was tightly covered with aluminum foil wrap and a thermocouple was inserted into the sonicated chamber through the aluminum foil wrap. The duration of the barrier material leaching and sonication was two hours and the maximum recorded temperature, due to the process of energy dissipation inside the sonicated solution, was 51.6 °C.

Another piece of the barrier material was also leached with ammonium carbonate solution for the same length of time but without ultrasonic treatment or even stirring of the solution. In this leaching test, which was also conducted at the same time as the sonicated test described above, the piece of barrier material was put into a Teflon® bottle already containing ammonium carbonate solution. This Teflon® bottle was isolated from the sonicated/vibrational region of the laboratory hood floor. This leaching test was also performed at an ammonium carbonate solution temperature of 20.5 °C inside a radioactive hood.

After the leaching tests, the two samples were retrieved from the ammonium carbonate solution and placed on a sheet of paper towel inside the hood and allowed to air-dry for 30 minutes before submission of the leached solids for digestion and analysis for Tc-99 and uranium isotopes by ICP-MS. The resulting, post leaching solutions (leachates) were clear and without any visible solid particles and were both submitted for Tc-99 and uranium isotopic analysis.

3.5 Flow Systems-Super-Heated Steam

The steam leaving the steam generator, shown in Figure 5, had to be maintained above its saturated temperature at all times or it would begin to condense; therefore, the flow system (transfer lines) to and through a test reactor had to be heated. Furthermore, the need to maintain the reactor and test specimen in a security safe meant that some of the tubing needed to be flexible and accessible. No modification of the safe was permitted. There were certain sections of the tubing that could only be heated by the steam itself, which meant temperature fluctuations could occur before the steam reached saturation conditions. This meant that there were occasionally accumulations of condensed steam so the temperature had to be periodically increased to boil off the liquid water to maintain supersaturated conditions for the test. Because the generator was operated at approximate 60 psig the temperature for saturated conditions was approximately 160 °C. As the system was brought up to temperature, steam was initially directed to bypass the safe in order to heat and maintain hot the pipe to the safe (steam transfer lines). That bypass system condensate, partially seen in Figure 5, was collected in a separate container. When flow and temperature through the bypass system were stable and above steam saturation point, the steam was slowly redirected to the reactor by shutting its flow through the bypass pipe. When the bypass valve was fully closed the entire stream travelled through the reactor and around test specimen.

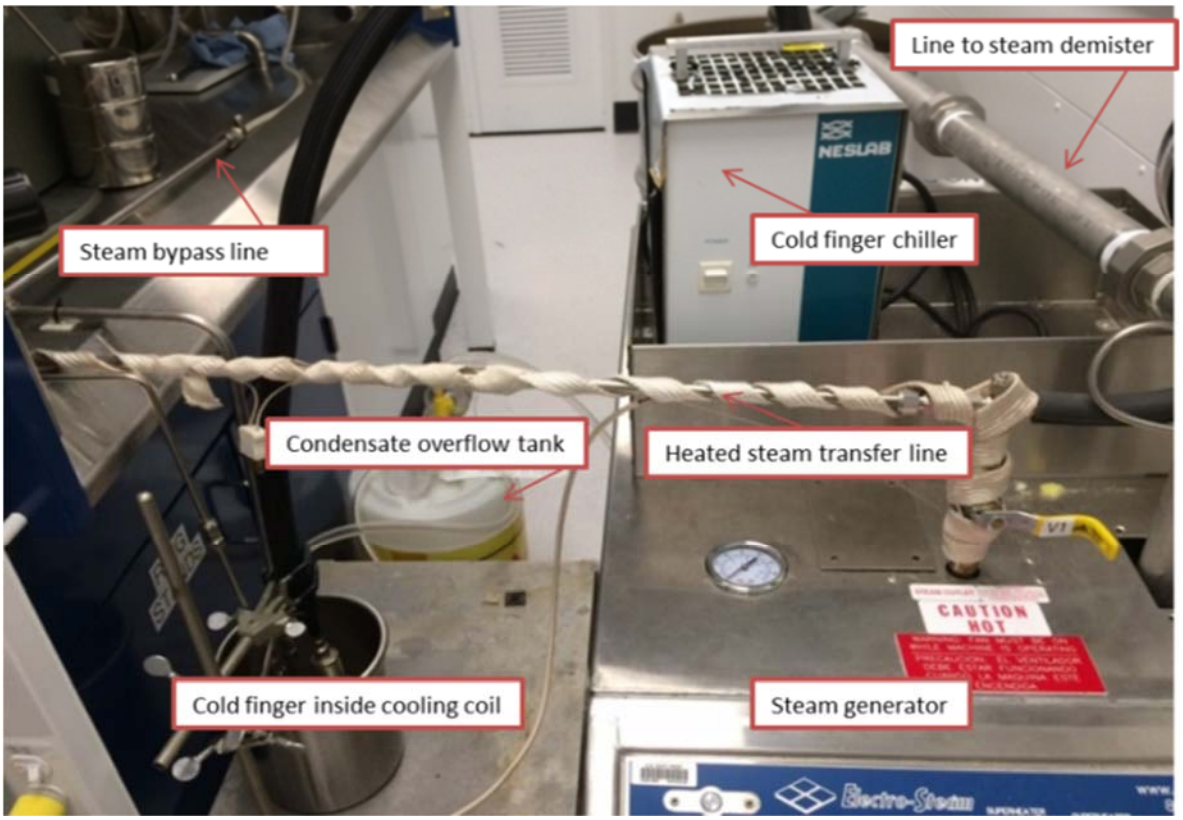


Figure 5 Steam generator placed next to radiological hood to supply steam to test reactor

4.0 RESULTS and DISCUSSION

4.1 Data Quality and Presentations for Radionuclides

In the analysis results presented in all tables in this report, values preceded by "<" (less than sign) indicate that the values were below the minimum detection limits (MDLs), and values proceeded by "≤" (less than or equal to sign) indicate that for replicates, at least one of the analysis values was at or above MDL and at least one of the analysis values was below the MDL. Thus, where replicate analyses were both above and below the detection limit, the average of all replicates above and below the detection limit is given and a "≤ "sign precedes the average value. The standard deviations reported in the analyte tables were calculated only for values that were all above the detection limits. The minimum detectable activity (MDA) is defined as the value above which instrument signal can be considered quantitative relative to the signal-to-noise ratio. The MDL as used in ICP-MS analyses is equivalent to three times the standard deviation of the blank measurements. In the ICP-MS analytical results, one sigma measurement uncertainty for Tc-99 and uranium isotopes reported in all tables is ±10% and this uncertainty is used in all graphing presentations.

4.2 Steam Operation Results

The running of each test, as shown in Table 1, was basically independent of the other tests; therefore, the discussions will be presented in the order of the test matrix in Table 1, although the tests were not performed in a chronological order, but as resources became available for each specific test.

4.2.1 Overall Temperature and Pressure Measurements

Before briefly discussing the results of each test, the overall measurements are shown in Table 2. The table contains all the test runs completed, but only a subset of the runs used flowing steam. The first three listed tests, i.e., 0-A, 0-B, and 0-C, were test specimens from the test material as was received. Those were analyzed for Tc-99 and uranium on several sections of the test material to obtain baseline concentrations in order to compare concentrations of other sections that received decontamination treatments. Tests 4-A and 4-B were specimens that received leaching treatments in aqueous solutions of 1.0 M ammonium carbonate, so for these two tests flowing steam was not used and therefore not applicable. The table shows the overall weight of each specimen before the test began and the average reactor pressure and temperatures during each test. With these values, the density of steam is given along with the flow rate of the steam and its superficial velocity, which is based on the inside diameter of the reactor. Of course, the actual local velocity in and around each specimen is expected to be higher because of the space occupied by the specimen itself and if the specimen was secured by the device used to force the steam through a specimen for tests 2, 3, 5, and 6.

A total of ten tests were conducted under a steam atmosphere as presented in Table 1. Of these ten steam tests, eight of them were conducted at 232 °C and the other two tests at a lower temperature of 121 °C (tests 5-A and 5B). With the exception of tests 1-A and 1B, all steam flow tests were performed with the new reactor design, which held a test sample in a fixed and defined location inside the reactor and permitted the exposure of the entire surfaces of the test samples to flowing steam.

In Table 1, the 1-hour and 4-hour steam tests, labelled tests 1-A and 1-B, were performed to determine if results from previous steam tests [1] could be reproduced with the new membrane material at 232 °C using the old reactor design where the sample under investigation may not have had full exposure to steam and the location of the test sample inside the reactor was not fully defined. The temperature and pressure profile for this 1-hour, 4-hour tests are shown in Figures 6 and 7. The two figures show that it was difficult to achieve the desired or target temperature of 232 °C, especially at the beginning of the tests.

The average superheated steam temperatures the test sample pieces were exposed to during the 1-hour and 4-hour tests were 230 ± 6 °C and 204 ± 20 °C, respectively. The fluctuations in temperature and pressure were much more pronounced with the 4-hour test where the average pressure was 61± 17 psig when compared with 65 ± 3 psig for the 1-hour test. As presented in Table 2, the calculated steam flow rates through the reactors containing the samples were identical at 16 mL/second.

Each of the next pair of duplicate 4-hour steam exposure tests was carried out with a new reactor design; one which held each test sample in a permanent position inside the reactor and allowed the flow of steam into all surfaces of the test sample. The only difference between this duplicate 4-hour tests and test 1-B, described earlier, is that all surfaces of this test sample were assumed to be exposed to flowing steam. As shown in Figures 8 and 9, the average temperature and pressure of this duplicate 4-hour runs were, respectively, 233 ± 10 °C/66 ± 2 psig and 233 ± 8°C/66 ± 2 psig. The fluctuations in both temperature and pressure inside the reactor were within expectations. The steam flow rates through the reactors containing the samples were not identical; the first duplicate test steam flow rate was 28 mL/second while the steam flow rate in the second duplicate test was 39 mL/second.

The duplicate alternating steam and vacuum test temperature/pressure profiles are presented in Figures 10 and 11. As earlier explained, this pair of tests was carried out to minimize steam blinding of the high surface area and porous nickel surfaces of the membrane pieces. The goal here was to see if this approach will enhance trapped and embedded Tc-99 steam desorption at 232°C. The average reactor temperature/pressure and vacuum conditions (steam desorption tests lasted for 4 hours before switching to overnight vacuum test condition) for the first duplicate test was 232± 13°C, 65 ± 2 psig and -4.5 ± 0.3 psig, respectively. The average reactor temperature/pressure and vacuum conditions for the second duplicate test was 231± 8°C, 64 ± 8 psig and -6.5 ± 0.03 psig, respectively. In all, the steam/vacuum test cycle for each sample followed a sequence of steam/vacuum/steam and vacuum treatments at 232°C. Both Figures 10 and 11 show regions in the pressure profiles where the steam run time pressure inside the reactor averaged about 65 psig (for 4 hours), while during overnight conditions, when the tests were put under vacuum, the pressure inside the reactor ranged from -4-5 to -6.5 psig. During the steam flow runs, in the day times, the reactor steam flow rate for the first duplicate run was 39 mL/second and in the second duplicate steam run the steam flow rate through the reactor was a slightly lower at 28 mL/second (Table 2). It is worth noting that the steam flow rates are based on the collected steam condensate accumulation rate inside the condensate reservoir.

The duplicate flowing steam test temperature/pressure profiles at a lower target temperature of 121 °C are presented in Figures 12 and 13. The average temperature and pressure of this duplicate 8-hour runs were, respectively, 121 ± 1 °C/14 ± 1 psig and 122 ± 3°C/15 ± 2 psig. There were no significant temperature fluctuations from the desired target value of 121°C. The steam flow rates through both reactors for the duplicate runs were almost identical at 60 mL/second and 55 mL/second for the second 8-hour run.

As documented in detail in previous Tc-99 thermal decontamination with superheated steam investigations [1], the cycling of the steam generator and the heated conditions of the steam tubes limited the stability of the test apparatus. That is, the pressure and steam were held constant within the limits of the steam generator used. The small steam generator used in this investigation needed to continually cycle its boiler to maintain the needed temperature and this cycling traveled through the entire system. In other words, the pressure fluctuation was a direct result of the main boiler heating elements being switched on and off to maintain the required output temperature. Thus, the temperature and pressure fluctuations observed during the superheated steam operations (±10 °C and 5 psig, respectively), contributed to the overall variations of both temperature and pressure from the target values for the experiments.

Table 2 Individual Sample Mass, Average Reactor Temperature and Reactor Steam Flow Rate

Test No.	Sample ID	Sample Weight grams	Average Reactor Pressure psig	Average Reactor Temp. °C	Reactor Steam Density x 10^3 g/mL	Reactor Steam Flow mL/s (1)	Steam Superficial Velocity in Reactor cm/s
0-A	As Received P 4-1	0.675	NA	NA	NA	NA	NA
0-B	As Received P 4-2	0.697	NA	NA	NA	NA	NA
0-C	As Received P 4-3	0.682	NA	NA	NA	NA	NA
1-A	1-Hour Steam-232°C-1	0.741	65	230	2.42	16	8
1-B	4-Hour Steam-232°C-2	0.689	61	204	2.44	16	8
2-A	SV-Pulse-4HR-232°C-1	0.702	65	232	2.41	39	20
2-B	SV-Pulse-4HR-232°C-1	Same	65	232	2.41	39	20
3-A	SV-Pulse-4HR-232°C-2	0.685	64	231	2.39	28	14
3-B	SV-Pulse-4HR-232°C-2	Same	64	231	2.39	28	14
4-A	Leach with Sonication	0.674	NA	NA	NA	NA	NA
4-B	Leach without Sonication	0.698	NA	NA	NA	NA	NA
5-A	8-Hour Steam-121°C-1	0.699	14	121	3.38	60	30
5-B	8-Hour Steam-121°C-2	0.687	15	122	3.38	55	27
6-A	HS-4HR-232°C-1	0.598	66	233	2.44	28	14
6-B	HS-4HR-232°C-2	0.650	66	233	2.44	39	19

Note to Table:

(1) Flow rates for the high-temperature Tests 1, 2, 3, and 6 were determined by using the valve setting in Table 4, however, for the low temperature, Test 5, two different valves were needed so the steam flowrate was determined by measuring the flow rate of condensate, which was 725.8 mL/h for Test 5-A and 667.7 mL for Test 5-B. Actually, for Test 5-B the flowrate started at 576 mL/h for the first two hours and then readjusted to the higher rate for the remainder of the 8 hours. The higher rate was used in this table.

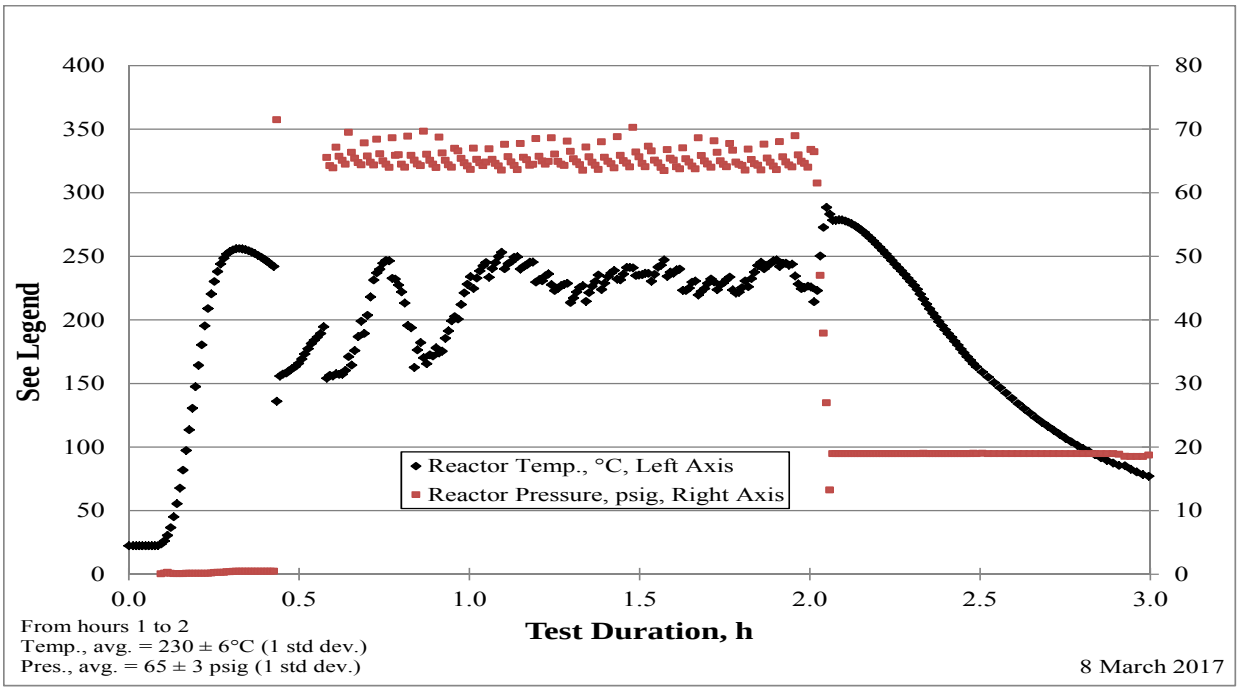


Figure 6 Test 1-A: Temperature & pressure profile for limited exposure of sample surface - 1-hour steam flow.

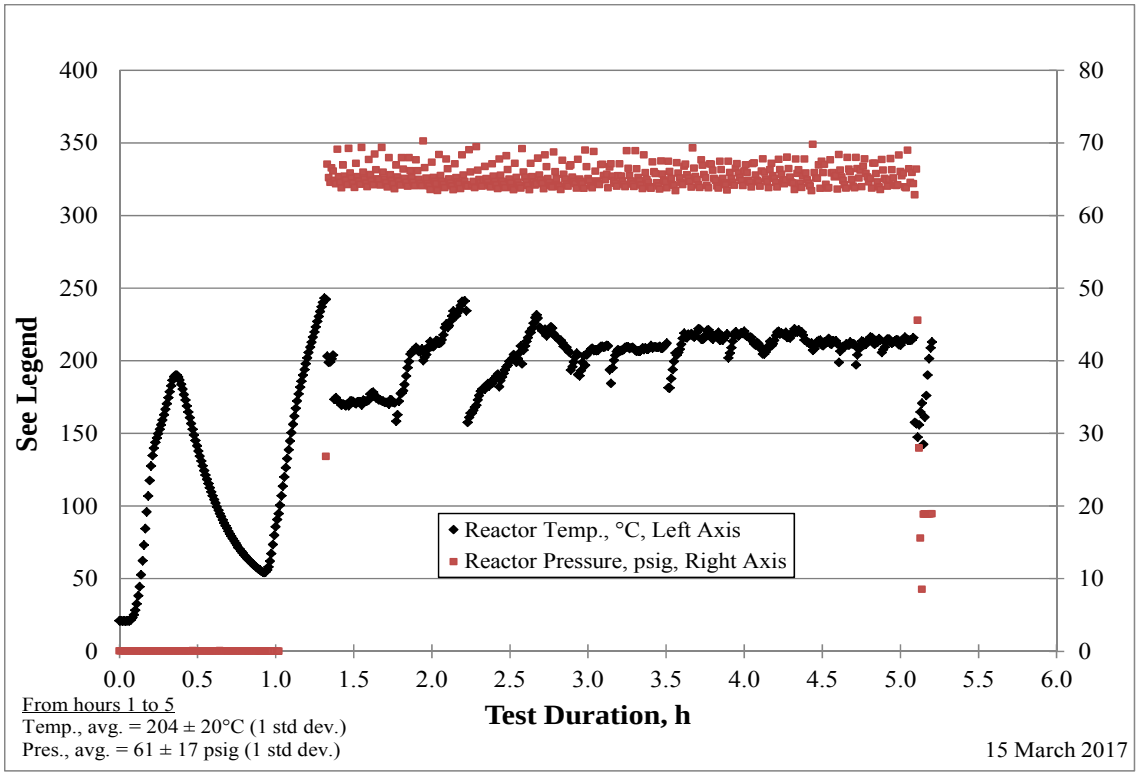


Figure 7 Test 1-B: Temperature & pressure profile for limited exposure of sample surface - 4-hour steam flow

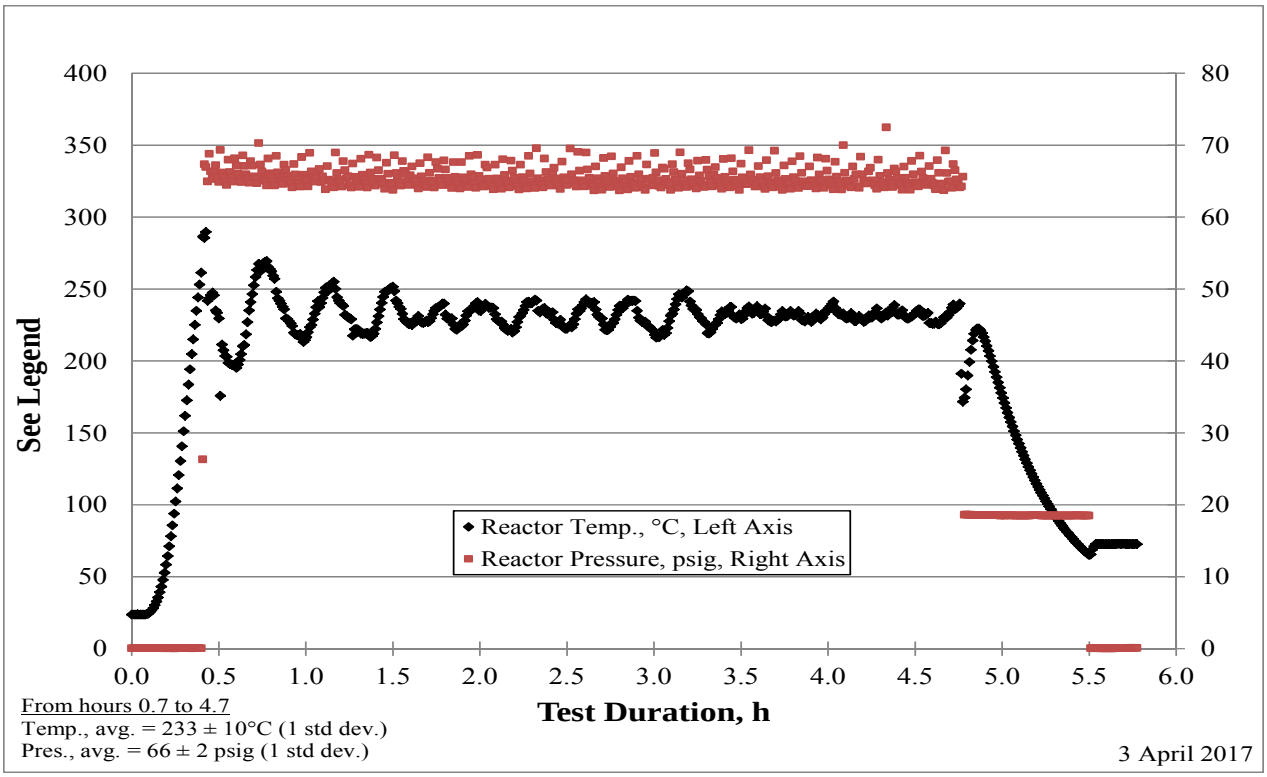


Figure 8 Test 6-A: Temperature & pressure profile for full exposure of sample surface - 4-hour steam flow.run-1

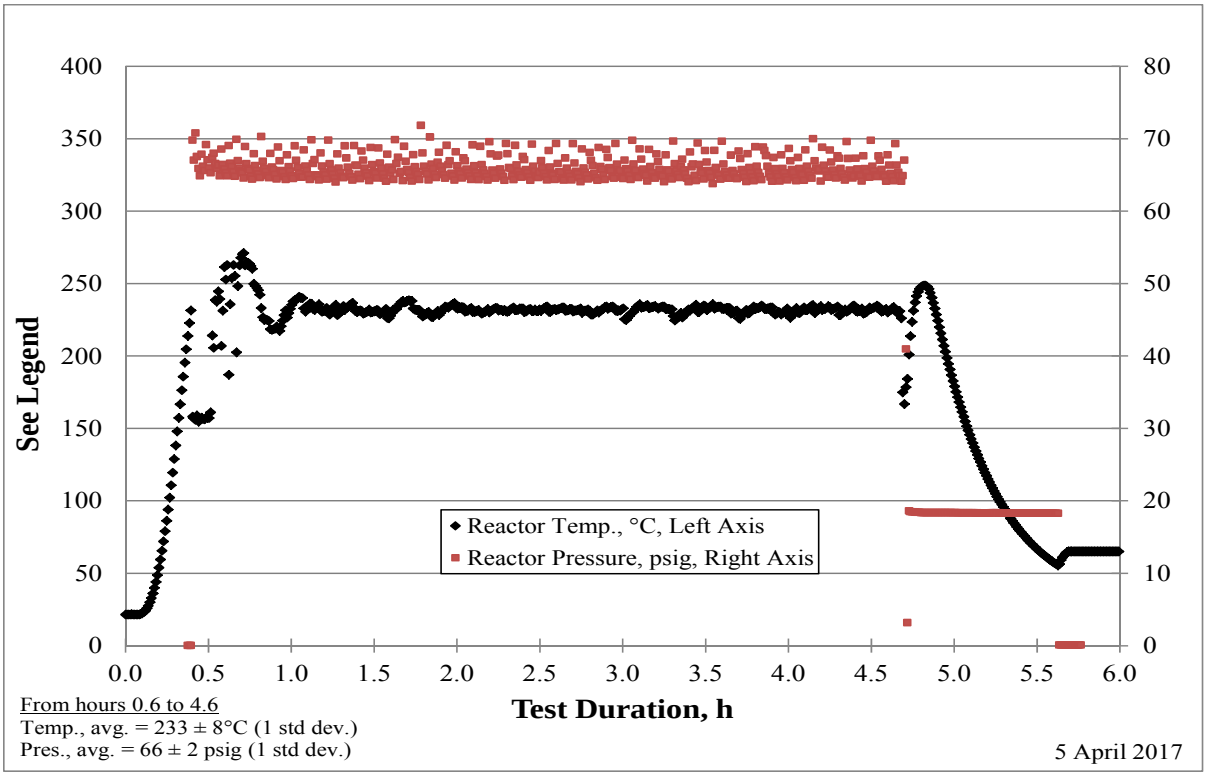


Figure 9 Test 6-B: Temperature & pressure profile for full exposure of sample surface - 4-hour steam flow.run-2

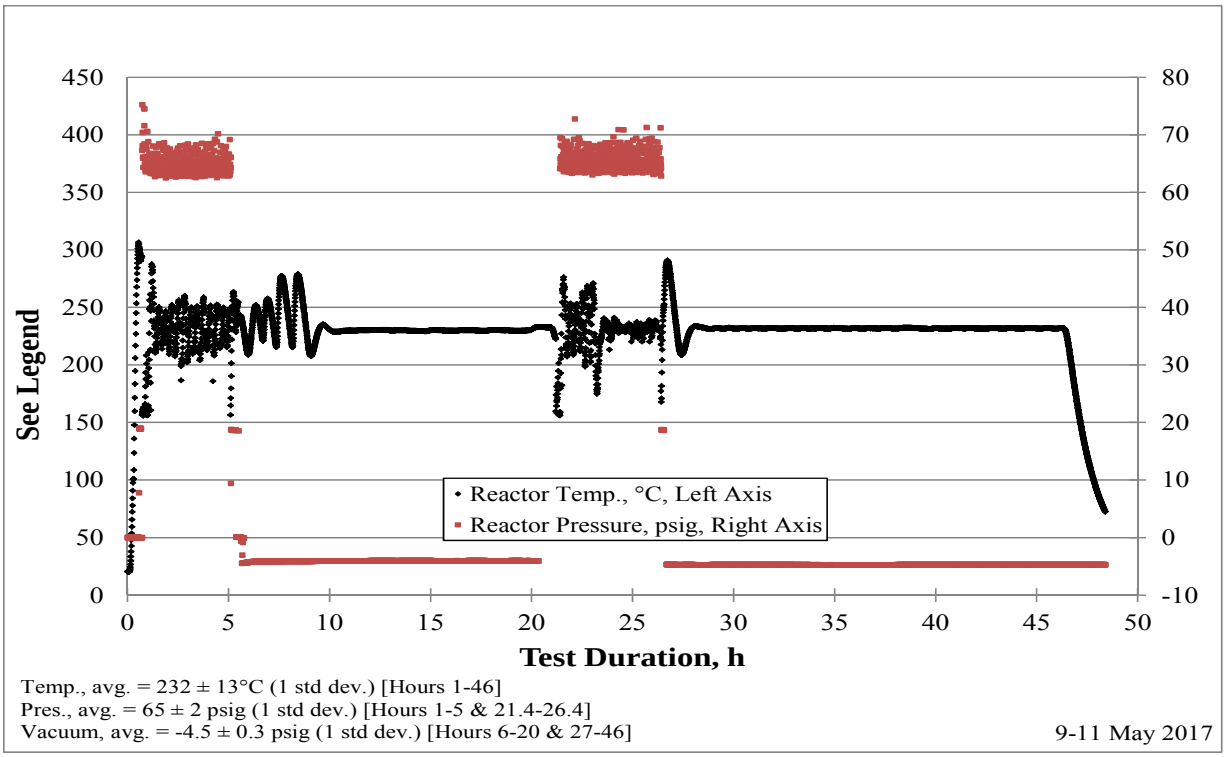


Figure 10 Test 2-A & 2-B: Temperature & pressure profile for full exposure of sample surface - alternating steam & vacuum run 1

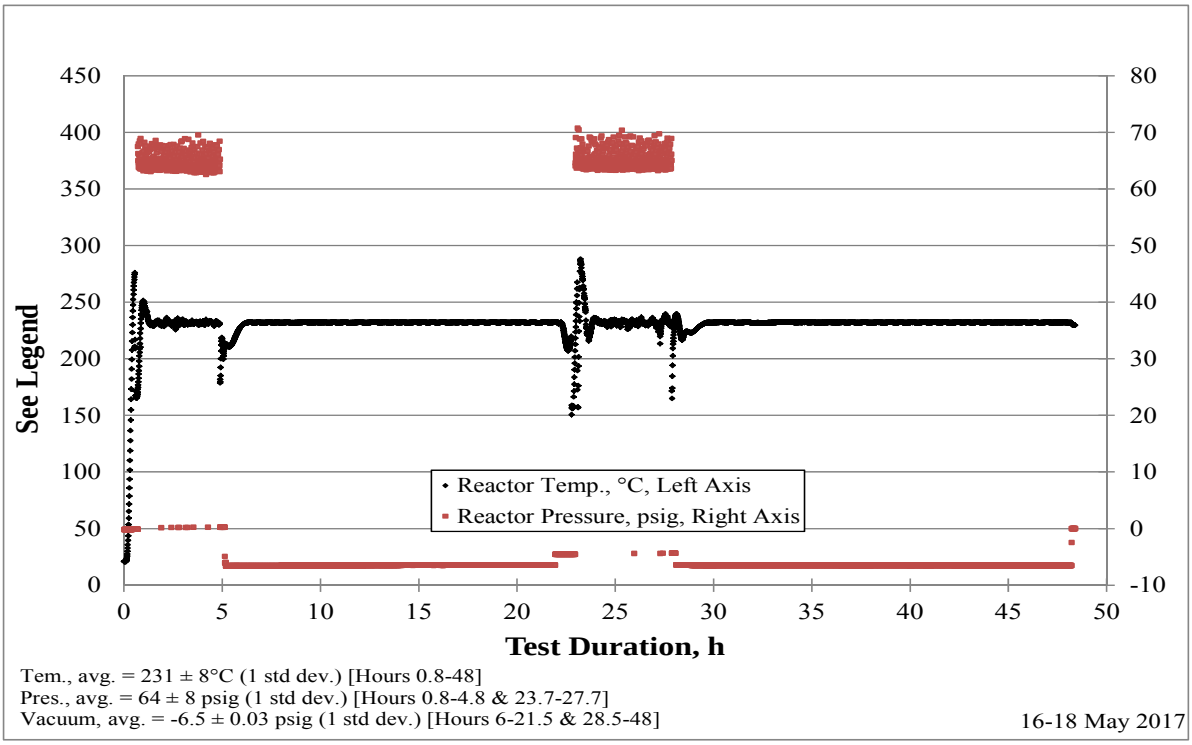


Figure 11 Test 3-A & 3-B: Temperature & pressure profile for full exposure of sample surface - alternating steam & vacuum run 2

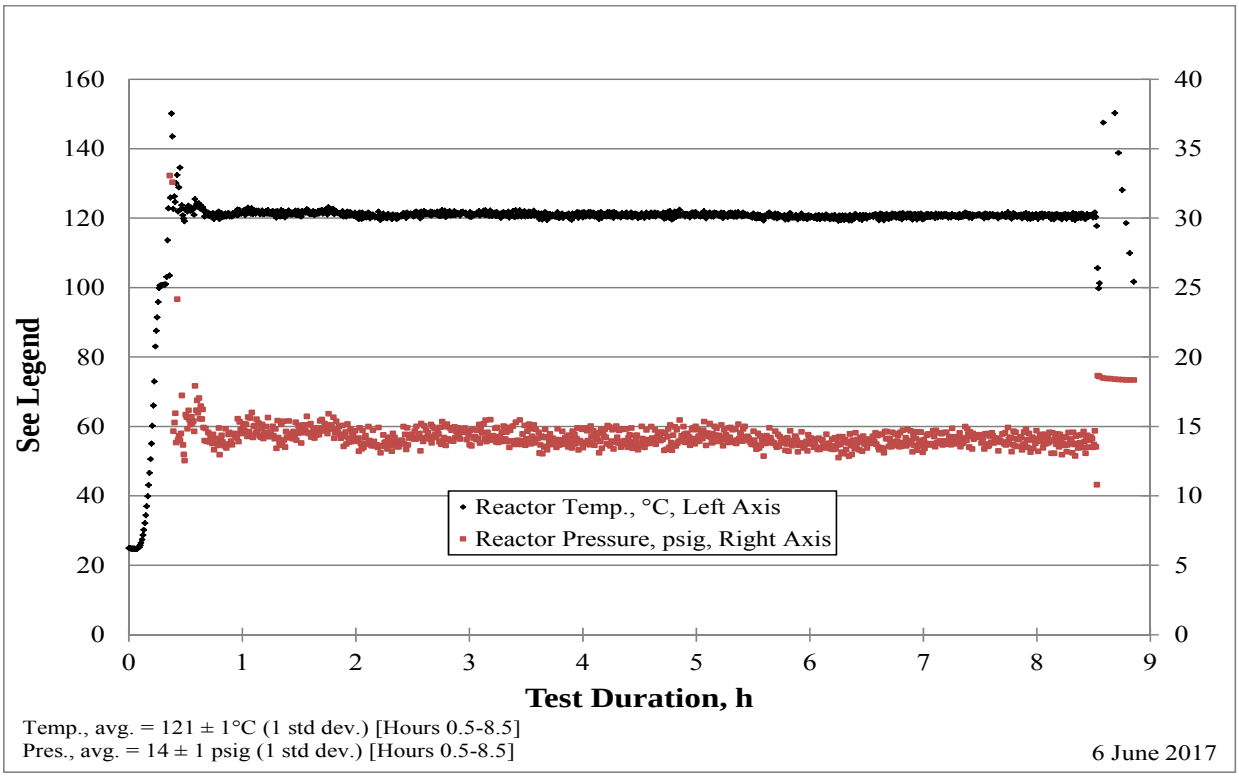


Figure 12 Test 5-A: Temperature & pressure profile for full exposure of sample surface - low temperature steam flow run 1

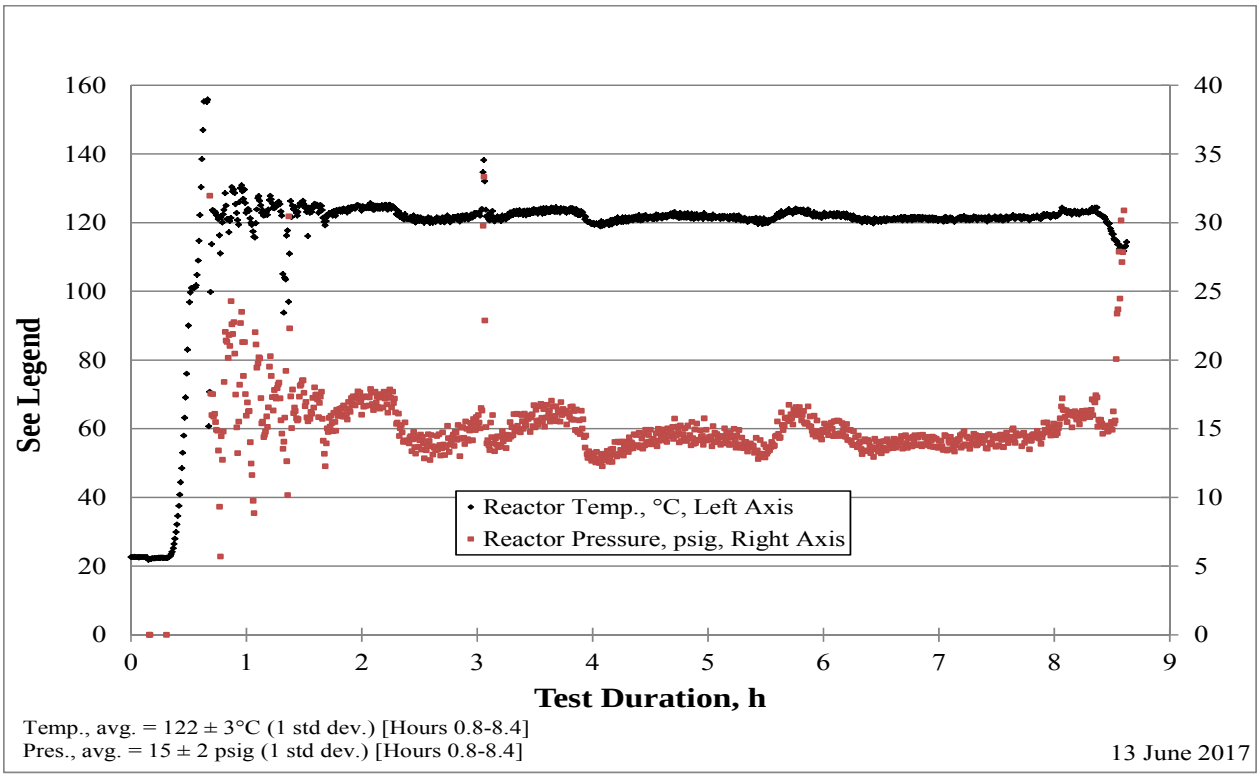


Figure 13 Test 5-B: Temperature & pressure profile for full exposure of sample surface - low temperature steam flow run 2

4.3 Technetium and Uranium Decontamination Results with Superheated Steam

4.3.1 Tests 1-A and 1-B: 1-Hour and 4-Hour Steam Reproduction Tests

Table 3 shows a summary of the average initial Tc-99, uranium isotopes and neptunium-237 concentrations in the "as-received" barrier material 23327-Mid along with the one sigma ICP-MS measurement uncertainty values. Table 4 shows the results for the removal of technetium, uranium isotopes and neptunium-237 from pieces of the barrier material that were placed in the reactor during steam exposures for 1 hour and 4 hours using the old reactor design and two 4-hour post steam treatments using the new reactors. As earlier described, the 1-hour and 4-hour steam tests (tests 1-A and 1-B) in which the old reactor design was used, meant to reproduce earlier tests using barrier material 23327-Mid to determine if steam treatment under these conditions could yield Tc-99 removal efficiency of about 27 percent as was obtained in previous tests with another barrier material sample (sample 23008-Mid) [1].

In these reproduction tests using barrier material 23327-Mid, the 1-hour test resulted in about 20% Tc-99 removal and an average of 73% uranium isotope removal (Table 5 and overlay graphs in Figures 14-17), which is in line with the previous results using the old reactor/sample 23008-Mid. However, strangely enough, the 4-hour steam treatment test at the same temperature failed to yield any measurable changes in Tc-99 and uranium concentrations when compared with the "as-received" Tc-99 and uranium concentrations as shown. It is worth pointing out that steam flow through each reactor during these two steam tests was identical at 16 mL/second, as presented in Table 2. In the previous 4-hour steam treatment test using barrier material 23008-Mid, about 52 % Tc-99 removal was observed under the same steam and temperature treatment conditions. The only difference was the initial Tc-99 concentration in the "as-received" materials; with an average of 1800 pCi/g compared to the current barrier material 23327-Mid which has an initial Tc-99 average concentration of 1350 pCi/g. These reproduction tests results seem to indicate that more Tc-99 contaminated materials may give better Tc-99 decontamination result with steam. Therefore, there may be some threshold under which Tc-99 decontamination from the barrier material with steam becomes ineffective.

4.3.2 Tests 6-A and 6-B: Full Surface Sample (Repeat of test 1-B with new reactor design)

The repeat of test 1-B (Tests 6-A and 6-B; steam treatment of sample at 232°C with a new reactor-Table 2) in duplicate also presented mixed results in both Tc-99 and uranium isotope removal from the barrier material. In the first of the 4-hour steam tests (4-hour steam treatment run 1; test 6A) with a new reactor in use, there was no measurable removal of both Tc-99 and uranium isotopes as shown in Table 5 and overlay graphs in Figures 14-17. However, the second 4-hour test with a new reactor (test 6-B) did show some measurable Tc-99 removal. With only about 6% Tc-99 removal, this was significantly lower than expectations. The Tc-99 concentrations in the duplicate 4-hour post steam treatment at 232°C of the barrier material, as presented in Figures 14 overlay plots (data from Table 5), in comparison to the average Tc-99 concentration in the "as-received" barrier material (1350 ± 135 pCi/g [± sigma]) does **Not** show a 68 % confidence that Tc-99 was thermally desorbed from the barrier material based on superheated steam treatments. The uranium isotope removal averaged only about 55%. The amount of Tc-99 left on the barrier material after these treatments does not meet Oak Ridge WAC limits. The poor Tc-99 thermal desorption with steam cannot be attributed to the slight difference in steam flow rate through both reactors, which was 28 mL/second for the first 4-hour test and 39 mL/second for the second 4-hour steam as presented in Table 2.

4.3.3 Tests 2-A and 2-B: Alternating Steam and Vacuum Treatment at 232°C and Tests 3-A and 3-B (Repeat of Tests 2-A and 2-B)

As earlier described, alternating periods of steam and vacuum treatments tests were designed to minimize membrane pore blinding due to the presence of steam/moisture in the pores of the nickel material membrane during steam treatment of the test specimens. Such pore blinding with steam will prevent thermal desorption of embedded Tc-99. It was assumed therefore that the Tc-99 decontamination factor would increase with such alternating steam/vacuum treatment process. In this alternating steam/vacuum treatment test at 232°C, the steam portion of the test lasted for a period of 4 hours during day time before switching the test condition to vacuum for an overnight duration. Thus, in a complete run the treatment sequence was steam for four hours followed by vacuum treatment overnight (12 hours), another steam treatment of the same sample for 4 hours the next day and finally the second vacuum test for another 12 hours. Therefore, each sample was exposed to steam a total of 8 hours at 232°C and vacuum conditions a total of 24 hours at 232°C.

The duplicate steam/vacuum alternating treatment results at 232°C for Tc-99, uranium isotopes and neptunium-237 are presented in Table 6. Note in Table 6 there is a single result from Tests 2-A and 2-B and a single result for Tests 3-A and 3-B. This is because when Test 2-A ended the specimen was not removed from the reactor and just continued on into Test 2-B. Tests 3A and 3B were a repeat of Tests 2-A and 2-B except a new reactor was used with a new specimen. Once again, when Test 3-A ended the specimen was not removed from the reactor and just continued on to Test 3-B.

The extent of Tc-99 thermal desorption with this alternating steam and vacuum approach was not that impressive; in both cases the removal of Tc-99 was less than 20%. In the first run, under this condition, only about 19% of the Tc-99 on the barrier material was thermally removed while about 13% of Tc-99 was removed during the second duplicate run as shown in Table 7 and overlay plots in Figure 14. This duplicate alternating steam/vacuum treatment of the barrier material gives only an average of 16% Tc-99 removal, which translates to a residual Tc-99 average concentration left on the barrier material pieces of about 1,128 ± 53 pCi/g. Therefore, relative to the Tc-99 concentration in the "as received" barrier material (1350 ± 135 pCi/g [± 1 sigma]), some Tc-99 was removed from the barrier material as a result of this treatment. The overlay graph in Figure 14 also shows that the Oak Ridge WAC limit requirement of less than or equal to 172 pCi per converter was not met in any of the steam and vacuum alternating tests.

An average of about 32% and 30% of the uranium isotopes and neptunium-237, respectively, were removed based on the duplicate runs as presented in Table 7 and in the overlay graphs in Figures 14 through 17.

Table 3 "As-received" Analytical results for Tc-99, uranium isotopes and neptunium-237 in sample 23327-Mid

Sample ID	Tc-99, pCi/g	U-234, pCi/g	U-235, pCi/g	U-238, pCi/g	Np-237, pCi/g
"As-received"-1	1.35E+03	5.40E+01	4.74E+00	1.96E+02	2.66E+00
"As-received"-2	1.38E+03	4.52E+01	3.84E+00	1.59E+02	1.74E+00
"As-received"-3	1.33E+03	5.08E+01	4.33E+00	1.80E+02	2.39E+00
Average	**1.35E+03**	**5.00E+01**	**4.30E+00**	**1.78E+02**	**2.27E+00**
10% analytical uncertainty (ICP-MS)	1.35E+02	5.00E+00	4.30E-01	1.78E+01	2.27E-01
Average plus one Sigma *	1.49E+03	5.50E+01	4.73E+00	1.96E+02	2.49E+00
Average minus one Sigma *	1.22E+03	4.50E+01	3.87E+00	1.60E+02	2.04E+00

*Average value +10% of the average value (one sigma plus) or average value –10% of the average value (one sigma minus)

Table 4 Post steam treatment Tc-99, uranium isotopes, and neptunium-237 concentrations at 232°C new and old reactor design

Component	1 hour steam treatment (old reactor)	4-hour steam treatment (old reactor)	4-hour steam treatment run-1 (new reactor)	4-hour steam treatment run-2 (new reactor)
Tc-99, pCi/g	1.09E+03	1.50E+03	1.48E+03	1.27E+03
U-234, pCi/g	1.39E+01	4.99E+01	5.16E+01	2.20E+01
U-235, pCi/g	1.13E+00	4.29E+00	4.45E+00	1.91E+00
Np-237, pCi/g	2.26E+00	2.79E+00	2.30E+00	1.66E+00
U-238, pCi/g	4.61E+01	1.79E+02	1.85E+02	7.97E+01

Table 5 Post Steam treatment percent removal of Tc-99, uranium isotopes and neptunium-237

Component	1 hour steam treatment (old reactor)	4-hour steam treatment (old reactor)	4-hour steam treatment run-1 (new reactor)	4-hour steam treatment run-2 (new reactor)
Tc-99	20	None removed	None removed	6#
U-234	72	None removed	None removed	56
U-235	74	None removed	None removed	56
Np-237	0	None removed	None removed	27
U-238	74	None removed	None removed	55

Insignificant Tc-99 removal

Table 6 Post steam/vacuum treatment: Tc-99, uranium isotopes and neptunium-237 concentrations

Component	Alternating Steam &Vacuum Test (2-A and 2-B) at 232°C	Alternating Steam &Vacuum Test (3-A and 3-B) at 232°C
Tc-99, pCi/g	1.09E+03	1.17E+03
U-234, pCi/g	3.14E+01	3.68E+01
U-235, pCi/g	2.77E+00	3.11E+00
Np-237, pCi/g	1.32E+00	1.88E+00
U-238, pCi/g	1.16E+02	1.29E+02

Table 7 Post Steam/Vacuum Treatment: Percent removal of Tc-99, uranium isotopes and neptunium-237

Component	Alternating Steam &Vacuum Test (2-A and 2-B) at 232°C	Alternating Steam &Vacuum Test (3-A and 3-B) at 232°C
Tc-99	19	14
U-234	37	26
U-235	36	28
Np-237	42	17
U-238	35	28

4.3.4 Tests 5-A and 5-B: Steam at Low Temperature

The duplicate post-steam thermal desorption treatment concentration results for Tc-99, uranium isotopes and neptunium, at a lower temperature of 121°C for the 8- hour runs, are presented in Table 8 and 9. Table 8 shows the concentration of these elements (Tc-99, uranium isotopes and Np-237) left on the barrier material surfaces after treatment while Table 9 results summaries the percent of these elements taken off the barrier material surface after steam treatment at 121°C for eight hours.

The extent of Tc-99 thermally desorbed from the barrier material sample after eight hours steam treatment at 121°C is relatively low, especially in the first 8-hour duplicate run. In the first 8-hour duplicate run only about 3.0 percent of Tc-99 was removed while in the second 8-hour run about 25.2 % of Tc-99 was removed. As presented in Table 9, for both duplicate runs, an average of 58 ± 1.4 % of the uranium isotopes was removed from the barrier material with this steam treatment of the barrier material sample at 121°C. More neptunium-237 was removed from the barrier material in the second 8-hour steam treatment at 121°C. It is interesting to note that although only about 3.0 % of Tc-99 was removed in the first 8-hour run, the amount of uranium isotopes removed from the barrier material sample in this first 8-hour run (57%) was comparable to the amount of these isotopes removed in the second 8-hour run (59%) where relatively more Tc-99 was removed through this steam treatment at 121°C. This suggested that the thermal desorption process for uranium isotopes from the barrier material is independent of the processes or chemistry involved in the thermal desorption of Tc-99. The overlay plots for Tc-99 and the uranium isotopes left on the barrier material surfaces after eight hours steam treatment at 121°C for both duplicate runs are shown in Figures 14 through 17.

The duplicate post-steam thermal desorption treatment concentration results for Tc-99 at 121°C for 8-hour runs show a residual technetium concentration average of 1,160 pCi/g in the post-steam treated samples, which indicates that some Tc-99 was removed from the barrier material as a result of this steam treatment relative to the Tc-99 concentration in the "as received" barrier material (1350 ± 135 pCi/g [± sigma]) as presented in the overlay plots in Figure 14. Figure 14 overlay plots also definitely shows that Tc-99 was removed from the barrier material with steam treatment at 121°C after the second 8-hour steam treatment but not necessarily the case with the first 8-hour steam treatment at 121°C. The overlay graph in Figure 14 also shows that the Oak Ridge WAC limit of less than 172 pCi per converter was not met in any of these 8-hour runs.

Table 8 8-hour post steam treatment percent removal of Tc-99, uranium isotopes and neptunium-237

Component	First 8-hour steam test at 121°C; Test 5A	Second 8-hour steam test at 121°C Test 5B
Tc-99, pCi/g	1.31E+03	1.01E+03
U-234, pCi/g	2.13E+01	2.08E+01
U-235, pCi/g	1.87E+00	1.75E+00
Np-237, pCi/g	1.30E+00	<1.04E+00
U-238, pCi/g	7.80E+01	7.26E+01

Table 9 8-hour post steam treatment percent removal of Tc-99, uranium isotopes and neptunium-237

Component	First 8-hour steam test at 121°C; Test 5A	Second 8-hour steam test at 121°C Test 5B
Tc-99	3#	25
U-234	57	58
U-235	57	60
Np-237	43	≥ 56
U-238	56	59

Insignificant Tc-99 removal

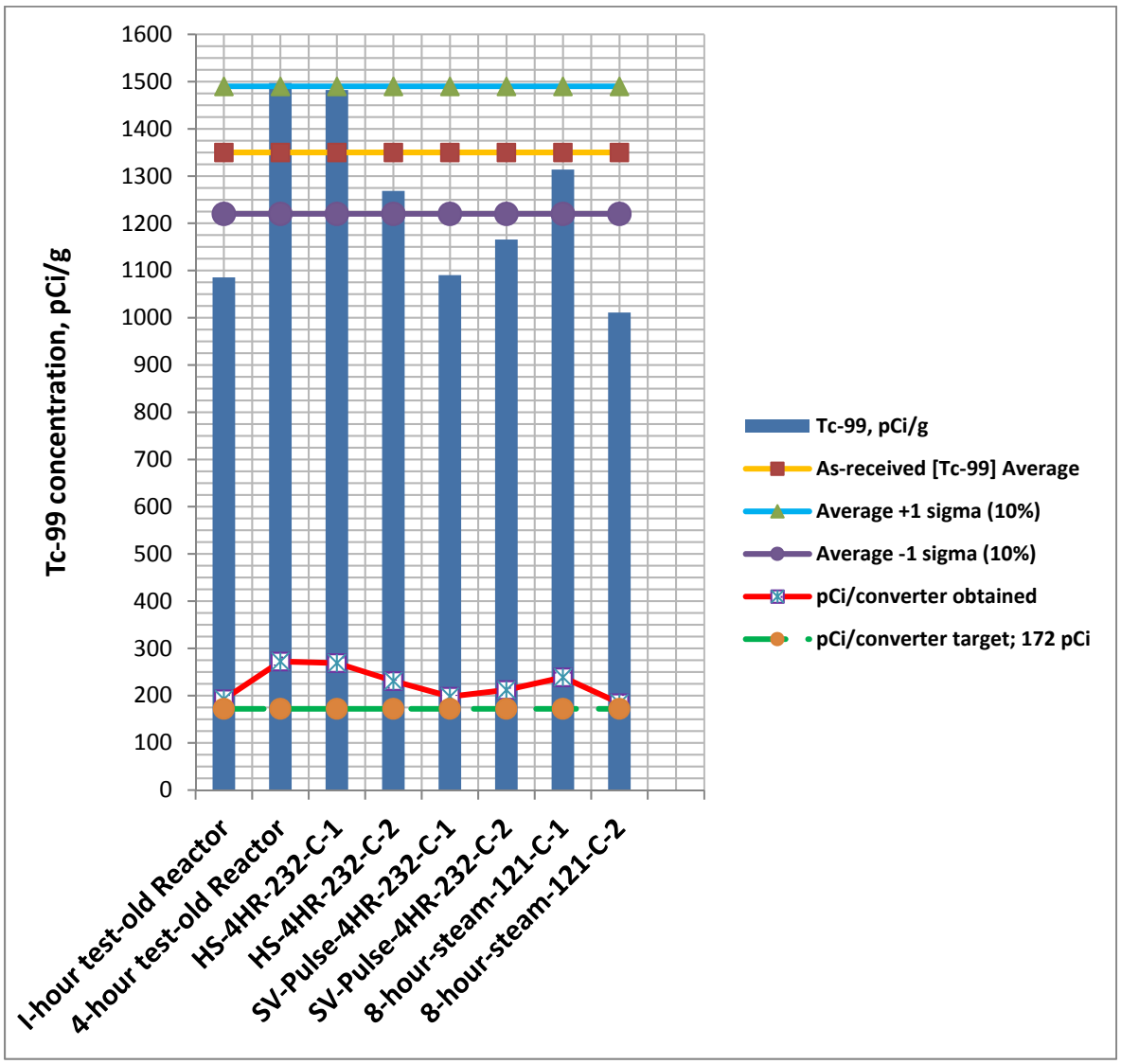


Figure 14 Overlay plots of average "as-received" Tc-99 concentration in the barrier material, ± 1 sigma values and post-steam treatment Tc-99 concentration at 232 °C and 121°C.

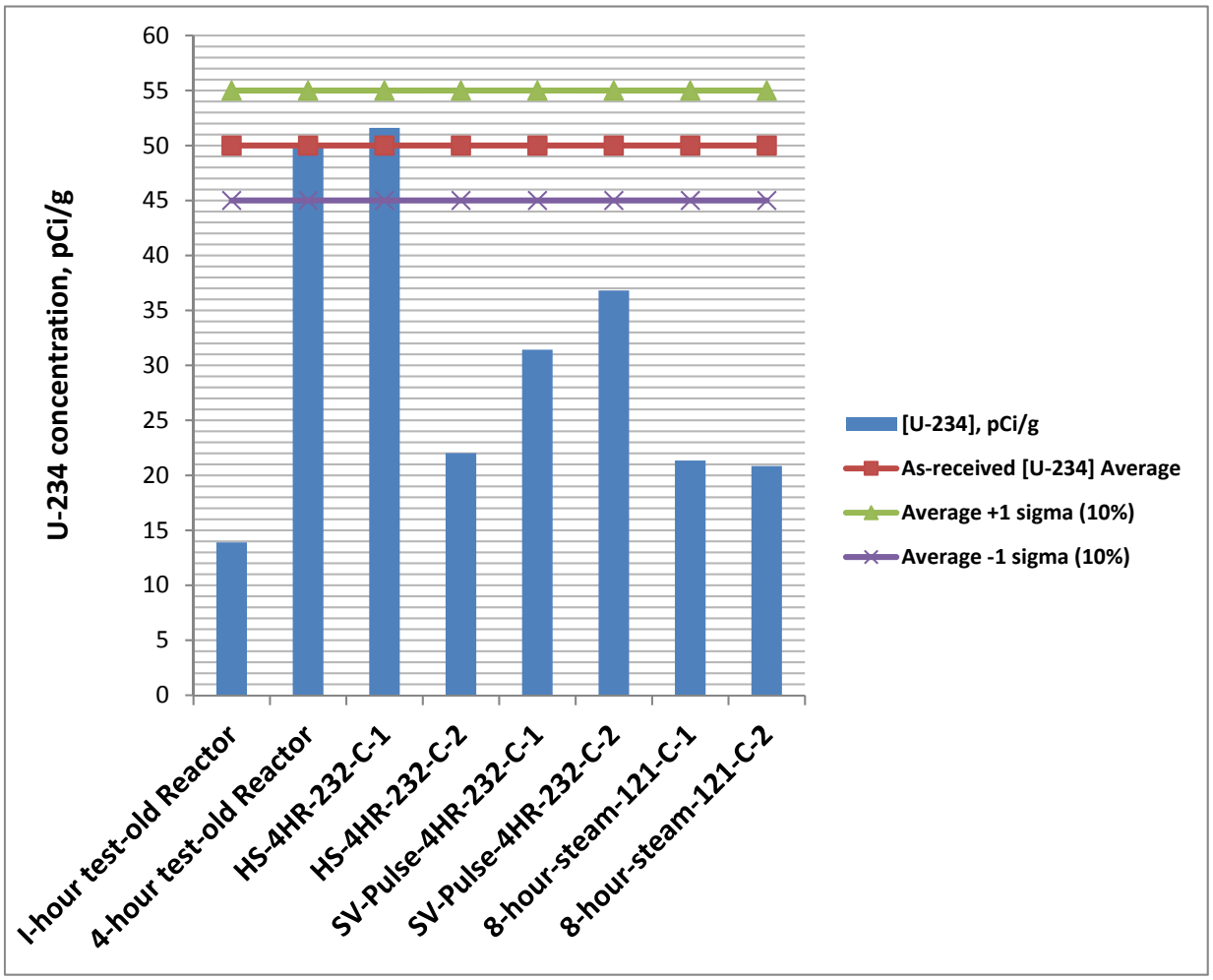


Figure 15 Overlay plots of average "as-received" U-234 concentration in the barrier material, ± 1 sigma values and post-steam treatment U-234 concentration at 232 °C and 121°C.

Overall, of the six steam treated sample runs, excluding the two reproduction tests (1-hour and 4-hour tests with the old reactor at 232°C) with barrier material 23327-Mid, only the duplicate alternating steam/vacuum treatment runs with the barrier material at 232°C showed any consistent removal of Tc-99 and uranium isotopes from the surfaces of the barrier material.

The average Tc-99 remaining on the barrier material sample 23327-Mid after alternating steam and vacuum treatment averaged 1,128 ± 53 pCi/g (Tables 6). To compare this barrier material Tc-99 decontamination test results with the Oak Ridge WAC limits of 172 pCi/g of converter (172 pCi/g of waste material), a conversion factor, as provided by Paducah, was used [6]. When this conversion is made the result is 205 ± 10 pCi/g of converter (1 sigma). This value of 205 ± 10 pCi/g of converter does not meet the Oak Ridge on-site disposal WAC of 172 pCi/g of waste [5].

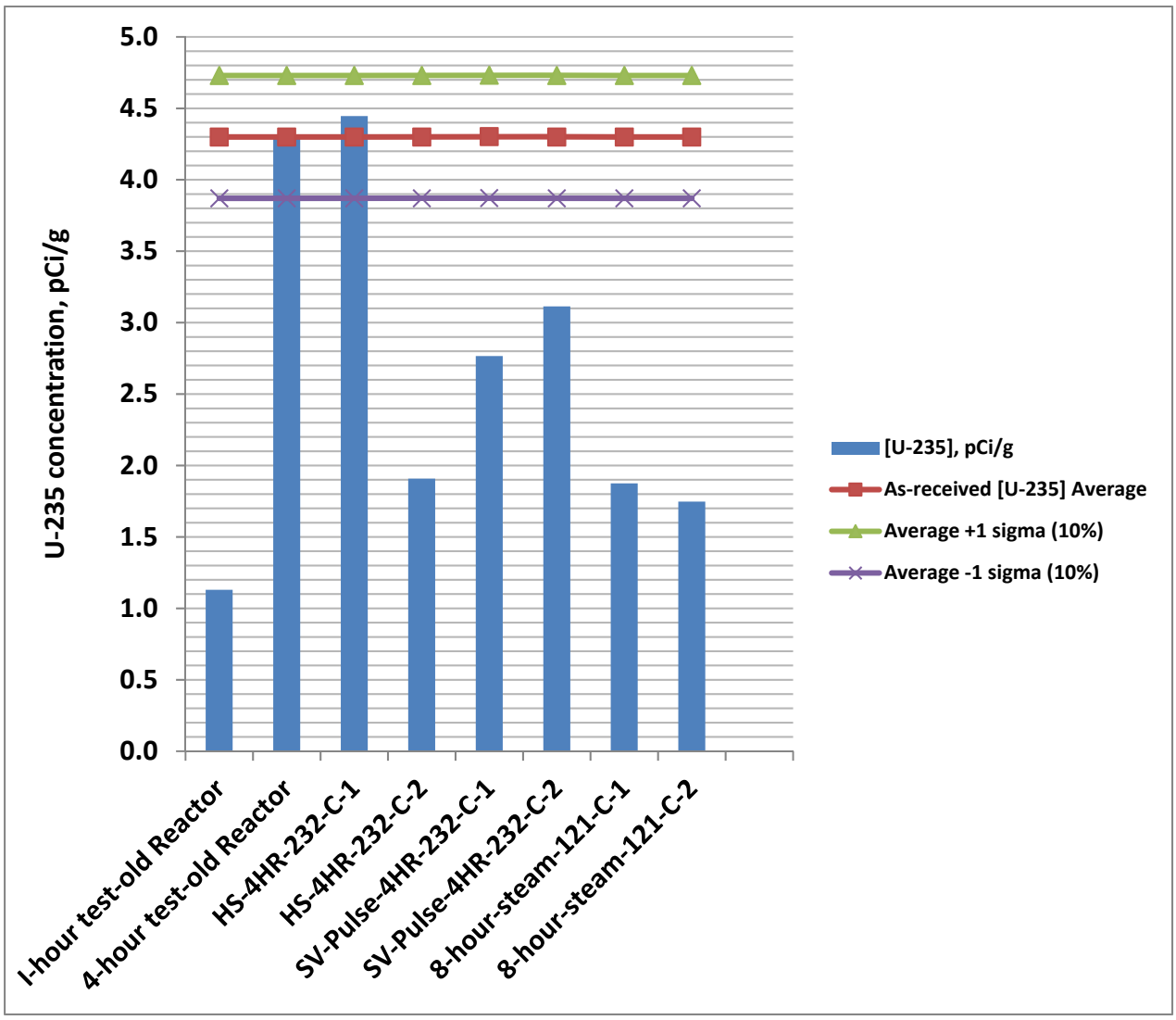


Figure 16 Overlay plots of average "as-received" U-235 concentration in the barrier material (± 1 sigma) and post-steam treatment U-235 concentration at 232 °C and 121°C.

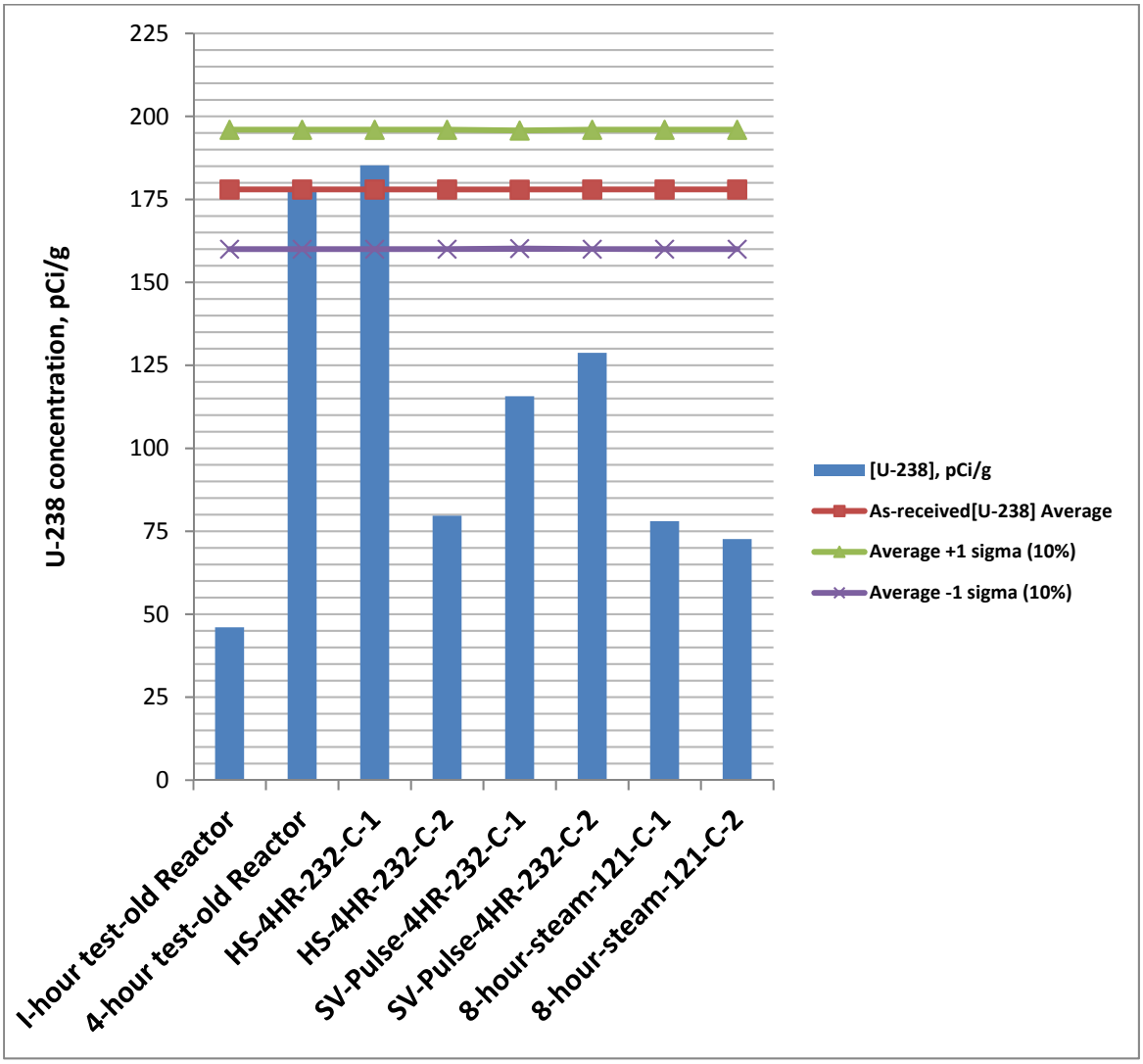


Figure 17 Overlay plots of average "as-received" U-238 concentration in the barrier material (± 1 sigma) and post-steam treatment U-238 concentration at 232 °C and 121°C.

4.4 Technetium and Uranium Decontamination Results with Ammonium Carbonate Leaching

The post aqueous ammonium carbonate leaching of Tc-99, uranium isotope and neptunium concentration changes in the barrier material, at room temperature, are shown in Table 10 along with the percent concentration changes and WAC disposal values obtained with and without sonication of the ammonium carbonate lexiviant. Treatment of the barrier material in ammonium carbonate solution, with and without sonication, resulted in significant leaching of Tc-99, uranium isotopes and neptunium from the test barrier material pieces at room temperature. Leaching of the barrier material for two hours *without* sonication or agitation removed about 42% of the Tc-99 on the barrier material piece, while sonication for the same length of time resulted in the removal of about 66% of the Tc-99 on the barrier material piece. As shown in Figure 18, these two leaching conditions led to Tc-99 WAC for disposal of 142.5 and 84 pCi/converter, respectively. These WAC disposal values are lower than the Oak Ridge WAC limit (172 pCi/converter).

The relative amounts of uranium isotopes (U-235 and U-238) left on the barrier material after leaching with ammonium carbonate solution with and without sonication is shown in the overlay plots in Figure 19. In both leaching scenarios, more than 98% of these uranium isotopes was removed from the original test material.

The concentration of U-234 after leaching under these two conditions were below the instrument detection limits, which averaged, <9 pCi/g as presented in Table 10. Since the post leaching U-234 concentrations were below MDLs it can be assumed that more than 98% of the U-234 was removed during both leaching conditions.

This significant removal and accumulation of uranium isotopes with ammonium carbonate solution leaching raises criticality concerns if this approach is used for Tc-99 removal from fissile barrier materials prior to disposal at Paducah.

Table 10 Technetium and uranium decontamination results: ammonium carbonate leaching

Component	**$(NH_4)_2CO_3$ Leaching without sonication, pCi/g Test 4B**	**% Removed & WAC limit per converter Test 4B**		**$(NH_4)_2CO_3$ Leaching with sonication, pCi/g Test 4A**	**% Removed & WAC limit per converter Test 4A**	
-	-	%Rem.	WAC limit per Converter		%Rem.	WAC limit per Converter
Tc-99	784	42	143	462	65.9	84
U-234	< 9.0	≥ 82	NA	< 9.7	≥ 81	NA
U-235	0.12	97	NA	0.01	99.7	NA
Np-237	1.6	29	NA	< 1.1	≥ 52	NA
U-238	4.0	98	NA	0.4	99.8	NA

4.4.1 Leachate analysis: Tc-99 and uranium isotope mass balance

As earlier described above, the leachates from the ammonium carbonate leaching of barrier material pieces (sonicated and non-sonicated ammonium carbonate solutions) were also analyzed for Tc-99 and uranium isotope (U-234, U-235 and U-238) concentrations after leaching. U-233 and U-236 concentrations were below instrument detection limits in the leachates. The post leachate analysis Tc-99 and uranium isotope concentrations are presented in Tables 11 and 12, respectively, for leaching without sonication and leaching with sonication. Mass balance calculations involving the use of concentrations of Tc-99 and the uranium isotopes in the leachates, residual amounts in the post leached barrier material piece coming from sample digestion and analysis and the concentrations of Tc-99 and uranium isotopes on the "as-received" barrier material was the basis of the mass balance data presented in Tables 11 and 12.

The Tc-99 mass balance is presented, therefore, as the total amount of Tc-99 left on the barrier material after leaching plus total amount of the Tc-99 in the leachate; this sum should equal the total amount of Tc-99 in the original "as-received" barrier material piece used for the leaching tests. In other words, the amount of each analyte in the leachate plus the corresponding analyte concentration on the barrier material after leaching should equal the analyte concentration in the original "as-received" barrier material used in the leaching tests. The same approach was used for the detectable uranium mass balances shown in Tables 11 and 12. The last columns in Tables 11 and 12 contains the percent differences between concentration of Tc-99 and uranium isotopes in the original barrier materials before leaching and sum of their concentrations from the leachates and residues left on the barrier material after leaching. The percent difference, which is the difference between the concentration of each analyte in the original "as-received" barrier material and the sum of the concentrations of the same analyte in the

leachate and post leached barrier material, is defined as the absolute concentration difference divided by the average concentration*100.

The Tc-99 mass balance percent difference, as defined above, for the test without sonication is less than 1% (0.7%), while the percent difference for the uranium isotopes in these un-sonicated runs ranged from 5-9 percent. For the sonicated leached sample, the Tc-99 mass balance percent difference was 4.4% and those for the uranium isotopes averaged about 16%.

These mass balance percent differences are within the expected analytical uncertainty for ICP-MS analysis of the barrier material for Tc-99 and uranium isotopes.

Table 11 Ammonium Carbonate Leaching *Without* Sonication Test 4B: Material Mass Balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amount on barrier after leaching, pCi	Original amount in 0.698 g barrier sample tested, pCi	% difference*
Tc-99	4.05E+02	5.48E+02	9.53E+02	9.46E+02	1.0
U-234	3.19E+01	<6.26E+00	3.2E+01 to 3.82E+01	3.49E+01	8-9
U-235	2.77E+00	8.05E-02	2.85E+00	3.00E+00	5.3
Np-237	9.51E-01	1.12E+00	2.07E+00	1.58E+00	27.0
U-238	1.15E+02	2.72E+00	1.18E+02	1.24E+02	5.4

*Percent difference (% difference) is defined as absolute difference/average*100.

Table 12 Ammonium Carbonate Leaching *With* Sonication Test 4A: Material Mass Balance

Component	Amounts in leachate, pCi	Residual amount on barrier material after leaching, pCi	Leachate + residual amounts on barrier after leaching, pCi	Original amount in 0.674 g barrier sample tested pCi	% difference*
Tc-99	6.43E+02	3.12E+02	9.54E+02	9.13E+02	4.4
U-234	3.93E+01	<6.52E+00	3.9E+01 to 4.58E+01	3.37E+01	15-30
U-235	3.41E+00	8.13E-03	3.41E+00	2.90E+00	16.3
Np-237	1.61E+00	7.35E-01	2.34E+00	1.53E+00	42.0
U-238	1.41E+02	2.67E-01	1.41E+02	1.20E+02	16.0

*Percent difference (% difference) is defined as absolute difference/average*100.

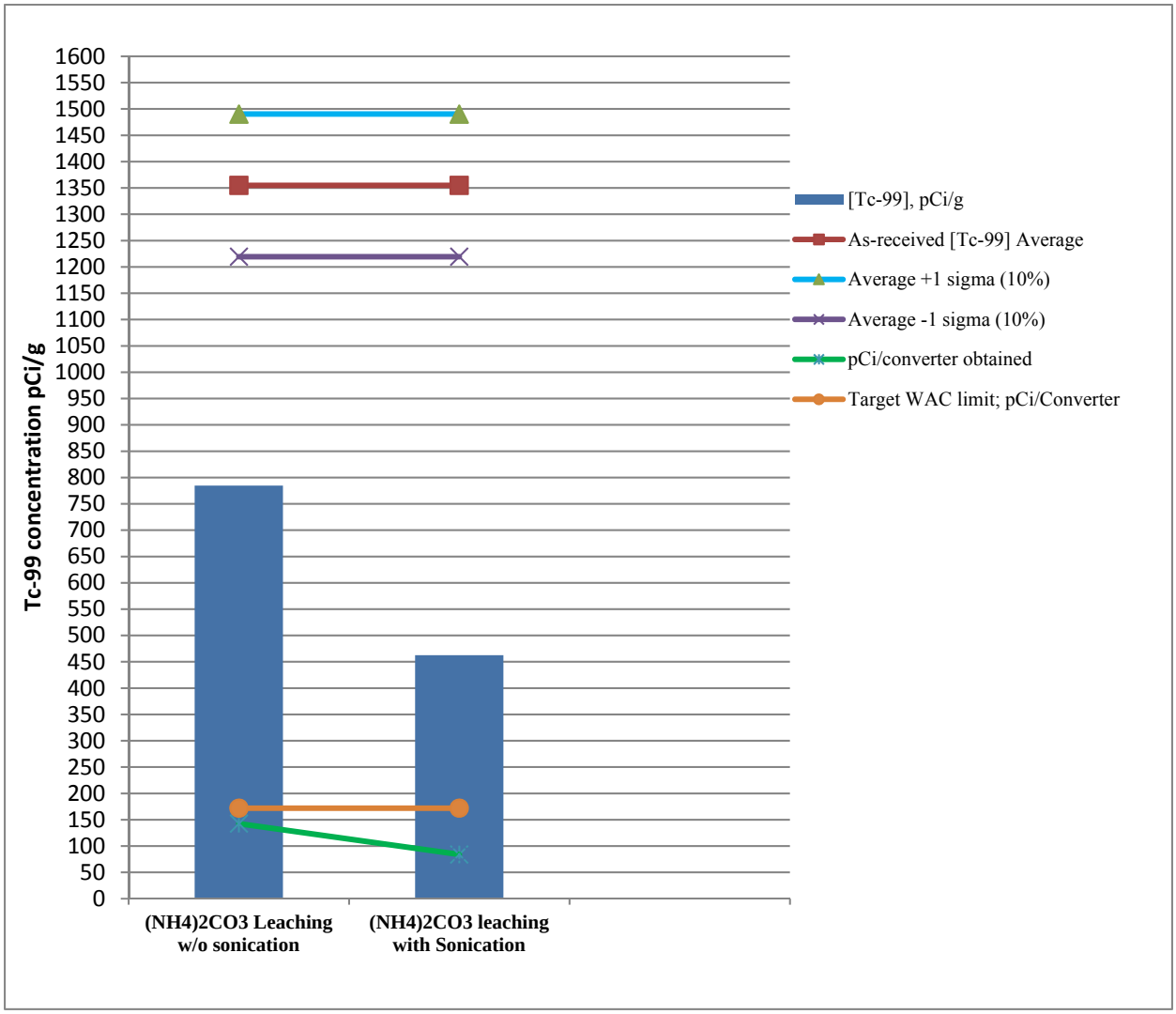
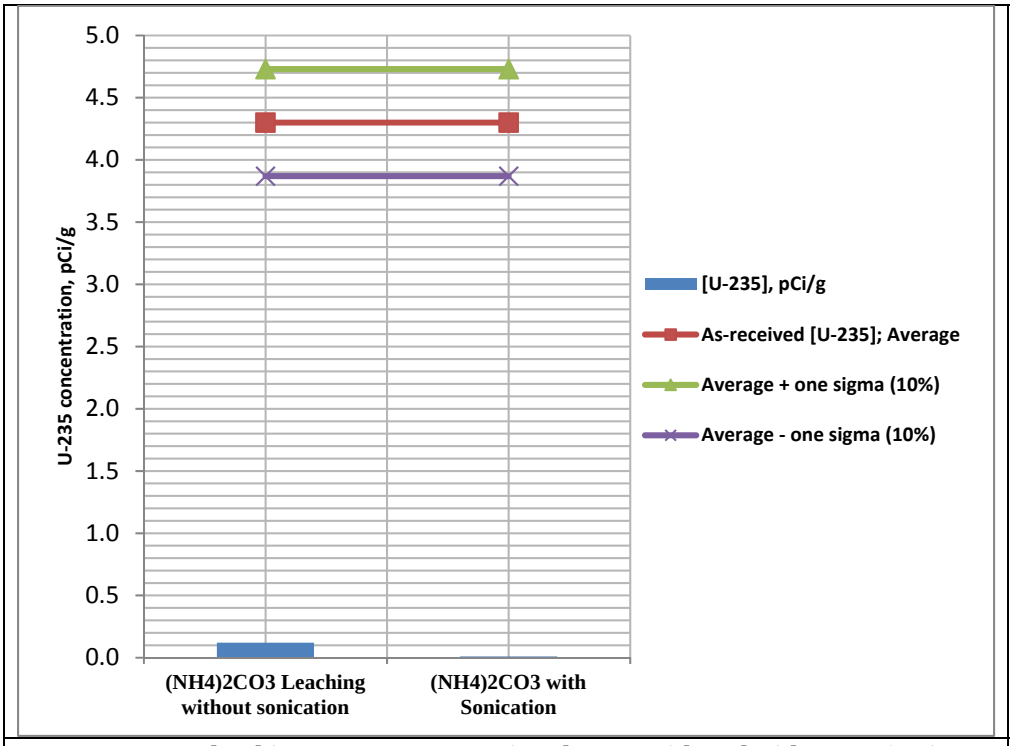
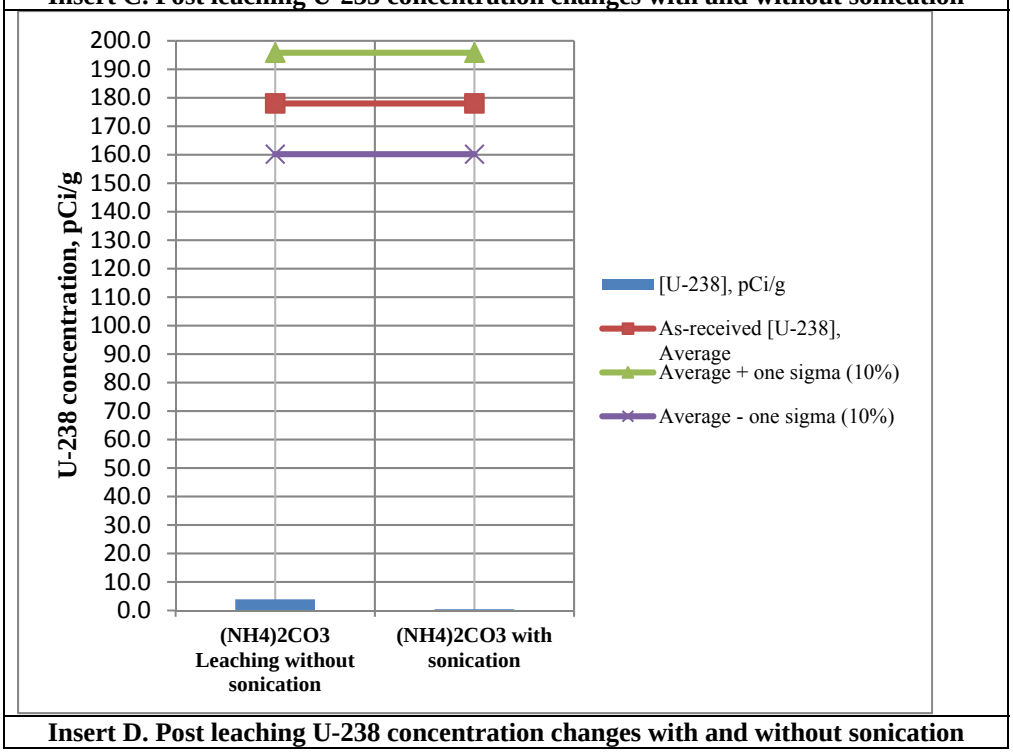


Figure 18 Ammonium carbonate leaching test results without sonication (Test 4B) and with sonication (Test 4A): Post treatment concentration changes for Tc-99 relative to the "as-received" Tc-99 concentrations.



Insert C. Post leaching U-235 concentration changes with and without sonication



Insert D. Post leaching U-238 concentration changes with and without sonication

Figure 19 Ammonium carbonate leaching test results without sonication (Test 4B) and with sonication (Test 4A): Post treatment concentration changes for-U-235 and U-238 relative to initial concentration.

5.0 CONCLUSIONS and RECOMMENDATIONS

The application of superheated steam was used to attempt to remove deposited Tc-99 on Paducah barrier material to determine if the waste acceptance criteria (WAC) for land disposal in a future landfill at the Paducah site could be attained. In Phase I of this steam testing application at 232 ° C (450 ° F), it was shown that it was possible to remove sufficient Tc-99 to levels which approached the Oak Ridge WAC limit of 172 pCi/ converter. In the current Phase I-Part B results presented in this report, barrier material with a starting concentration lower than the starting concentration of the barrier in Phase I was exposed to superheated steam at 232 ° C (450 ° F) or 121 ° C (250 ° F) in attempt to show further removal of Tc-99 from the barrier material. The Phase I, Part-B results did not show any further reduction in Tc-99 concentrations with superheated steam treatment of the barrier material.

This superheated steam treatment of the barrier material at 232 ° C (450 ° F) or 121 ° C (250 ° F) did not consistently reduce the Tc-99 concentrations in the Paducah barrier material to levels complying with the Oak Ridge WAC limit, especially when the Tc-99 concentration in the "as-received' barrier material is low. The reason for this inconsistent thermal desorption results for Tc-99 can be attributed to several factors, one of them being the possibility that superheated steam at 232 ° C (450 ° F) or lower temperatures may be converting the volatile oxy-fluoride Tc-99 compounds in the barrier material to oxides of Tc-99 when the material is exposed to superheated steam. If this is the case, then it will not be possible to use superheated steam to dislodge technetium oxides from the barrier material unless the temperature of the test conditions are above the 300 °C (592 ° F); the thermal desorption temperatures for Tc-99 oxides. On the other hand, this may be the limit of the technology to remove Tc-99 from the standpoint of superheated steam being able to reach all surfaces of the barrier material. The chemistry of the deposited Tc-99 species may be different in different locations within the barrier as Phase I and Phase I, Part-B used different barrier materials.

A temperature above 300 °C (592 ° F) is greater than the maximum scoping experimental thermal desorption temperature of 232 ° C (450 ° F) at which this testing was performed. Thus, thermal desorption of Tc-99 from these types of barrier materials may require greater efforts than hydrothermal treatment at 232 ° C (450 ° F) or lower to dislodge all the technetium compounds from the barrier materials to meet or exceed the WAC limit for barrier material disposal at Paducah. If thermal desorption options are the preferred means to attain the Oak Ridge WAC disposal limits then thermal desorption experiments at temperatures nearer to 350 °C (662 ° F) are preferable.

The extent of desorption of uranium compounds from the barrier material with superheated steam does not seem to correlate with the extent of Tc-99 desorption with steam treatment. On occasions when only small amounts of measurable Tc-99 was removed with steam treatment it was observed that significant amounts of uranium isotopes (U-234 through U-238) are desorbed, which will seem to suggest that that the thermal desorption process for uranium isotopes from the barrier material is independent of the processes or chemistry involved in the thermal desorption of Tc-99.

Leaching of the barrier material with aqueous ammonium carbonate, with and without sonication, significantly reduced the amount of Tc-99 and uranium isotopes on the barrier material. The post ammonium carbonate leached barrier material met the Oak Ridge Tc-99 waste disposal WAC limit of 172 pCi/ converter. However, laboratory leaching of the barrier material resulted in the accumulation of uranium isotopes, which in practice, may lead to criticality problems if neutron absorbers/poison agents are not employed with ammonium carbonate leaching of the barrier material.

The following recommendations are proposed:

- Ammonium carbonate-based lixiviant or other leaching agents, doped with neutron poison agents to address criticality concerns which may result from the accumulation of uranium isotopes with leaching of the barrier material, should be considered for further studies. This leaching study will also include the evaluation of other Tc-99 target lixiviants, leaching time, ammonium carbonate concentrations, pH, solid/liquid ratio (phase ratio), and temperatures effects on Tc-99 and uranium isotope removal efficiency with and without sonication.

- The use of fluorinating agents, such as environmentally compatible nitrogen trifluoride, which under thermal conditions will convert the technetium compounds in the barrier material into more volatile technetium compounds, should be considered as a means of attaining the desired Oak Ridge Tc-99 waste disposal WAC limit.

- Thermal decontamination of both Tc-99 and uranium isotopes from the Paducah barrier materials should be performed with emphasis on superheated steam treatment at more elevated temperatures; temperatures greater than the boiling temperature of technetium oxides.

6.0 QUALITY ASSURANCE

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

The Task Technical and Quality Assurance Plan (TTQAP) details the planned activities and associated quality assurance implementing procedures for the Tc-99 Decontamination of a Gaseous Diffusion Membrane - Phase I (TTQAP, SRNL-RP-2016-00180, Rev. 0, April 30, 2016) task. The documents referenced in the TTQAP include the following: Laboratory Notebook SRNL-NB-2016-00005. Various AD notebooks contain the analytical data.

7.0 REFERENCES

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[5] DOE/OR/01-1909&D3, Attainment Plan for Risk/Toxicity-Based Waste Acceptance Criteria at the Oak Ridge Reservation, Oak Ridge, Tennessee, October 2001, Appendix A, Final Waste Acceptance Criteria, Page A-4.

[6] P2S-15-198, Submittal of Paducah Technetium-99 Sampling Results Graph, Professional Project Services, Inc., September 21, 2015.

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[8] B. Lanning, "Statistical Experimental Design for ^{99}Tc Removal in Shut Down Cells," FBP-WM-NDA-11-00071, February 29, 2012.

[9] B. Lanning, "Statistical Experimental Design for 99Tc Removal in Shut Down Cells," FBP-WM-NDA-11-00122, May 14, 2012.

[10] D. W. Simmons, "An Introduction to Technetium in the Gaseous Diffusion Cascades," K/TSO-39, September 1996.

APPENDIX A: Piping and instrument diagram: Superheated steam Setup.

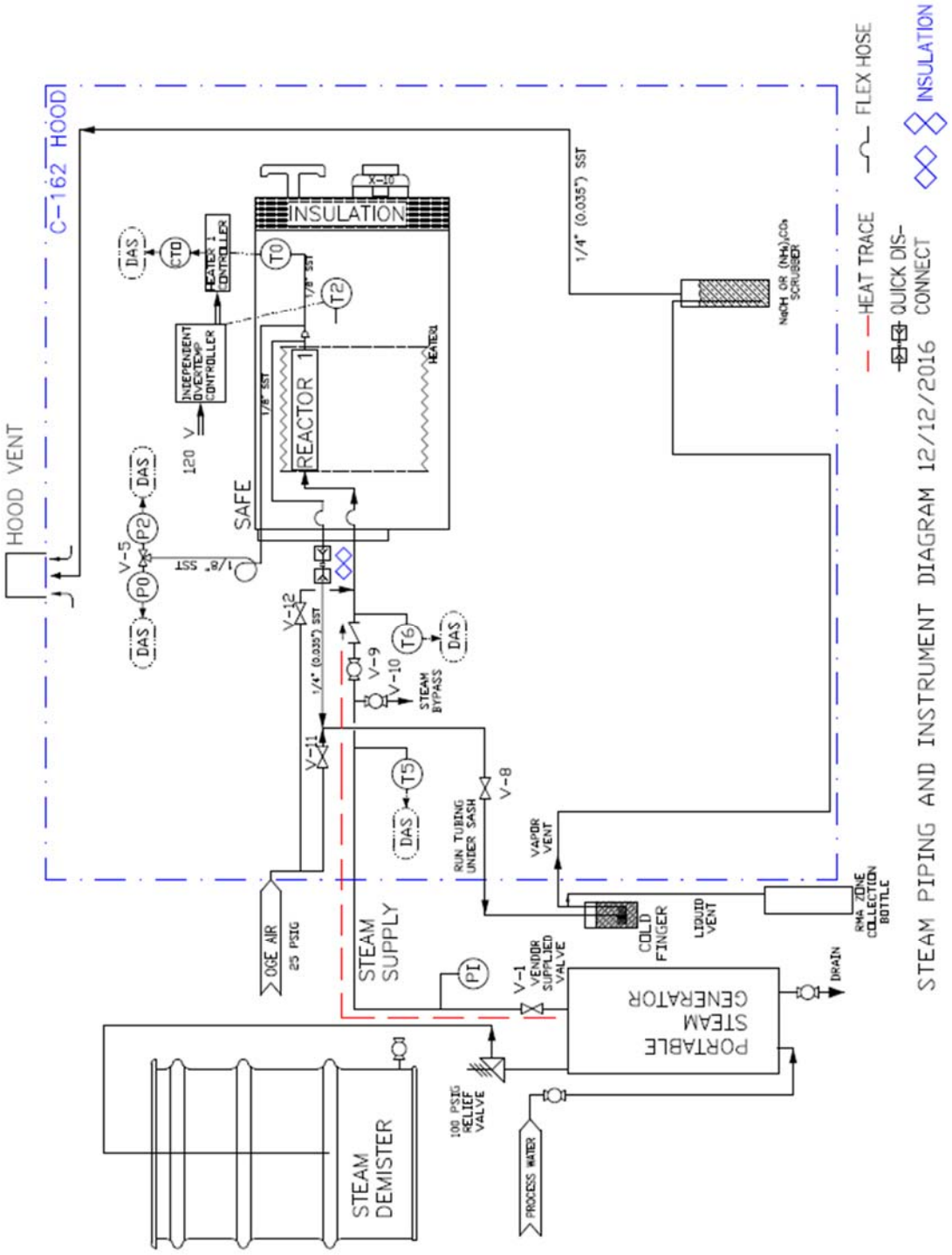

Figure 20 P&ID Steam Flow System

APPENDIX B: Data Acquisition System Set Up (Outside the Radiological Hood)

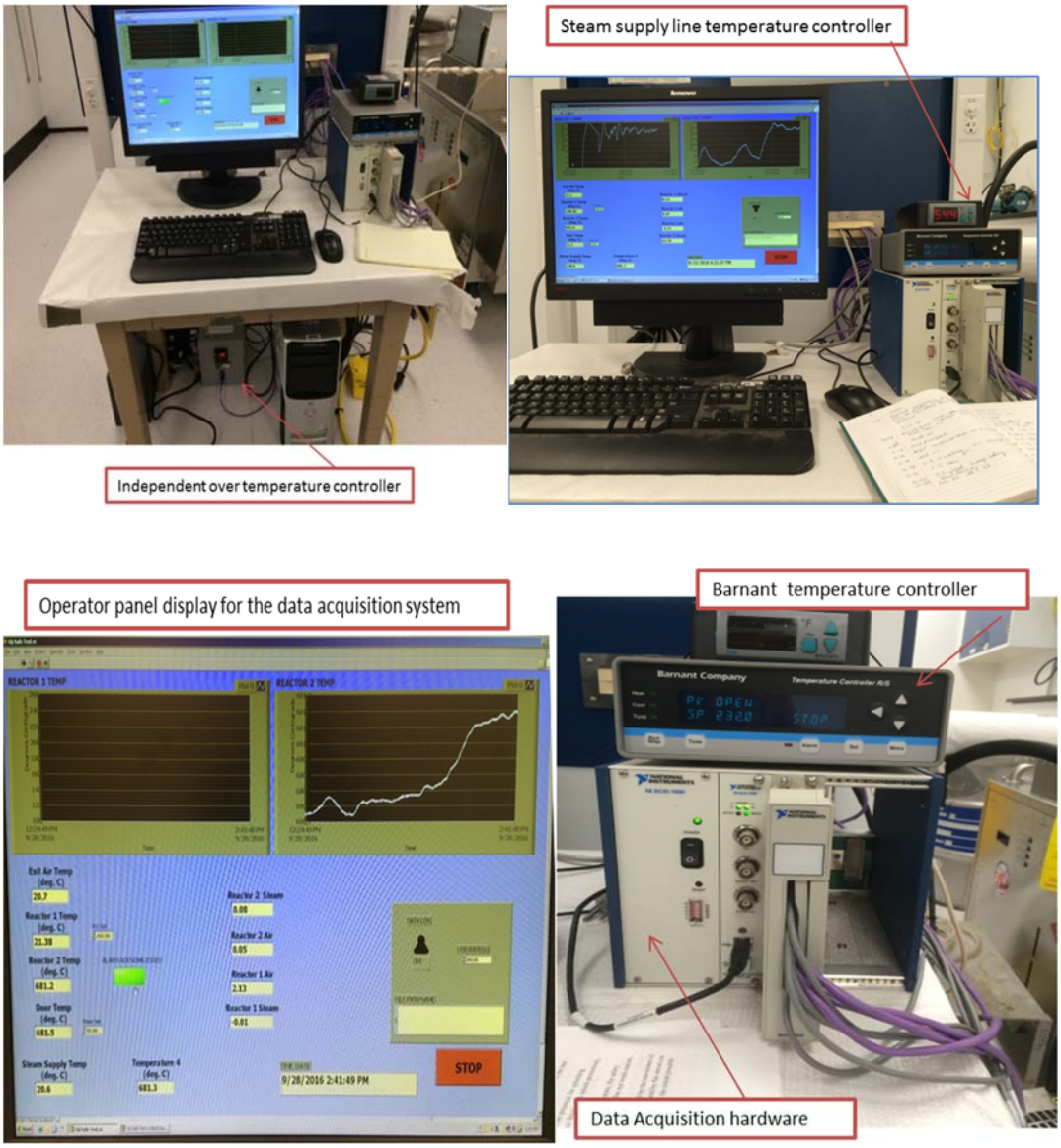

Figure 21 Various Photos of the Test Rig, including the Data Acquisition System

APPENDIX C: General Equipment list

The following is a list of the equipment/instrumentation used for the data acquisition:

Channel Name	Description	M&TE Number	Range
T0	Reactor 1 Temperature	TR-40080	0-300 °C
T1	Reactor 2 Temperature	TR-01518	0-300 °C
T2	Security Safe Internal Temperature	N/A	0-300 °C
T3	Reactor 1 Trap Temperature	N/A	0-300 °C
T4	Reactor 2 Trap Temperature	N/A	0-300 °C
T5	Rotameter Temperature	TR-01516	0-100 °C
T6	Steam Inlet Temperature	TR-40011	0-300 °C
T7	Security Safe Door Lock Temperature	TR-02827	0-300 °C
P0	Reactor 1 Steam Pressure	TR-40019	0-150 PSIG
P1	Reactor 2 Steam Pressure	TR-40018	0-150 PSIG
P2	Reactor 1 Air/Vacuum Pressure	TR-03498	0-30 PSID (Low/High Pressure Taps)
P3	Reactor 2 Air/Vacuum Pressure	TR-03745	0-30 PSID (Low/High Pressure Taps)
PI	Rotameter Pressure	TR-03788	0-15 PSIG/0-30 in Hg
PI-SG	Steam Generator Pressure	TR-03801	0-200 PSIG
FI	Flow Rotameter	TR-40284	0-2 SCFH
	Over-Temperature Controller, Custom	786-A-MLR-OTC-1	0-100 °C
	Heater Controller, Barnant Temp Controller R/S	N/A	0-300 °C
	Steam Generator, Electro Steam LG-10	N/A	0-500 °C, 0-85 PSIG
	Steam Inlet Heater, Briskheat ETC1311	N/A	0-800 °C
	Neslab CC-65 cold Finger (Cryotro)	N/A	

Data Acquisition hardware

Dell 9200 Tower running Windows™ XP

National Instruments™ Hardware

SCXI-1000 4-Slot Chassis

SCXI-1600 USB Data Acquisition and Control Module

SCXI-1102 with 1303 Terminal Block, Signal Conditioner for thermocouples and 4-20 mA Instruments

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