Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Scoping Tests of Technetium and Iodine Removal from Tank Waste Using SuperLig® 639 Resin

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September, 2013

SRNL-STI-2013-00538, Revision 0

SRNL.DOE.GOV

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2013-00538
Revision 0

Keywords: *Technetium*
Iodine
High Level Waste

Retention: *Permanent*

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REVIEWS AND APPROVALS

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EXECUTIVE SUMMARY

The primary chemical form of ^{99}Tc found in Hanford Low Activity Waste (LAW) is pertechnetate anion (TcO_4^-), which is highly soluble in water, and is mobile if released to the environment. Pertechnetate will not be removed from the aqueous waste in the Hanford waste treatment plant, and the primary disposition path is immobilization in the LAW glass waste form, which will be disposed in the Integrated Disposal Facility (IDF). Due to the soluble properties of pertechnetate, and the potential for impact to the Performance Assessment (PA), effective management of ^{99}Tc is important to the overall success of the River Protection Project mission. Washington River Protection Solutions (WRPS) is developing some conceptual flow-sheets for LAW treatment and disposal that could benefit from technetium removal. While ^{99}Tc is the primary radionuclide of interest, ^{129}I also contributes to the calculated future dose of disposed LAW, and it would be of interest to examine if removal is possible.

SuperLig® 639[a] resin had previously been tested extensively and found highly effective for removing the pertechnetate form of ^{99}Tc from Hanford tank wastes. Two new batches of resin were produced by the vendor as part of an overall program to mature the Technetium removal technology level. One batch of the new resin was tested to examine the effectiveness of removing both ^{99}Tc and ^{129}I from a sample of actual tank waste. The sample of tank waste used in testing was from Tank 50H at SRS. Although this waste did not originate at Hanford, its composition is very similar to many tank wastes at Hanford, and is expected to have pertechnetate and iodine chemistry comparable to Hanford tanks that do not contain appreciable organic complexants. SRS waste has been used previously as a substitute for some Hanford waste types, and appears to have comparable performance for technetium behavior.

Results indicate that the resin is highly effective for removal of ^{99}Tc, and also moderately effective for removal of ^{129}I. The Distribution Coefficient (K_d) was 582 mL/g for ^{99}Tc, and 49 mL/g for ^{129}I at a phase ratio of 100:1. This is the first time that a separation process has been shown to selectively remove ^{129}I from radioactive aqueous LAW from decontaminated HLW. Many tests in the past have shown that the ^{99}Tc can be readily eluted from this resin with warm water, and it is expected that the ^{129}I will likely be elutable as well, although this demonstration of this was not practical in this test. These results indicate that a process could be developed that could remove at least some portion of the ^{129}I from tank wastes using a regenerable resin, and isolate it along with ^{99}Tc in a waste form. To further examine the practicality of an ^{129}I removal process, tests are needed to determine if first removing the competing ^{99}Tc improves the removal of ^{129}I, and to determine if the ^{129}I can be eluted. Tests would include sequential batch contacts, column testing and elution testing to determine the loading and elution cycles and to measure the achievable decontamination factor.

[a] SuperLig is a trademark of IBC Advanced Technologies, Inc., American Fork, UT

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g	gram
IDF	Integrated Disposal Facility
K_d	Distribution Coefficient
LAW	Low Activity Waste
M	Molar
mL	milliliter
ORP	Office of River Protection (DOE)
PA	Performance Assessment
pCi	picoCurie (1E-12 Ci)
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
WRPS	Washington River Protection Solutions

1.0 Introduction

The primary chemical form of ^{99}Tc found in Hanford Low Activity Waste (LAW) is as pertechnetate anion (TcO_4^-). Pertechnetate is highly soluble in water, and is mobile if released to the environment. Pertechnetate will not be removed from the aqueous waste in the Hanford waste treatment plant, and its disposition path is immobilization in the LAW glass waste form, which will be disposed in the Integrated Disposal Facility (IDF). Because ^{99}Tc has a very long half-life (211,000 years) and is highly mobile [Icenhower, 2008, 2010], it has potential to be a major dose contributor to the Performance Assessment (PA) of the IDF [Mann, 2003]. Due to the soluble properties of pertechnetate, and the potential for impact to the PA, effective management of ^{99}Tc is important to the overall success of the River Protection Project mission. While ^{99}Tc is the primary radionuclide of interest, ^{129}I also contributes to the calculated future dose in the PA due to its 15.7 million year half-life, and it would be of interest to examine if removal is possible. No effective methods have been demonstrated for selectively removing ^{129}I from the aqueous phase of LAW. Tests have been done with simulants, and with analytical samples of Melton Valley Storage Tank waste at ORNL [Gula, 1998].

Removal, followed by off-site disposal of technetium from the LAW, would eliminate a key risk contributor for the IDF PA for supplemental waste forms, and has potential to reduce treatment and disposal costs. Washington River Protection Solutions (WRPS) is developing some conceptual flow-sheets for LAW treatment and disposal that could benefit from technetium removal. One of these flow-sheets will specifically examine removing Tc from the LAW feed stream to supplemental immobilization and will support a Tri-Party Agreement Milestone (M-062-40ZZ), which is a one-time report on supplemental immobilization technology that is scheduled for October 31, 2014. To enable an informed decision regarding the viability of technetium removal, further maturation of available technologies is being performed. One of the technologies, SuperLig® 639, is an elutable ion exchange resin available from IBC Advanced Technologies. Although this resin is selective for pertechnetate (TcO_4^-), it has potential to also remove iodine species because of their similar charge and configuration, particularly if present as periodate (IO_4^-). The resin also interacts with nitrate ion (NO_3^-). Even though the nitrate interaction is fairly weak, its high concentration in tank waste causes interference with removal of the target pertechnetate ion. This document summarizes testing performed to examine the effectiveness of removing both ^{99}Tc and ^{129}I from a sample of actual tank waste using a new batch of SuperLig® 639. This also furthers the maturation of the technology by demonstrating technetium removal with a sample of resin manufactured to SRNL-developed acceptance criteria and produced at bench-scale batch size (~4 L) [Bruening, 2013].

The sample of tank waste used in testing was from Tank 50H at SRS. This tank primarily receives Low Activity Waste that has been decontaminated for ^{90}Sr and actinides using Monosodium Titanate in the Actinide Removal Process, and decontaminated for ^{137}Cs in the Modular Caustic Side Solvent Extraction Unit at SRS. Although this waste did not originate at Hanford, its composition is very similar to many tank wastes at Hanford. SRS tank waste has been used before as a substitute for Hanford waste during ^{99}Tc

removal testing [King, 2000] and ^{99}Tc immobilization testing by Fluidized Bed Steam Reforming [Jantzen 2013], and is expected to have comparable pertechnetate and iodine chemistry with Hanford tanks that do not contain appreciable organic complexants. It is important to use actual tank waste for this test because the speciation of iodine in tank waste is not well understood. Iodine can take many chemical forms in aqueous solution, such as periodate (IO_4^-), iodide (I^-), and triiodide (I_3^-), and it is not known which is dominant. Use of actual tank waste as a first step will ensure that the right species are present, even if it is not yet known which are extracted by the resin.

2.0 Experimental Procedure

2.1 Tank 50H Sample Characterization

A sample of Tank 50H at SRS was obtained from a routine subsampling of the tank (Sample I.D.: 1QCY13). The complete composition has been reported [Bannochie, 2013], and the results are reproduced in Appendix A for radionuclides and chemicals that could impact the outcome of this test, excluding extensive trace radionuclides and constituents that are reported for regulatory purposes. The analysis was on the complete sample, including trace insoluble solids. However, the sample was filtered for the current testing, so any insoluble species would have been removed. This is not expected to be significant for the components shown in the Appendix, since they are expected to be soluble, and the trace insoluble solids (estimated maximum of 0.4 wt%, $\sigma = 0.7$) would not contribute significantly versus the total solids of 28.5 wt%. Approximately 100 mL of the sample was filtered with a 0.45 micron Nalgene® filter prior to performing the tests.

2.2 Distribution Coefficient Testing

The Distribution Coefficient (K_d) was tested using a batch of SuperLig® 639 produced in May, 2013 (Lot # 130611552-56). Generally, approximately 0.25 g of resin was placed in a poly bottle, approximately 25 mL of the filtered Tank 50H sample was added by weight, and the bottles were agitated in a shaker oven at 25 °C +/- 1 °C for 49.5 hours. At the end of shaking, the samples were filtered to remove the resin and analyzed for ^{99}Tc and ^{129}I by chemical separation and beta counting by liquid scintillation. An initial feed sample that had not been contacted with resin was also analyzed. The analytical results for the initial concentration for both isotopes shown in Table 1 was the result from a single analysis of this initial feed sample. The initial feed was not measured in duplicate since it is nearly identical to the result reported in triplicate analyses shown in the Appendix, and was analyzed alongside the test samples.

The F-factor (moisture content) of this batch was reported as <0.2% in the acceptance report [Bruening, 2013], so was ignored in calculations. The resin was used as received with no preconditioning.

2.3 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.

This report fulfills the scope described in the Task Technical and Quality Assurance Plan for Task 4.3 of SRNL-RP-2012-00708, Rev. 1.

3.0 Results and Discussion

Results of the Distribution Coefficient Tests are shown in Table 1. Calculation of the Distribution Coefficient was performed utilizing Equation 1:

$$K_d = [(C_i/C_f)-1][V/M*F] \qquad \text{(Eqn. 1)}$$

where

C_i = initial concentration
C_f = final concentration
V = Volume of liquid (mL)
M = mass of resin (g)
F = resin dry weight correction factor (ignored due to <0.2 wt% moisture)

Table 3-1. Distribution Coefficient Test Results

Resin (g)	**Liquid (mL)**	**^{129}I initial (pCi/mL)**	**^{129}I final (pCi/mL)**	**^{129}I K_d (mL/g)**	**^{99}Tc initial (pCi/mL)**	**^{99}Tc final (pCi/mL)**	**^{99}Tc K_d (mL/g)**
0.2504	24.97	11.8 (5.22E-7 M)	5.9	102	2.06E4 (1.23E-5 M)	3.04E3	578
0.2499	24.94		10.2	15.8		3.17E3	551
0.2498	25.99		9.2	29.4		2.98E3	617
			Average	49		Average	582
			Standard Deviation	46		Standard Deviation	34

For comparison, the K_d for ^{99}Tc was also calculated for this sample using the equilibrium computer model. The nitrate concentration of the sample composition used in the model was mathematically increased to 2.28 M versus the measured 1.82 M in the actual Tank 50H sample to balance the charge. This increase would have the effect of lowering the calculated K_d. Results indicated that the K_d was predicted to be 636 mL/g for ^{99}Tc [Smith, 2013], although the composition of the solution was altered for the calculation to achieve charge balance. The Tc loading on the resin is strongly dependent on the nitrate:pertechnetate ratio. Overall, the calculated and measured K_d agree reasonably well.

A prior test with an SRS Tank 44 sample [King, 2000] exhibited a K_d of 950 mL/g, but that sample had very low nitrate and high potassium concentrations, which would cause high distribution coefficients. A subsequent column test with that Tank 44 sample reached 45% breakthrough after nearly 600 bed volumes had been processed, which was very good performance. By comparison, the current sample would be expected to reach 50% breakthrough at more than 300 bed volumes processed, which is still good performance, indicating that Tc removal with SuperLig® 639 is a viable process.

Selective removal of ^{129}I from tank waste with a regenerable resin has not previously been demonstrated with radioactive tank waste samples. Although the K_d is moderate (49 mL/g) and the standard deviation (46 mL/g) is nearly as large as the distribution coefficient, the results indicate that some ^{129}I can be removed in a ^{99}Tc removal process using SuperLig® 639, if incorporated into an overall strategy for managing long-lived radionuclides. Based on these results, a rough estimate for the fraction of ^{129}I removed is comparable to the ratio of the Distribution Coefficients for the isotopes, i.e., roughly 8% of the ^{129}I would be removed from this waste in a Tc removal-based process using this resin. Although, because of the high standard deviation of the results, additional testing is needed to obtain a better estimate of the process parameters. The removal could be increased somewhat by more frequent elution cycles. It was not practical in this test to show that ^{129}I can be eluted with water, so the process is not proven viable, but the results do indicate that a potential method for removing a fraction of the ^{129}I from the waste may be possible with SuperLig® 639 resin. There could also be differences in the iodine chemistry in the various waste tanks, which would lead to better or worse performance. Similarly, since this test was a "competitor" test, where the ^{99}Tc and ^{129}I were both competing for removal, and it is possible that removal of ^{99}Tc with two columns in series could remove that competition, allowing for increased removal of ^{129}I in a third column. At this time, it is not known if competition from pertechnetate or chemical speciation of iodine are the dominant factors affecting absorption of ^{129}I. Similarly, although it is assumed that 48 hours of contact time is sufficient for reaching Tc equilibrium, it is not known if it is sufficient for I with this batch of resin.

4.0 Conclusions

The new batch of SuperLig® 639 resin that was tested was very effective at removing the ^{99}Tc from the sample of SRS Tank 50H waste, and was moderately effective at removing ^{129}I. The measured value for the Tc K_d (582 mL/g) was in general agreement with the model-based calculation (636 mL/g). The model-based calculation included the vendor-measured capacity of this batch of resin, which is higher than the estimated capacity used in prior work. This resin batch appears to exhibit good distribution coefficient performance; at least equivalent to previous batches.

5.0 Future Work

Removal of ^{99}Tc with SuperLig® 639 from radioactive tank waste has been demonstrated several times, but this is the first concurrent measurement of ^{129}I removal from LAW from decontaminated HLW. The next step in determining if removal of ^{129}I can be developed into a viable process are sequential batch contacts, column testing and elution testing. These tests would be designed to evaluate the sorption behavior of the radionuclides onto this resin in a flowing system to determine the loading and elution cycles and to measure the achievable decontamination factor. This effort would also include work to identify which iodine chemical specie(s) is being extracted by the resin (e.g. metaperiodate (IO_4^-), iodide (I^-), triiodide (I_3^-), etc.). Testing would also determine whether the ^{129}I can be eluted for separate disposal, and then allowing for reuse of the resin.

6.0 References

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Appendix A. Partial Results of Characterization of 1st Quarter 2013 Tank 50H Slurry Sample

Complete characterization data has been documented [Bannochie, 2013].

Table A-1. Results for Chemical Contaminants for the 1st Quarter 2013 Tank 50H Slurry Sample

Chemical Name	Method	Average Concentration (mg/L)	Standard Deviation
Ammonium (NH_4^+)	IC	<5.00E+01	NA
Carbonate (CO_3^{2-})	TIC	1.20E+04[a]	5.00E+01
Chloride (Cl^-)	IC	<2.50E+02	NA
Fluoride (F^-)	IC	<2.50E+02	NA
Free Hydroxide (OH^-)	Total base	3.38E+04[a]	1.96E+02
Nitrate (NO_3^-)	IC	1.13E+05	4.04E+03
Nitrite (NO_2^-)	IC	1.42E+04	9.94E+02
Oxalate ($C_2O_4^{2-}$)	IC	4.35E+02	4.71E+01
Phosphate (PO_4^{3-})	ICP-ES	4.27E+02	2.19E+00
Sulfate (SO_4^{2-})	IC	4.05E+03	2.08E+02
Arsenic (As)	ICP-ES	<4.12E+00	NA
Barium (Ba)	ICP-ES	<4.61E-01	NA
Cadmium (Cd)	ICP-ES	<7.31E-01	NA
Chromium (Cr)	ICP-ES	3.55E+01	1.89E-01
Lead (Pb)	ICP-MS	6.08E-01	3.10E-02
Mercury (Hg)	AA	5.03E+01	6.09E-01
Selenium (Se)	ICP-ES	<7.90E+00	NA
Silver (Ag)	ICP-ES	<9.74E-01	NA
Sodium (Na)	ICP-ES	1.20E+05	6.34E+02
Aluminum (Al)	ICP-ES	3.86E+03	1.43E+01
Potassium	ICP-ES	2.76E+02	8.22E+00
Nickel Hydroxide	ICP-ES	<2.85E+00[d]	NA
n-Butanol	VOA	<5.00E-01[b]	NA
i-Butanol	VOA	<5.00E-01[b]	NA
i-Propanol	VOA	<2.50E-01[b]	NA
Phenol	SVOA	<1.00E+01[b]	NA
Isopar L	SVOA	<2.67E+01 ppm [b,c]	NA
Total organic carbon	TOC	3.31E+02[a]	4.16E+00
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00	NA

a. Measurement performed on filtered supernate samples.
b. Measurement performed on duplicate samples rather than triplicate samples.
c. Result is calculated from the reported concentration of < 33 mg/L and the density of the slurry sample listed in Table A-3
d. Result is calculated from the measured Ni concentration assuming all of the Ni is present as the hydroxide compound.

Table A-2. Results for Radionuclides in 1st Quarter 2013 Tank 50H Slurry Sample.

Radionuclide	**Method**	**Average Concentration (pCi/mL)**	**Std. Dev.**
Technetium-99 (^{99}Tc)	Tc-99 Liquid scintillation	2.07E+04	1.02E+03
Iodine-129 (^{129}I)	I-129 (w/ separation) Liquid scintillation	1.24E+01	6.31E-01
Cesium-137 (^{137}Cs)	Gamma Scan	9.55E+05	4.68E+04

Table A-3. Results for Properties in 1st Quarter 2013 Tank 50H Slurry Sample.

Property	**Method**	**Value**	**Std. Dev.**
pH	Calculated	>13	NA
Density (slurry)	Measured (21.9ºC)	1.2346 g/mL	0.0019
Total Solids	Measured	28.53 wt%	0.123
Total Insoluble Solids	Calculated	0.400 wt%	0.744

Distribution:

S. L. Marra, 773-A
T. B. Brown, 773-A
D. R. Click, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
R.A. Robbins, WRPS
P.A. Cavanaugh, WRPS
D.J. Swanberg, WRPS
W.G. Ramsey, WRPS
A.D. Cozzi. 999-W
K.M. Fox, 999-W
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