(SRR) Savannah River Remediation
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SRR-CWDA-2017-00050
Revision 0
RSM Track #: 10667

MAY 0 8 2017

Sherri R. Ross, Program Manager
Waste Removal and Tank Closure
Waste Disposition Programs Division
Savannah River Operations Office

Dear Ms. Ross:

ACTION ITEM FOLLOW-UP IN SUPPORT OF U.S. NUCLEAR REGULATORY COMMISSION SALT WASTE DISPOSAL MONITORING ACTIVITIES

Ref:

1. SRR-CWDA-2015-00086, *Savannah River Site Salt Waste Disposal NRC Onsite Observation Visit July 7-8, 2015*, Savannah River Site, Aiken, SC, Revision 1, July 2015.
2. SRR-CWDA-2016-00052, *Savannah River Site Salt Waste Disposal NRC Onsite Observation Visit April 19-21, 2016*, Savannah River Site, Aiken, SC, Revision 1, April 2016.
3. K-ESR-Z-00006, Williams, R. J., *Construction Phase Settlement Monitoring Report for Saltstone Disposal Unit 6 (SDU 6)*, Savannah River Site, Aiken, SC, Revision 0, March 2017.
4. SREL Doc. No.:R-17-0002, Seaman, J.C. and Cochran, J., *Sulfate Attack Testing of SDU Concretes: Coated and Uncoated SDU6 Concrete, and Uncoated Type II and Type V Shotcrete*, Savannah River Ecology Laboratory, Aiken, SC, Revision 0, December 2016.
5. SRNL-STI-2009-00473, Kaplan, D.A., *Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site*, Savannah River National Laboratory, Aiken, SC, Revision 1, July 2016.
6. SREL Doc. R-13-0004, Seaman, J. C., and Chang, H. S, *Impact of Cementitious Material Leachate on Contaminant Partitioning*, Savannah River Ecology Laboratory, Aiken, SC, Version 1.0, September 2013.
7. SRNL-STI-2016-00106, Reigel, M.M. and Hill, K.A., *Results and Analysis of Saltstone Cores Taken from Saltstone Disposal Unit Cell 2A*, Savannah River National Laboratory, Aiken, SC, Revision 0, March 2016.
8. SRR-CWDA-2017-00007, *Savannah River Site Salt Waste Disposal NRC Onsite Observation Visit January 25, 2017*, Savannah River Site, Aiken, SC, Revision 1, January 2017.

The following information is being provided in follow-up to open Action Items from previous Onsite Observation Visits (OOV) by the U. S. Nuclear Regulatory Commission (NRC). The Action Items include the following:

- NRC # SDF-CY15-02-001 (Action Item #12 from 7/2015 OOV, Reference 1)
  - *DOE will provide NRC with information on SDS 3A, SDS 3B, SDS 5A, and SDS 5B fill height restrictions related to resolution of mercury Potential Inadequacy in Safety Analysis.*

- NRC # SDF-CY16-01-005 (Action Item #4 from 4/2016 OOV, Reference 2)
  - *DOE to provide NRC with SDS 6 settlement marker elevation data.*

- NRC # SDF-CY16-01-015 (Action Item #23 from 4/2016 OOV, Reference 2)
  - *DOE to provide NRC results of disposal structure concrete testing.*

- NRC # SDF-CY16-01-023 (Action Item #21 from 4/2016 OOV, Reference 2)
  - *DOE to provide NRC additional information on the basis of cement leachate factors from SRNL-STI-2009-00473, Rev. 0, "Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site".*

<u>NRC # SDF-CY15-02-001 (Action Item 12 from 7/2015 OOV)</u>
As discussed during previous NRC onsite Observation Visits, in response to the issuance of a Potential Inadequacy in Safety Analysis (PISA) pertaining to the Saltstone Facility Documented Safety Analysis (DSA), beginning with a 6/24/2015 restart of Saltstone Processing Facility operations the fill height for Saltstone Disposal Unit (SDU) cells 3A, 3B, 5A and 5B was limited to a height of 19 feet (previously 21.5 feet). The PISA was issued after Tank 50 sample analysis results indicated that the concentration of monomethyl mercury, an organic constituent of mercury, in Tank 50 exceeded the concentration assumed in the Saltstone Facility DSA. The fill height restriction was put in place pending the evaluation of potential impacts of the higher concentrations versus DSA assumptions. The grout fill height limit is established to ensure that the flammable constituents of the cell vapor space, a combination of organics, ammonia and hydrogen, remain below the Composite Lower Flammability Limit (CLFL). An update to the Saltstone Facility DSA was completed which included, among other things, an evaluation of impacts resulting from higher than previously assumed monomethyl mercury concentrations. As a result of evaluations supporting the DSA update, the fill height limits for SDU cells 3A, 3B, 5A and 5B have been restored to the original 21.5-foot value.

NRC # SDF-CY16-01-005 (Action Item 4 from 4/2016 OOV)

Document K-ESR-Z-00006 Revision 0, *Construction Phase Settlement Monitoring Report for Saltstone Disposal Unit 6 (SDU 6),* was previously provided to NRC on 3/8/2017 via e-mail from Sherri Ross to Harry Felsher. The referenced report provides the settlement marker elevation data for SDU 6 (Reference 3, NRC Accession # ML17068A166).

NRC # SDF-CY16-01-015 (Action Item #23 from 4/2016 OOV)

Document SREL Doc.:R-17-0002, *Sulfate Attack Testing of SDU Concretes: Coated and Uncoated SDU6 Concrete, and Uncoated Type II and Type V Shotcrete*, provides the results of SDU 6 concrete testing that was being carried out at Savannah River Ecology Laboratory (SREL) during the April 2016 NRC OOV. A copy of the report is being provided with the transmittal of this document (Reference 4).

NRC # SDF-CY16-01-023 (Action Item #21 from 4/2016)

Document SRNL-STI-2009-00473, Rev. 0, *Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site,* was revised (Reference 5) to incorporate, among other things, additional available information regarding cement leachate factors that had been published since the original issuance of the SRNL-STI-2009-00473. Studies done at SREL related to measuring the cement leachate factors for radionuclides of interest to the performance assessment (Reference 6) were reviewed as part of the update to SRNL-STI-2009-00473. The conclusions of the review resulted in no changes to the original recommended cement leachate factors. At this time, no other additional information is available. Document SRNL-STI-2009-00473, Revision 1, was previously provided to to NRC on 2/9/2017 via e-mail from Sherri Ross to Harry Felsher, Robert Gladney and Lloyd Desotell.

The following additional information is being provided in follow-up to a recent request for information via e-mail by the NRC. The e-mail request is the following:

Email request from Harry Felsher to Sherri Ross 4/17/2017

- The NRC technical staff received the DOE response to the previous NRC question about the units in Table 2-4 of SRNL-STI-2016-00106:
  - The previous NRC question: *Verify that the units used in the table are correct (g/L) or, if not correct, then provide the NRC with the correct units for the table.*
  - The DOE response: *The units (g/L) are correct.*
- As a follow up, the NRC technical staff requests additional clarifying information from the DOE:
  - Table 2-4 of SRNL-STI-2016-00106 provides the composition of the leachate used; however, the document does not provide a basis for that solution composition.

- That basis is unclear to the NRC staff because the solution appears to be more than three orders of magnitude more concentrated in major ions (e.g., Ca2+, Cl-, Na+) than SRS groundwater; but does not have the expected composition (e.g., high nitrate concentration) of saltstone-leachate-impacted water.
- *Please clarify the basis for the solution composition provided in Table 2-4 of SRNL-STI-2016-00106.*
- *If the composition of the leachate differs from anticipated field conditions, then please describe how that may impact radionuclide release.*

Response to 4/17/2017 e-mail request

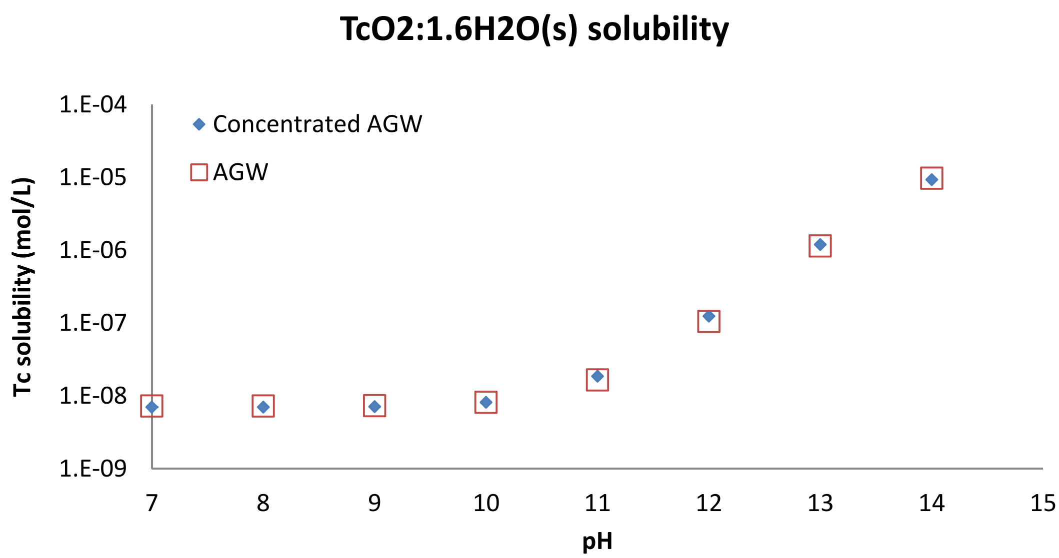
Cored samples of saltstone from SDU Cell 2A were provided to Savannah River National Laboratory (SRNL) to determine radionuclide (i.e., ^{99}Tc) solubility and/or partitioning behavior in a series of desorption experiments conducted under anoxic and ambient oxic conditions (Reference 7). Material from the interior of the cores was used to negate the potential impact of ^{99}Tc oxidation at the exposed exterior of the core surface. The resulting samples were ground to fine powder for testing. Triplicate 1 gram samples of the powdered saltstone were added to 10 mL of an artificial groundwater solution (AGW) and then equilibrated on an end-over-end shaker at 15 rpm for seven days. The solution phase was then filtered (0.45 µm pore size) and analyzed for ^{99}Tc. Samples of the same SDU cores were digested with concentrated acid to determine the initial total solid-phase activity for ^{99}Tc. After testing and analysis had been completed it was determined that a concentrated AGW stock solution was used in testing rather than the intended 1,000 times diluted AGW stock solution. The following discusses the potential impacts of using the concentrated AGW on the solubility data. It is important to note that the constituents of the AGW solution are not redox active, and would not alter the redox speciation of the target radionuclide contaminants regardless of their concentration.

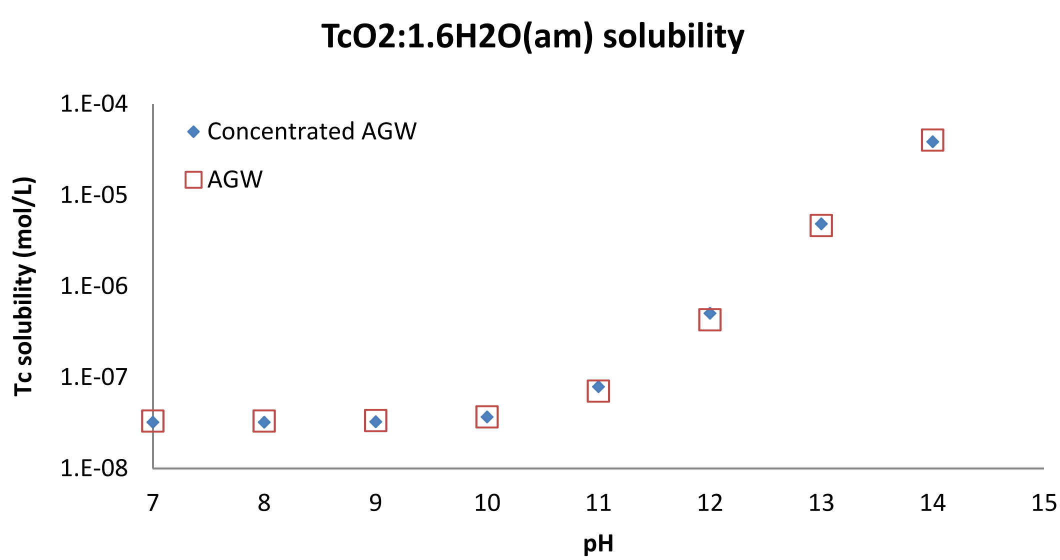
Technetium-99 retention was quite similar for all SDU samples regardless of the equilibration atmosphere, with the final concentration of ^{99}Tc ranging from ≈ 7.02 x 10^{-9} to 3.95 x 10^{-8} *M*. The solubility of several technetium phases at the pH of the batch test is presented in Table 1. Solubility estimates as a function of solution conditions were determined using the PHREEQC Version 3 computer code for aqueous geochemical calculations (Parkhurst, D.L., and Appelo, C.A.J., 2013) and the accepted thermodynamic databases (Thermoddem_V1.10; LLNL Database). Under anoxic conditions the solid phase retention of ^{99}Tc is generally considered to be controlled by the solubility of Tc(IV)-oxide (i.e., TcO_2), with the final concentrations of ^{99}Tc observed in the SRNL tests similar to the levels predicted for Tc(IV)-oxide solubility at the observed pH values. The solubility of $TcS_{2(s)}$ would support much lower ^{99}Tc concentrations than the values reported in the current study. Figure 1 illustrates the solubility of two potential Tc(IV)-oxide solid phases as a function of pH in the low ionic strength AGW solution and the more concentrated version. As illustrated in Figure 1, the ionic strength of the background solution has a very limited impact on the solubility of the Tc(IV)-oxide.

Table 1. Molar Tc solubility related to potential pure Tc solid phases in concentrated AGW (database Thermoddem_V1.10; LLNL Database).

Compounds	Tc solubility at pH 9	Tc solubility at pH 10	Tc solubility at pH 10.5	Tc solubility at pH 12
Tc (element)	$2.562\ 10^{-16}$	$9.328\ 10^{-17}$		$1.971\ 10^{-16}$
Tc_2O_7	$1.695\ 10^{1}$			
TcS_3	Not soluble			
TcOH	$8.611\ 10^{-19}$	$4.183\ 10^{-19}$		$1.461\ 10^{-18}$
TcO_3	$1.000\ 10^{1}$			
Tc_4O_7	$8.417\ 10^{-12}$	$8.407\ 10^{-12}$	$1.033\ 10^{-11}$	$1.031\ 10^{-10}$
Tc_3O_4	$3.887\ 10^{-19}$	$3.053\ 10^{-19}$	$3.335\ 10^{-19}$	$2.464\ 10^{-18}$
$Tc(OH)_3$	$8.947\ 10^{-16}$	$7.737\ 10^{-16}$	$8.861\ 10^{-16}$	$7.390\ 10^{-15}$
$Tc(OH)_2$	$7.684\ 10^{-20}$	$4.980\ 10^{-20}$	$4.947\ 10^{-20}$	$2.877\ 10^{-19}$
$KTcO_4$	$1.113\ 10^{-1}$	$1.113\ 10^{-1}$	$1.114\ 10^{-1}$	$1.127\ 10^{-1}$
$HTcO_4$	8.476			
$Na(TcO_4){:}4H_2O(s)$	4.357	4.357	4.357	4.341
$TcO_2{:}1.6H_2O(s)$	$7.126\ 10^{-9}$	$8.173\ 10^{-9}$	$1.068\ 10^{-8}$	$1.243\ 10^{-7}$
$TcO_2{:}2H_2O(am)$	$3.253\ 10^{-8}$	$3.674\ 10^{-8}$	$4.686\ 10^{-8}$	$5.038\ 10^{-7}$
$TcS_2(s)$	-	-	-	$7.421\ 10^{-40}$
Tc_2S_7	Not soluble			

Figure 1. Solubility of $TcO_2 \cdot 1.6H_2O_{(s)}$ (upper graph) and $TcO_2 \cdot 1.6H_2O_{(am)}$ (lower graph) as a function of pH in the AGW solution and the more concentrated version ($[CO_2] = 0$ mol/L).





Computer Code and Database information supporting 4/17/2017 e-mail request:

- LLNL Database: Data are from 'thermo.com.V8.R6.230' prepared by Jim Johnson at Lawrence Livermore National Laboratory, in Geochemist's Workbench format. Converted to PHREEQC format by Greg Anderson with help from David Parkhurst.
- Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at https://pubs.usgs.gov/tm/06/a43/.
- Thermoddem_V1.10: PHREEQC database Thermoddem_V1.10, Version V1.10. Data from thermoddem V1.10 Code version 1.07_2.06. Thermochemical Database from the BRGM institute (French Geological Survey).

After providing the information included in this document, one Action Item from the April 2016 NRC OOV (Reference 2) remains open at this time. The remaining Action Item is the following:

- NRC # SDF-CY16-01-013 (Action Item #13 from April 2016 NRC OOV)
  - *DOE to provide NRC with velocity field and cross-section through Z-Area.*

One Action Item from the January 2017 NRC OOV (Reference 8) remains open at this time. The remaining Action Item is the following:

- NRC # SDF-CY17-01-002 (Action Item #3 from January 2017 NRC OOV)
  - *DOE to provide NRC with a map identifying the locations for the pictures from the tours.*

If you have any questions please contact me at 557-8960.

Sincerely,

Steven A. Thomas
Manager
Waste Disposal Authority

st/lr

c:

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