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Hanford Low-Activity Waste Processing: Demonstration of the Off-Gas Recycle Flowsheet - 13443

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ABSTRACT

Vitrification of Hanford Low-Activity Waste (LAW) is nominally the thermal conversion and incorporation of sodium salts and radionuclides into borosilicate glass. One key radionuclide present in LAW is technetium-99. Technetium-99 is a low energy, long-lived beta emitting radionuclide present in the waste feed in concentrations on the order of 1-10 ppm. The long half-life combined with a high solubility in groundwater results in technetium-99 having considerable impact on performance modeling (as potential release to the environment) of both the waste glass and associated secondary waste products.

The current Hanford Tank Waste Treatment and Immobilization Plant (WTP) process flowsheet calls for the recycle of vitrification process off-gas condensates to maximize the portion of technetium ultimately immobilized in the waste glass. This is required as technetium acts as a semi-volatile specie, i.e. considerable loss of the radionuclide to the process off-gas stream can occur during the vitrification process. To test the process flowsheet assumptions, a prototypic off-gas system with recycle capability was added to a laboratory melter (on the order of $1/200^{th}$ scale) and testing performed. Key test goals included determination of the process mass balance for technetium, a non-radioactive surrogate (rhenium), and other soluble species (sulfate, halides, etc.) which are concentrated by recycling off-gas condensates. The studies performed are the initial demonstrations of process recycle for this type of liquid-fed melter system. This paper describes the process recycle system, the waste feeds processed, and experimental results. Comparisons between data gathered using process recycle and previous single pass melter testing as well as mathematical modeling simulations are also provided.

INTRODUCTION

The Hanford Site maintains approximately 57 million gallons of radioactive waste, a legacy of cold war weapons plutonium production. This waste is stored in underground single shell and double shell tanks at the site, located in southeastern Washington State. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being constructed to separate this waste into low-activity and high-level fractions and vitrify the soluble and insoluble solids, generating Immobilized Low-Activity Waste (ILAW) and Immobilized High-Level Waste (IHLW) products. These waste forms are to be suitable for long-term disposal, IHLW at a federal repository and ILAW, at the Hanford Site Integrated Disposal Facility (IDF). [1]

ILAW glass will contain nominally one percent of the tank waste radioactivity (total inventory currently ≈175M Curies). This will include the majority of the sites' technetium-99 inventory (≈0.026M Curies). Technetium-99 is a long-lived (210,000 year half-life) beta emitting

radionuclide. It is most commonly found as the soluble pertechnetate (Tc^{+7}) ionic specie, though a significant fraction is predicted to be complexed with organic compounds to an insoluble form (nominally Tc^{+4}). During the vitrification process, technetium acts as a semi-volatile specie, with slightly over 1/3rd of the technetium fed to the melter being incorporated in glass (ILAW canisters) each single pass. The majority of Tc, then, must be recycled back through through the system multiple times. [2-6]

While technetium is not associated with penetrating gamma emissions, nor is it fissile, its longevity mandates it as a principal contributor to long-term risk in performance assessments of the on-site disposal facility. As such, verification of the fate of technetium, i.e. distribution within ILAW or IHLW versus secondary solid or liquid waste, is of considerable interest. [7,8]

The fraction of technetium to be disposed on-site includes the ILAW and secondary waste streams produced by WTP. However, WTP, as it is currently being constructed, cannot process all Site LAW inventory within the required mission duration. A Supplemental LAW processing facility will be constructed. Based on the projected flowsheet, this facility will process ≈60% of the total LAW mass. Effectively, therefore, technetium to be stored on-site will be generated as ILAW from WTP and Supplemental LAW and their aggregate secondary waste. [1]

Supplemental LAW is projected to be a larger version of the WTP LAW vitrification facility, fed by a common pre-treatment facility (WTP-PT). This feed will not only include freshly decontaminated LAW, but also WTP LAW off-gas condensates recycled via WTP-PT. As described above, a significant fraction of the technetium volatilizes prior to incorporation within the melt/glass and must be recycled. This is also projected for Supplemental LAW vitrification – leading to the recycling of Supplemental LAW off-gas condensates. In short, based on the current System Plan 6 baseline mission scenario process modeling, accounting for facility interaction and process off-gas recycling, the technetium inventory will be dispositioned between primary wastes forms as follows: 5.6% of Tc within IHLW glass, 22% of Tc within ILAW glass, and 70% of Tc within ILAW glass generated by Supplemental LAW. The mission scenario also projects less than 1% of Tc will be dispositioned as secondary waste. This is roughly consistent with the 2003 Supplemental LAW risk assessment, which assumed 99.9% incorporation of technetium into a glass form as a "best estimate." [1,7]

At the time System Plan 6 was generated, no detailed testing of process recycle had been performed. Mathematical modeling was used to determine the efficacy of process recycle, based on single-pass melter tests, off-gas component testing, and the assumption of no systematic purge of recycle streams or components. It was recognized that integrated process testing should be performed. The primary facets of the Tc / LAW Recycle Test Program included the design and construction of a prototypic WTP system that coupled feed, melter, and off-gas components with a process off-gas system suitable for safe, reliable operations. The specific test objectives included determination of the following:

1) Recycle flowsheet mass balance,
2) Technetium (^{99m}Tc) retention in the melt (glass),
3) Technetium speciation within the feed / melter / off-gas process loop,
4) Direct comparison of Rhenium (common Tc surrogate) alongside ^{99m}Tc,
5) Retention and recycle concentration of sulfate, nitrate, chromium, and halides,
6) Implications of LAW recycle flowsheet on process control and glass formation,

7) Implications of LAW recycle on the secondary waste flowsheet.

The project, a joint effort of WRPS, Energy Solutions and the Vitreous State Laboratory (VSL) of the Catholic University of America, was authorized and commenced April 4, 2011. [8,9]

PROJECT DESCRIPTION

The initial project scope included off-gas recycle testing at bench (DM10 – 1/200th) and pilot (DM1200 – 1/8th) WTP LAW scale. The plan was to upgrade the DM10 to include a prototypic off-gas with recycle capability and perform testing followed by an associated upgrade to the DM1200. The technetium isotope selected for testing, ^{99m}Tc, has a very identifiable gamma signature, but only a six hour half-life. Detailed modeling and initial DM10 test results demonstrated the difficulty in incorporating the ^{99m}Tc radioisotope at the larger scale because of the longer sump residence times in comparison to the half-life of ^{99m}Tc. Accordingly, the DM1200 upgrade and testing was deferred and ultimately de-scoped (for FY12) to allow more focus on the DM10 operations. [2,10]

Initial operations demonstrated design limitations (primarily in the delivery of the ^{99m}Tc "spike" to the feed) that were systematically remedied. The final configuration of the DM10 melter system with recycle capability is provided in Figure 1, a schematic of the system including unit operations and sampling points. Figure 2 is a corresponding photo of the DM10 system as installed at the VSL. [10,11]

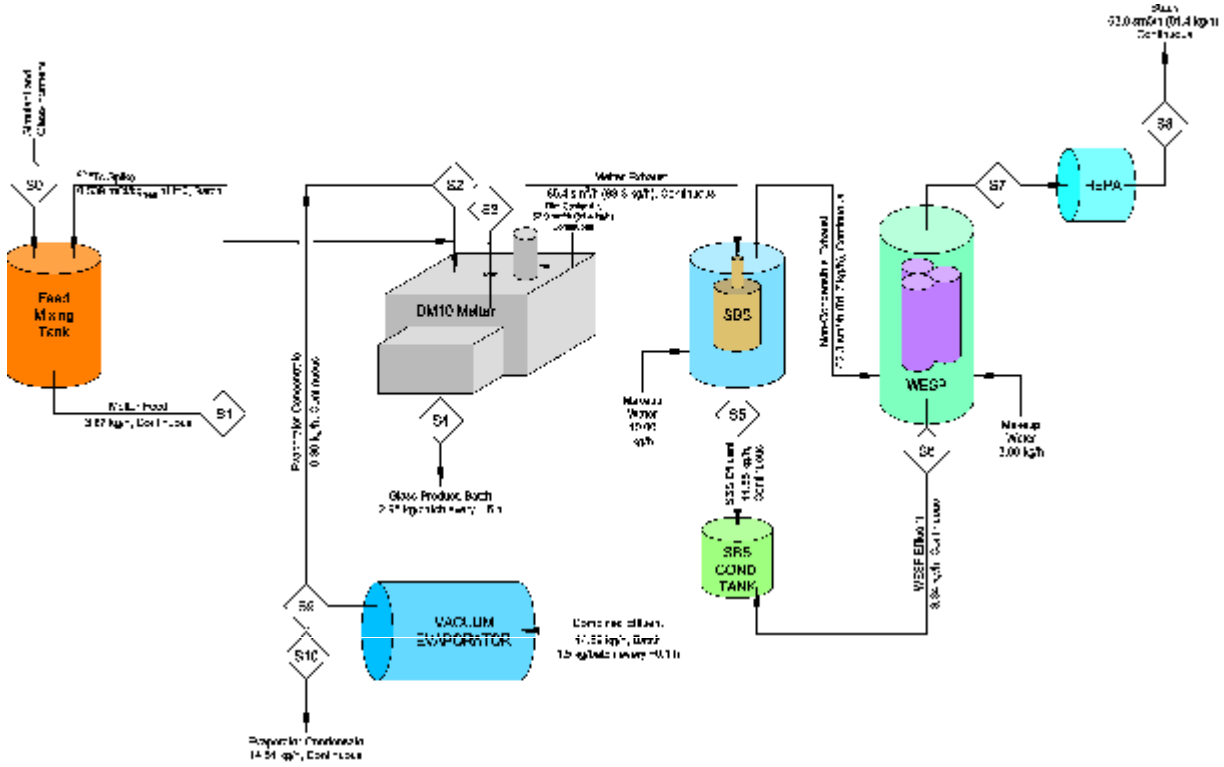

Figure 1. Schematic Diagram Showing DM10 System Components and Process Design Mass Flow. Sampling points designated by diamond shapes.

Acronym Key:	SBS	Submerged Bed Scrubber
	WESP	Wet ElectroStatic Precipitator
	HEPA	High-Efficiency Particulate Filter

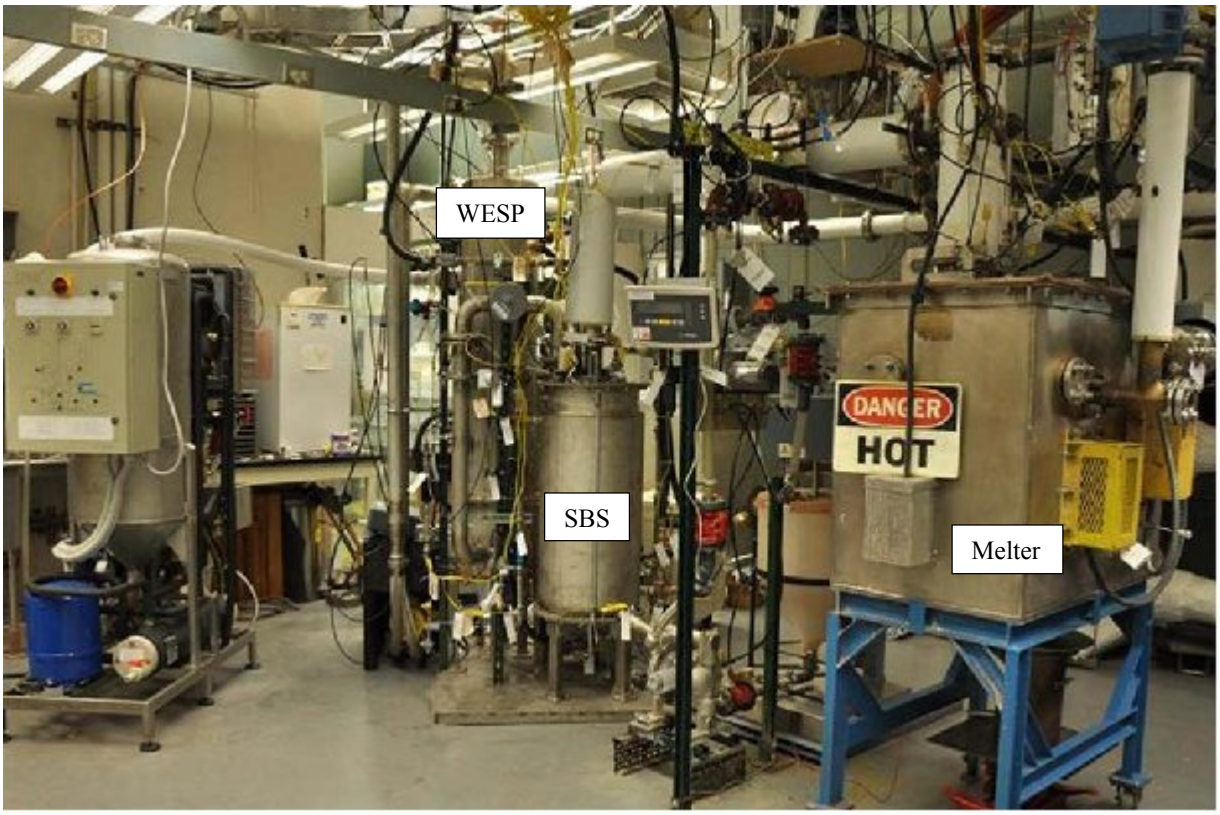

Figure 2. Photograph of the DM 10 System as per Figure 1 and as Operated During this Test Series.

A test matrix for the project was developed based on the feed/glass formulations used to develop the correlation that defines the LAW processing region. Likewise, these identified feed/glass compositions have been those used for single-pass Tc retention studies. Approximately 70 such single-pass tests have been performed previously with either ^{99m}Tc, Re, or both. Table 1 provides the recycle test matrix (as per the DM10 Test Plan) and rationale/objectives for each feed. Four tests were conducted in FY11, the remaining five tests were conducted in FY12. [5,6,11,12]

Table I. Recycle Demonstration Test Matrix. Glass formulations designate compositions developed for specific tank wastes as shown. These compositions have been used extensively for WTP process development testing.

Test	Glass Formulation	Tanks Waste Simulant	Rationale/Objective
1	LAWE4H	AN-105	Most extensively tested formulation / System shakedown
2	LAWE4H	AN-105	Most extensively tested formulation[1]
3	LAWE5H	AN-107	Test each LAW simulant
4	LAWE10H	AZ-102	LAW simulant with highest single-pass retention
5	LAWE6H	AN-104	Test each LAW simulant
6	LAWE3	AP-101	LAW simulant with lowest single-pass retention
7	LAWE4H	AN-105	Most extensively tested formulation
8	LAWE7H	AN-102	Test each LAW simulant
9	LAWE9H	AZ-101	Test each LAW simulant

Each test operation targeted a 72 hour period, a duration calculated to achieve steady state conditions for the melter with respect to Tc incorporation and still allow for effective detection of ^{99m}Tc content in process samples. Samples were collected throughout each individual test run, with post–run system equipment disassembly, rinsing, and additional sampling in order to obtain detailed mass balance information. Due to the 6-hour half-life of ^{99m}Tc, the required gamma counting analyses were performed as soon as reasonably achievable upon sample acquisition. The samples were then set aside to allow for decay sufficient to handle as non-radioactive samples for associated whole element chemistry determination and other prescribed analyses. [11]

[1] *The nominal glass production rate for this test series was 2250kg/m^{2}day, consistent with the target rate used for single pass testing. This rate was not attainable with the LAWE4H (AN 105) feed. Test 2 was performed at a target rate of 1500 kg/m^{2}day to ensure consistent mass flow. All other feed types were successfully processed at the target rate.*

RESULTS AND DISCUSSION

Test data confirm the retention of technetium and other volatile and semi-volatile species in glass to be significantly increased by process recycle. Technetium retention averaged 68 percent at steady-state and ranged as high as 85 percent, as illustrated in Figure 3. In addition to the fraction retained in glass, Tc is also dispersed throughout the processing system. Test end mass balance charts, such as Figure 4, also provide a useful medium for analyzing the distribution of Tc during processing. These charts reflect the total amount of Tc as delivered to the melter (radioactive decay mathematically adjusted) residing in the various glass packages poured, the Tc remaining within the melter, as well as the Tc residing in the off-gas and recycle system vessels and process piping (process hold-up). Figure 4 reflects the as-analyzed mass balance for the DM10 run with LAWE10H (AZ-102) melter feed, the feed with the highest single pass Tc retention in glass and the lowest process hold-up of this test series. [10,11]

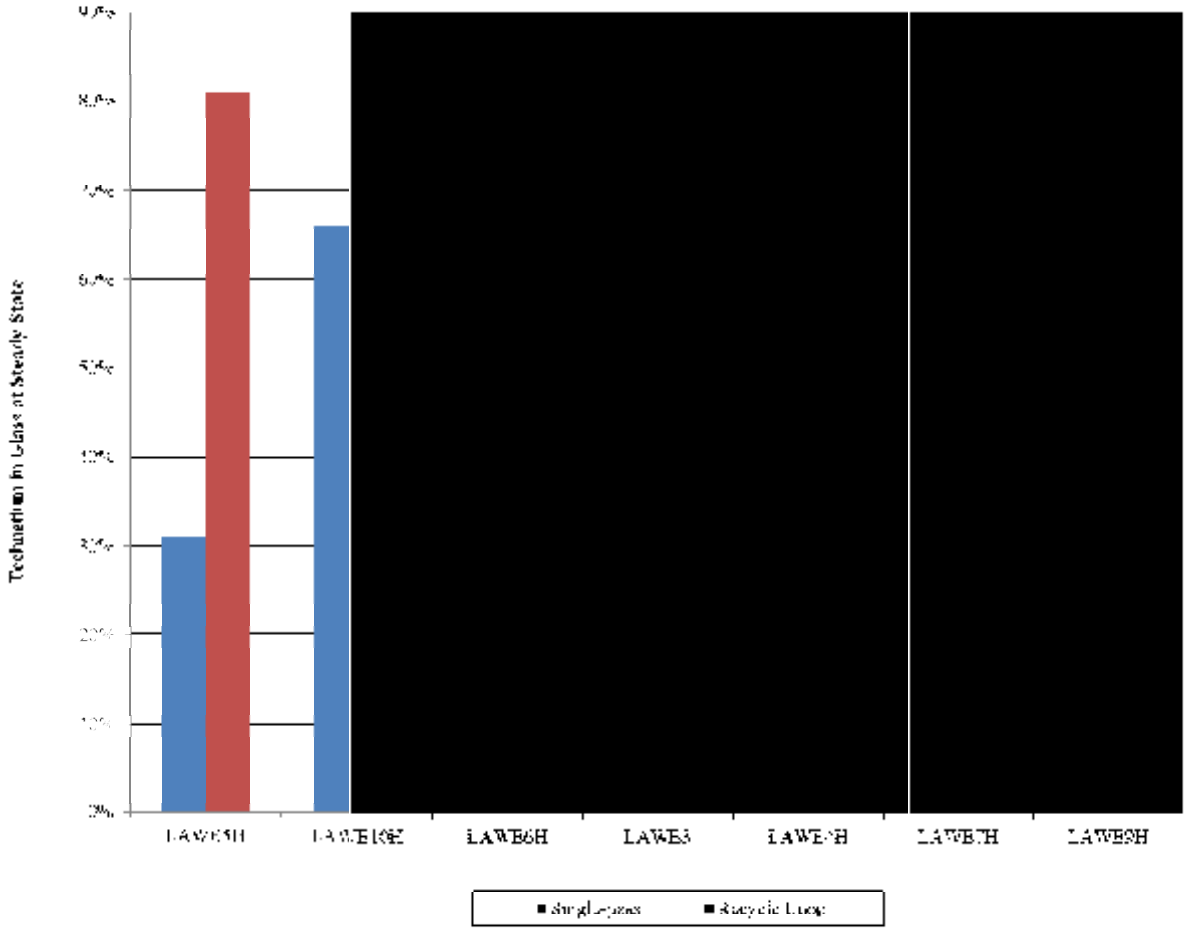

Figure 3. Comparison of Technetium Retention in Glass: With and Without (Single-Pass) Process Recycle.

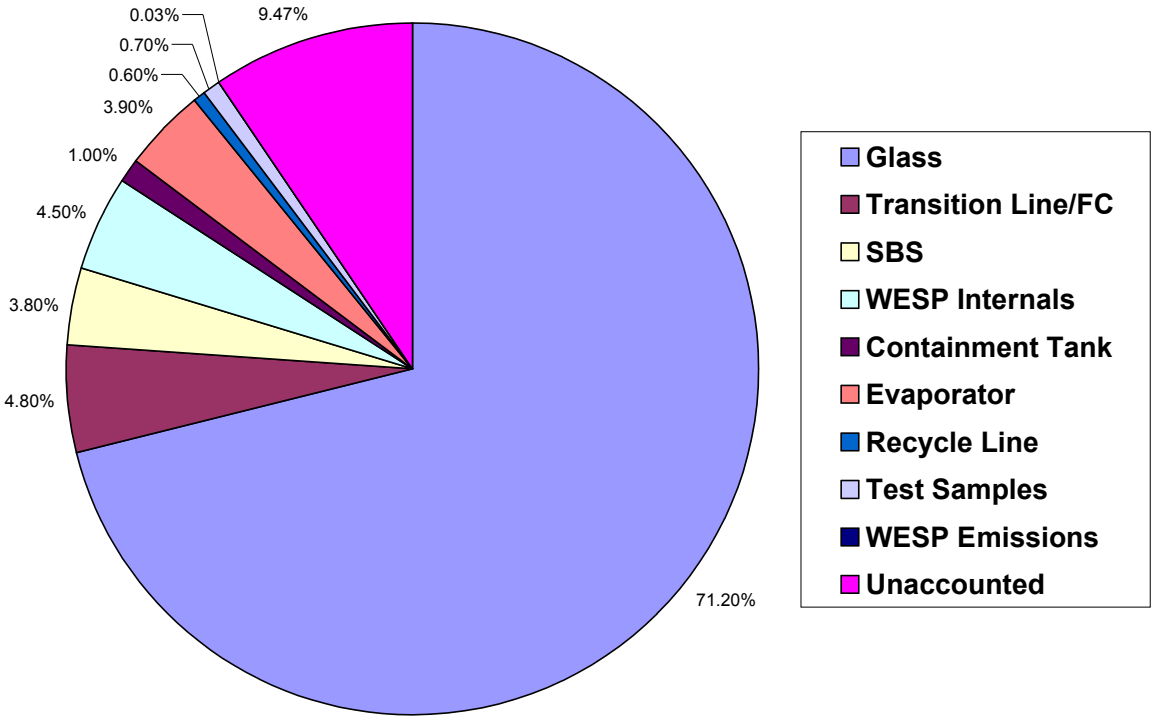

Figure 4. Technetium Mass Balance at End of Test 4.[2] Melter Feed Designation: LAWE10H. Formulated Previously for Tank AZ-102 Supernatant Liquid.

[2] *Note: The Tc content in glass per the above chart is 71.2%. This represents the sum of Tc captured in all glass containers poured, plus the amount residing in the melter at test end, as a function of the total Tc introduced to the system throughout the campaign. This is not to be confused with the information provided in Figure 3, which reflects the concentration of Tc in glass samples obtained at the end of the test relative to the concentration of Tc in the base feed. Using single pass test data as a reference, the retention per pass increased from 66 percent to effectively 85 percent as the volatilized Tc was captured and recycled.*

To better reflect the dispersion of technetium during operations, the aforementioned process models (used for system design) were updated to reflect the measured process hold-up. These model projections and corresponding test data for two melter runs are provided in Figures 5 and 6. Figure 5 charts the Tc mass balance data obtained for the DM10 run with LAWE7H (AN-102) melter feed. This feed had been previously identified as having one of the lowest single-pass Tc retentions. Figure 6 is the corresponding chart for the DM10 run with LAWE9H (AZ-101) melter feed. This feed had been previously determined to have the single-pass Tc retention closest to the arithmetic average for all feeds (and the 37.5% target value for WTP). Comparison of the two charts indicates significantly higher levels of Tc in the LAWE9H glass samples. Likewise, the impact of process hold-up is significantly greater for the LAWE7H tests, as more Tc exits the melter per pass. These results are consistent with single pass results and imply that feed with lower Tc retention in glass is more challenging for off-gas treatment and recycle purposes. [10,11]

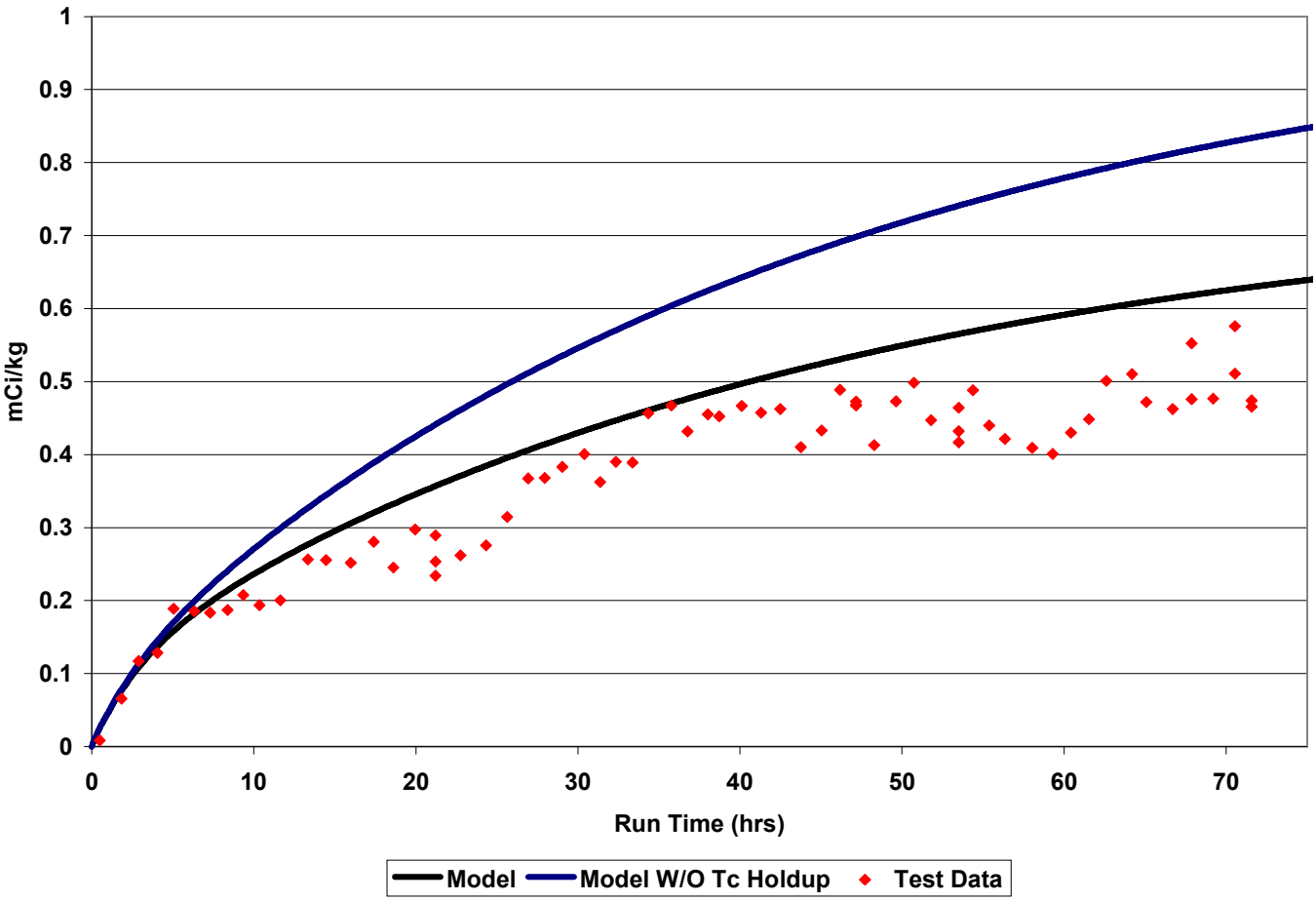

Figure 5. Technetium Concentration (mCi/g) in Glass as Measured for Test 8 Samples. Melter Feed Designation: LAWE7H. Formulated Previously for Tank AN-102 Supernatant Liquid.

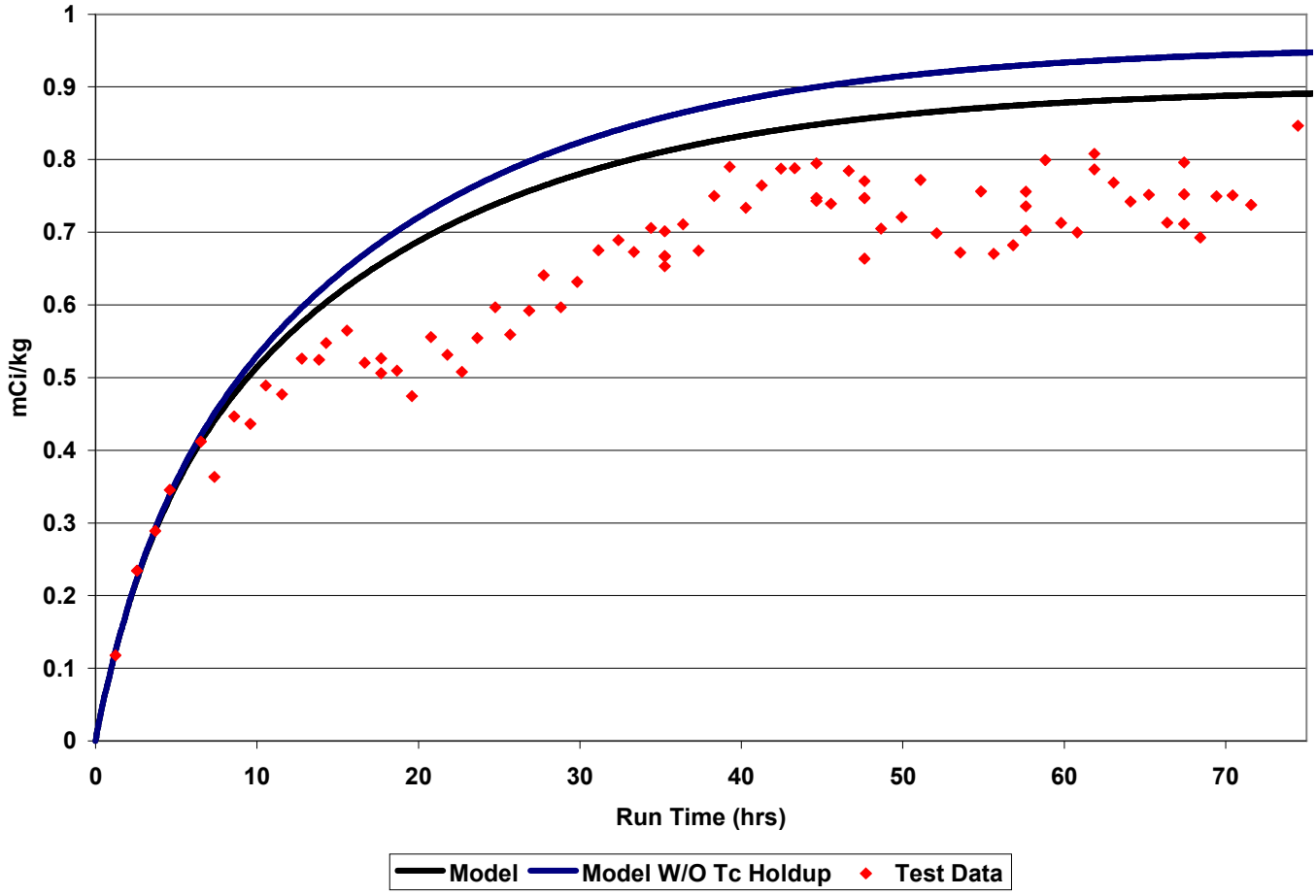

Figure 6. Technetium Concentration (mCi/g) in Glass as Measured for Test 9 Samples.[3] Melter Feed Designation: LAWE9H. Formulated Previously for Tank AZ-101 Supernatant Liquid.

These tests produced the initial data on the recycling melter off-gas as a process as opposed to a theoretical mathematical exercise. As described above, Tc incorporation was significantly increased by applying a recycle flowsheet. Process hold-up was identified as having a significant impact, effectively limiting the retention of Tc in glass. Feeds with lower single pass Tc retention lead to a greater fraction of Tc in the melter off-gas and recycle fluids, a greater potential for hold-up, and a consequent lower total Tc incorporation in glass. Longer tests would be required to determine the extent to which such feeds ultimately approach the levels of incorporation seen for other feeds. Feed chemistry, therefore, remains highly pertinent to Tc retention, process operations, and the efficacy of a recycle flowsheet. [11,13]

[3] *Note the steeper increase in Tc concentration relative to results shown in Figure 5, indicative of the higher single pass retention and accordingly reduced impact of process hold-up. One overarching trend is the deviation from theoretical modeling predictions as tests progressed through the 72 hour duration.*

OBSERVATIONS

The system tests have demonstrated Tc (and Re) retention in glass at levels significantly beyond that achieved in corresponding single pass tests. However, technetium retention in glass was limited to levels below those in previous projected mass balances and assumptions used in the ILAW PA. Process hold-up of material in the system, particularly in the Wet Electrostatic Precipitator (WESP) internals, the film cooler, and the off-gas transition piping retained on the order of 15 to 30 percent of the technetium introduced to the system.

1) Technetium retention in glass averaged 68 percent during recycle test operations, compared with a nominal average of 35 percent retention for a single melter pass.
2) Rhenium retention in glass averaged 79 percent during recycle test operations, compared with a nominal average of 43 percent retention for a single melter pass.

Test data indicate the fraction of Tc exiting the system via the off-gas system (e.g. to the HEPA filters) is heavily dependent on the performance of the WESP. Projections of Tc in liquid secondary wastes are strongly influenced by the WESP performance; although the evaporator overheads also become part of that stream, the measured Tc decontamination factors are so high as to make that a minor contributor, The extent of process hold-up of Tc could also affect the amount of Tc in secondary solid waste.

1) The fraction of feed Tc exiting through the WESP exhaust during nominal operations ranged from 0.01 to 0.5 percent.
2) During WESP malfunction, however, the fraction of Tc exiting in the WESP exhaust and thus lost to secondary waste rose to greater than 10 percent (i.e. by a factor of 500 or more). Similar behavior would be expected during the WESP downtime for the daily “deluges” (wash-down of collected particulate) planned for WTP off-gas system maintenance.

Test data are consistent with many assumptions regarding scale-up and the recycle of process off-gas condensates. The impact of recycled sulfate and halides must likewise be accounted for during process control and mission modeling.

1) Retention factors for Re at key points, specifically the WESP and Submerged Bed Scrubber (SBS) are very consistent with measurements taken during DM 1200 (a 60X larger scale melter) operations.

2) Key constituents, e.g., sulfur and the halides Cl, F, and I, were recycled along with Tc and resulting increases in constituent retention in glass were measured.

3) Sulfate salt phases were observed on the melt pool surface at the conclusion of two tests. These formations were consistent with the increased sulfate and halide concentrations per the recycle of condensates. The technetium concentration in the salt phases was enriched approximately 50X above the level observed in the glass. [13]

CONCLUSIONS

Recycle of WTP LAW vitrification process off-gas condensates does increase the retention of technetium in ILAW product glass. Process hold-up, however, retards the efficacy of Tc recycling to levels significantly lower than previously assumed. Further, halides and other soluble condensates are returned to the system along with technetium. The impact of these constituents on process control and glass production requirements must be included in subsequent process modeling and performance assessments.

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