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SAVANNAH RIVER NATIONAL LABORATORY
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Single-Pass Melt Pool Retention Based on the Ratio of Cesium to Technetium

Attached is the response to the Department of Energy Office of River Protection's questions pertaining to the impact of cesium on the retention of technetium in the direct feed low activity waste process flowsheet.

Attachments:

Attachment A. Single-Pass Melt Pool Retention Based on the Ratio of Cesium to Technetium

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Attachment A: Single-Pass Melt Pool Retention Based on the Ratio of Cesium to Technetium

Issue: The ratio of cesium to technetium in DFLAW may impact the single pass retention of these species in the LAW melter.

Concerns: The ratio of Tc to Cs was noted to be a possible reason for low single pass retention of Cs during selected pilot scale testing of the LAW vitrification process at VSL.[1] Lower single pass retention of Cs in glass leads to concerns that Cs-137 will build up in the off-gas system through the recycle strategy. This would ultimately increase the dose in the facility and could increase the dose in the some of the glass containers.

Response to Concerns: The ratio of Tc to Cs-137 is large in the DFLAW feed vectors when comparing the *molar* concentrations of each at the Feed Acceptance Limit[2], i.e. the concentration of Tc is large compared to Cs-137. Pretreated LAW waste envelopes A, B, and C found in reference 3 show the Tc molar concentration is more than a factor of 100 higher than Cs, where envelope B had 0.556 mmolar (millimoles/liter) Tc and 3.00E-3 mmolar Cs-137.[3] However, the highest Cs-137 (1.8e-5 Ci/mole Na) is found in envelope C and is about half the Cs-137 feed limit (3.18e-05 Ci/mole Na). The influence of Tc on Cs retention based on the large ratio would be notable in testing and Cs retention would be expected to be as low or lower than Tc retention. Likewise, the impact that Cs has on the Tc retention would be small.

Increases in Cs volatility above the assumed amounts (~25% in current system models) could lead to higher than expected dose rates in the LAW facility. The VSL testing did not attribute any variations in Tc retention to variations in Cs concentrations, but some literature sources indicate higher Tc volatilization in the presence of Cs.[1] It should be noted that the retention of all semi-volatile species is variable in the melting process and can be significantly impacted by a number of processing conditions. For example, increased volatility will be noted when the melters are idled. The authors of RPP-54130 acknowledge the data on Tc retention varies widely even for identical runs using identical conditions. The literature data presented there is not convincing enough to suggest there is a synergistic relationship between Tc and Cs volatilization.

The BARD[4] acknowledges this issue and provides two proposed mitigation strategies to remove excess Cs should it accumulate in the off-gas system and the recycle stream. The first option is to dilute the Cs-137 with Cs-133 (non-radioactive). The cesium would be expected to increase the single pass retention of cesium in the glass by decreasing the Tc:Cs ratio. The second option is to reroute the recycle stream through the ion exchange columns in the pre-treatment system, an option not readily available during DFLAW although some recycle could be purged by transfers to the Tank Farms. A third option is to

[1] RPP-54130, "Technetium Retention in WTP LAW Glass with Recycle Flow-Sheet: DMIO Melter Testing", 2012, Washington River Protection Solutions, Richland, WA.
[2] 24590-WTP-ICD-MG-01-030, "ICD 30- Interface Control Document for Direct LAW Feed," River Protection Project, Richland, WA.
[3] 24590-WTP-PL-RT-03-001, "ILAW Product Compliance Plan", Rev. 5, River Protection Project, Richland, WA.
[4] 24590-WTP-RPT-PT-02-005, "Bases, Assumption, and Requirements," Rev. 8, River Protection Project, Richland, WA.

reduce the waste acceptance criteria (WAC) for Cs. This will be discussed in the Recommendations section.

Recommendations:

This topic should be presented and discussed in the Flowsheet Technology Advisory Committee meeting in February. A thorough, updated literature review should be performed to cite and understand the literature available. This should include data and reports from DWPF, VSL-Atkins, WTP, and other references that have direct bearing on the topic. The literature review may not be able to be completed in time for the presentation, but could be guided by the discussion in that meeting.

The Savannah River Site started operations of the Tank Closure Cesium Removal (TCCR) demonstration on January 16^{th}, 2019. Performance data from the CST ion exchange columns should be evaluated as soon as it is available to give a perspective of what to expect from the related Tank-Side Cesium Removal (TSCR) facility being installed at Hanford Tank Farms.

There is a gap with the feed limits for Cs to LAW and the Cs limit in glass when processing at high waste soda loadings. The current acceptable Cs feed limit is 3.18E-5 Ci per mole of sodium (Na)[3]; with a waste loading of 20% waste soda, the resulting glass will have a Cs content of 0.55 Ci/m^3. The acceptable limit for glass is 0.3 Ci/m^3. In order to reach the 0.3 Ci/m^3, either the waste loading or the amount of Cs per mole of Na needs to be reduced. Reducing the waste loading to $<$ 10.8% will meet the 0.3 Ci/m^3 limit with feed at the limit for Cs-137/Na ratio and no added soda during processing. The second option would be to lower the waste feed limit in the WAC to 1.72E-5 Ci/mole of Na. This could potentially require more ion exchange resin. These options should be evaluated and compared to processes planned to deliver feed from tank farms. Currently, waste preparation in tank farms is underway that relies on the present WAC limits to be successful. Section 1.2 in RPP-54130, reviews some literature data available at the time of the report. The authors acknowledge there is wide variation in the retention of Tc even in runs of identical conditions. This could be an issue if this were the case with Cs-137. A sudden increase in Cs-137 loading may exceed the 0.3 Ci/m^3 limit.

Melter idling is also be a major concern for all volatile species in the melter. Tc and Cs, in particular, have low decontamination factors and in turn will volatilize fast during idling. Section 3.3.5 of the BARD describes the impacts of melter down time (or idling) and also explains the derivation of the *concentration* half-life[5] using the decontamination factors of semi volatile species. Using this derivation, it can easily be estimated that Tc and Cs will be nearly completely volatilized from the melter into the off gas system within 72 hrs. of melter idling. Condensation of the radioactive species in the off gas system should be a concern. DWPF studies have shown that Cs_2SO_4 will precipitate if not properly mitigated.[6]

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[5] The half-life in this case refers to the decrease in concentration of a species in the melt pool with respect to time, not to be confused with the radioactive half-life

[6] WSRC-TR-90-00205, "Glass Melter Off-Gas System Pluggages: Cause, Significance, and Remediation.", WSRC, Aiken, SC.