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Savannah River Site Liquid Waste Optimizations – 23353

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ABSTRACT

The Salt Waste Processing Facility (SWPF) initiated Hot Commissioning (HC) in October 2020 and started the initial the One Year Operations (OYO) phase in January 2021 under the SWPF Engineering, Procurement, Construction (EPC) Contractor auspices. Although the SWPF was able to achieve the maximum design capacity, 0.00112 m^3/s (9.3 Mgal/yr), during the Cold Commissioning (CC) phase, during HC and subsequent OYO, throughput was limited to ~7570 m^3 (2 Mgal) during OYO and was primarily impacted by 2 processing related factors:

1) Lower than expected filter flux through the Cross Flow Filters (CFF) in the Alpha Strike Process (ASP)

   During CC filtration was able to achieve and sustain maximum design throughput. It was anticipated that when moving from simulants in CC to real waste feed the filtration performance would increase due to the lower amount of solids being processed.

2) Fouling of Caustic Side Solvent Extraction (CSSX) process equipment

   During HC and OYO operations, fouling of CSSX processing equipment was noted. This fouling was not noted during the entirety of CC and no cleaning of the CSSX process equipment was required during CC.

Throughout the CC period, plant performance was not hampered by the items above. Two significant changes occurred on the transition from CC to HC which potentially impact the performance of SWPF:

1) Introduction of real waste feed versus the use of simulants throughout CC.
2) Significant recycling of spent acid from cleaning CFF's.

Savannah River Mission Completion (SRMC) assumed responsibility for Liquid Waste (LW) operations on February 27, 2022, and SWPF operational responsibility on March 28, 2022. SRMC developed an optimization plan to better understand the mechanisms above, potential impacts, and minimize influence on throughput. A series of test through the facility while changing conditions will highlight aspects of these mechanisms.

These tests will evaluate the following elements

1) Transfer of Spent Cleaning Acid directly to the Sludge Solids Receipt Tank (SSRT)

   Acid is utilized to clean the cross-flow filters when they become fouled. The current process recycles the spent cleaning acid to the head end of the process. The adjusted spent acid contains precipitates (including Titanium (Ti)) which increases the solids content that is being processed by the CFF's, potentially impacting filtration rate. Alternatively, the adjusted spend acid can be sent to the SSRT during the washing cycle.

2) Addition of Filter Aid

Filter aid is a standard method for improving filtration of a stream that contains fine particulate. Sludge simulant was used during the CC period and is well understood and has good filtration performance. Therefore, utilizing sludge simulant to demonstrate a filter aid with controlled and known material characteristics.

3) Reducing the Amount of Mono-Sodium Titanate (MST)

   Fouling of CSSX process components has been shown to contain a Ti bearing solids that presumably pass through the CFF's as a soluble or colloidal species. MST is the only significant source of Ti in SWPF, the reduction of MST effectively reduces the amount of Ti being processed within SWPF which may reduce fouling in CSSX.

4) Reducing the Amount of MST plus addition of a filter aid

   Similar to reducing the amount of MST above and the addition of a filter aid this combines the two. This may have additive or synergistic benefits from the combination of the two items.

5) MST Strike in the Alpha Finishing Facility (AFF) vs ASP (reduced MST in ASP + full MST in AFF)

   Reduction in MST may not allow for sufficient removal of Plutonium (Pu) and Strontium-90 (Sr-90). To achieve the benefits of reducing MST while achieving sufficient removal of Pu and Sr-90 may require an additional strike with MST in AFF. Thus, reduced fouling in CSSX and increased filter performance in ASP can be realized and the second strike in AFF post CSSX will ensure that sufficient removal Pu and Sr-90.

6) Reduced MST Strike in the ASP with Reduced MST Strike in AFF

   Operate the reduced MST Strike ASP flowsheet and CSSX process with additional filtration in AFF with reduced MST in AFF. This will demonstrate a combined ASP and AFF flowsheet with filtration rates achievable based on reduced MST contributions.

In addition, Savannah River National Laboratory (SRNL) is completing radiation damage studies on MST and mercury species interaction with crown ether-type moieties (i.e., CSSX Solvent) to help determine these potential impacts on overall SWPF throughput.

The proposed runs above provide a controlled set of test cases to help elucidate the influence of the mechanisms above on SWPF throughput. After collecting the information then additional mitigative actions can be put into place to maximize throughput of SWPF. Results collected to date will be presented.

INTRODUCTION

The Salt Waste Processing Facility (SWPF) initiated Hot Commissioning (HC) in October 2020 and started the initial the One Year Operations (OYO) phase in January 2021 under the SWPF Engineering, Procurement, Construction (EPC) Contractor auspices. Although the SWPF was able to achieve the maximum design capacity, 0.00112 m^3/s (9.3 Mgal/yr), during the Cold Commissioning (CC) phase, during HC and subsequent OYO, throughput was limited to ~7570 m^3 (2 Mgal) during OYO and was primarily impacted by 2 processing related factors and a third factor not related to processing:

1) Lower than expected filter flux through the Cross Flow Filters (CFF) in the Alpha Strike Process (ASP)

   During CC filtration was able to achieve and sustain maximum design throughput of 0.00112 m^3/s (9.3 Mgal/yr). Cold Commissioning used an aqueous phase salt solution simulant (non-radioactive) and a sludge simulant that is characteristic of the sludge in the tank farms and added at the design basis concentration of 600 mg/L. Also, during preparation of the simulant, a small amount of fine particulate naturally forms as part of the preparation process that is not expected to be present in the real waste material. Since, waste being received from the tank farm has undergone a lengthy settling process the amount solids actually received is significantly less than the design basis 600 mg/L (e.g., Salt Batches 1 and 2 were <<100mg/L). Therefore, it was anticipated that when moving from simulants in CC to real waste feed the filtration performance would actually increase due to the lower amount of solids being processed. However, filtration performance (i.e., filter flux) actually significantly decreased. During CC a typical cross flow filter would produce approximately $6.3\times10^{-4} – 9.5\times10^{-4}$ m^3/s (10-15 gpm) of filtrate. Once, feed from the tank farm was introduced into SWPF, a typical cross flow filter would only produce approximately $3.2\times10^{-4} – 5.0\times10^{-4}$ m^3/s (5-8 gpm) of filtrate flow. Filtration is currently the rate limiting step for SWPF and limiting SWPF throughput to 0.00048 – 0.00060 m^3/s (4-5Mgal/yr). Evaluating methods for improving performance needs to be investigated.

2) Fouling of CSSX process equipment due to solids accumulation

   During HC and OYO operations fouling of CSSX processing equipment was noted. The initial indications were increasing differential pressure (dP) on the Strip Effluent Coalescer (SEC). The SEC is used in a similar fashion as the DSSC above. The SEC removes residual traces of solvent in the strip effluent product to below required limits. Since it is a spun stainless steel fiber that creates a fine mesh, it also behaves as a particulate filter. Therefore, particulate matter that forms or passes into the CSSX system can be collected causing fouling of the media which is indicated by increasing dP across the media. Once, the dP reaches the maximum value, the CSSX process is shut down and it is acid cleaned to restore it. In addition to fouling being noted in the SEC, fouling has been noted in other CSSX process equipment (e.g., HX-217 A/B, EXT-202 A/B, EXT-201 P, etc). These have also required periodic acid cleaning to restore performance. Samples of the particulate matter fouling the equipment have indicated a titanium and mercury bearing solid that does not appear to be Mono-Sodium Titanate (MST). This fouling was not noted during the entirety of CC and no cleaning of the CSSX process equipment was required. This is currently not the rate limiting step (i.e., CSSX can be shut down, the equipment cleaned, and CSSX restarted before ASP filtration is impacted). However, when filtration performance improves then routine fouling in CSSX process equipment will limit throughput. Therefore, evaluating methods to minimize formation of the fouling agents in CSSX needs to be investigated.

3) Material component failure of gasket material in the Decontaminated Salt Solution Coalescer (DSSC).

   The downstream Saltstone facility from SWPF has stringent requirements on the amount of organic material that can be transferred to it. This is part of their flammability control program.

The salt solution in the Caustic Side Solvent Extraction (CSSX) process comes into intimate contact with an organic solvent containing Isopar L (essentially Kerosene) as the diluent. Therefore, the Decontaminated Salt Solution (DSS) passes through a coalescer prior to being collected for ultimate transfer to Saltstone. This coalescer removes residual traces of solvent in the DSS to below required limits. The DSSC contains elements of spun stainless steel fiber that creates a fine mesh. This mesh allows for fine solvent droplet coalescence which can then float to the surface of the liquid and be skimmed off. The elements were attached to a distribution tube sheet utilizing a Viton gasket, normally a much harder Teflon gasket would be used in this application. However, SWPF initially had a blanket prohibition against the use of Teflon in any applications regardless of potential radiation exposure (Teflon does not typically perform well at elevated radiation levels). During OYO higher than expected solvent was detected in DSS several times and was attributed to poor gasket performance and the gaskets required replacement several times. The poor gasket performance was primarily due to the softness of the Viton gasket. Eventually, SWPF was able to employ a graded approach for utilizing Teflon. Since, the DSSC is very low radiation the gaskets were able to be replaced with a Teflon material. Following the change to Teflon performance of the DSSC has been excellent. This item was not indicative of any significant processing or throughput issues, but replacement of the gaskets resulted in ~4 cumulative months of downtime to complete the repairs plus additional time to reprocess out of spec material. Since this item is not expected to impact operations/throughput going forward, no additional immediate action is needed.

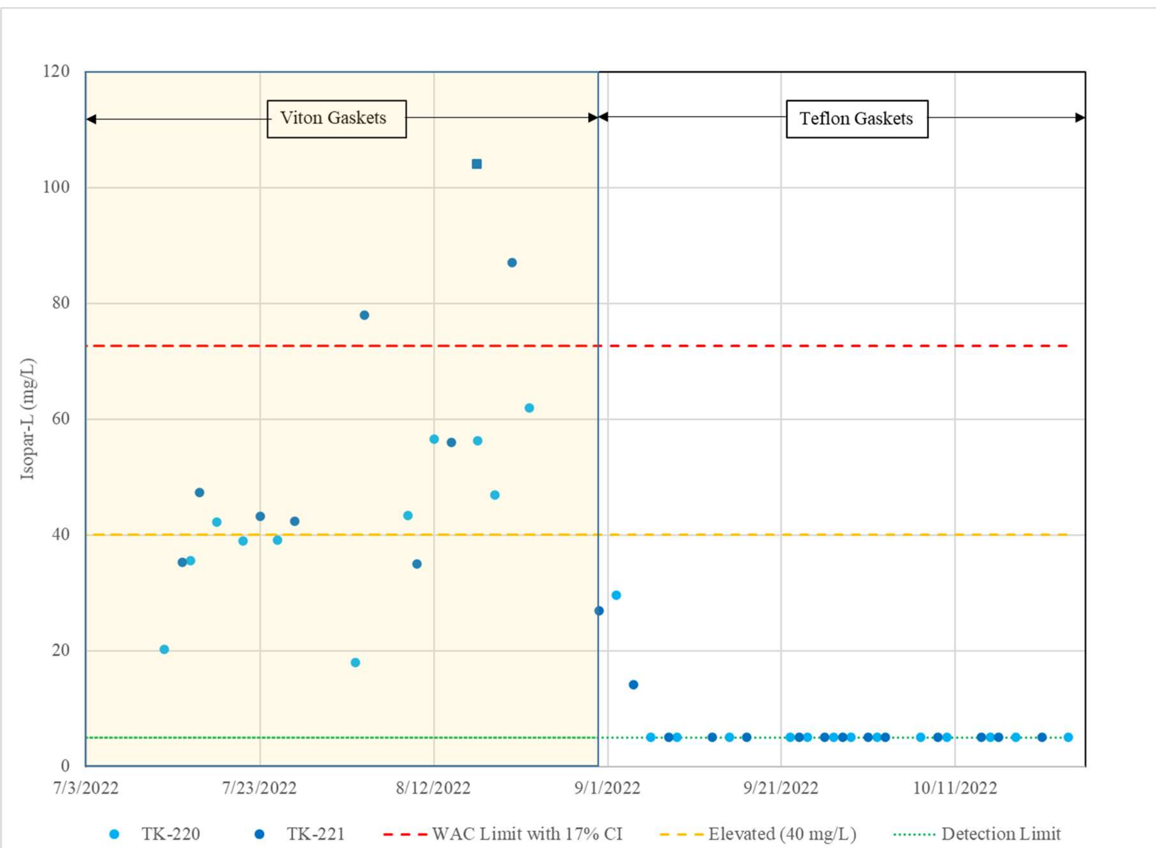

Figure 1. Isopar L in DSS After Change to Teflon Gaskets.

Throughout the CC period, plant performance was not hampered by the items above. Two significant changes occurred on the transition from CC to HC which potentially impact the performance of SWPF and are enumerated below:

1) Introduction of real waste feed from the SRS tank farm versus the use of simulants throughout CC.
2) Significant recycling of spent acid from cleaning CFFs.

These two differences may contribute to the effects described above (items 1 &2). Filtration performance can be significantly impacted by filtering particles that are of similar size to the filter pore. The CFFs have a 0.1 μm filter pore and simulants (e.g., sludge simulant) had a particle size distribution that is significantly greater than that (i.e., mean particle size ~1-10 μm). Potential sources of material that could create 'fines' that may increase the fouling rate / decrease filter performance are:

1) Solid particle size distributions in real waste feed may contain some fines of a similar size to the CFF pore size.

   The solid simulant utilized in CC was characteristic of tank farm sludge samples and was prepared in a manner that well approximates the sludge properties. However, during preparation of the salt solution it is allowed to undergo settling periods to minimize solids that are actually entrained in the feed solution. These settling periods can allow accumulation of finer material in the solids that are actually entrained through sedimentation separation. Although this won't impact bulk sludge properties and associated processes (e.g., mixing) it can cause additional fouling on the CFF's.

2) MST interaction with real waste (radiological or chemical) may result in generation of MST / Ti fines.

   The MST actively adsorbs the radioactive materials Plutonium (Pu) and Strontium-90 (Sr-90). This allows for close intermingling of the radioactive material with the MST. When the radioactive material decays and ejects a particle, alpha or beta it may interact with the MST matrix and 'knock-off' small amounts of MST or Ti solids, which would have a very small particle size. Although bulk MST radiation damage has been tested and it does not significantly impact its ability to retain radionuclides evolution of small amounts of MST or Titanium (Ti) solids from radiation damage has not been studied.

   Additionally, it is possible that MST interaction with chemical constituents in the real waste may result in the production of fines.

3) Recycle of spent acid from cleaning CFFs.

   During CC spent acid from cleaning CFFs was typically disposed of through outside vendors versus being recycled in the facility to facilitate simulant management. As the CFF foul due to accumulation of sludge solids and MST they require cleaning. To clean the filters, they are flushed with a 1M NaOH solution, then cleaned with a hot 20 wt% HNO_3 solution, and then flushed with a 1M NaOH. The spent acid dissolves the sludge solid and MST residues and creates an acidic solution containing Ti, Fe, Al, etc. Before the spent acid is recycled it is chemically adjusted (i.e., made caustic to ~1M NaOH). This adjustment causes the dissolved metals in the cleaning acid to precipitate as oxides/hydroxides (e.g., Ti forms $TiO2$). The formation of these precipitates could create fines that foul the CFFs as this material is recycled to the head end of the process upstream of the filtration step.

In addition to potentially impacting Filtration, the two differences from CC to HC may contribute to the fouling observed in CSSX. The fouling observed in CSSX has been primarily due to a Ti bearing solid. The significant source of Ti within SWPF originates with MST. The Ti appears to be passing through the CFFs in a soluble (or colloidal) form and then precipitating in CSSX either due to slow kinetics or change in process chemistry (e.g., slight acidification by scrub solution). Potential sources for formation of soluble (or colloidal) Ti material that could increase fouling in CSSX are:

1) MST interaction with real waste (radiological or chemical) that may result in generation soluble species or colloidal Ti that can pass through the CFFs.

   Similarly, to the above when the radioactive material sorbed onto the MST decays and ejects a particle it can interact with the MST matrix and 'knock-off' small amounts of Ti which may form a soluble species through free radical type reactions or colloidal Ti compounds. Again, although bulk MST radiation damage has been tested and it does not significantly impact its ability to retain radionuclides evolution of small amounts of soluble or colloidal Ti from radiation damage has not been studied.

   Additionally, it is possible that MST interaction with chemical constituents in the real waste may result in the production of fines.

2) Recycle of spent acid from cleaning CFFs.

   Also, similarly to above when the spent cleaning acid is chemically adjusted (i.e., made caustic to ~1M NaOH) there could be the formation of soluble Ti or colloidal species that can pass through the CFFs

Path Forward and Next Steps

Savannah River Mission Completion (SRMC) assumed responsibility for Liquid Waste (LW) operations on February 27, 2022, and SWPF operational responsibility on March 28, 2022. We wish to evaluate some of the mechanisms described above in order to better understand their potential impacts and minimize their influence on throughput. This will be accomplished through a series of test runs through the facility while changing conditions that should highlight aspects of mechanisms described above. These are detailed below:

1) Transfer of Spent Cleaning Acid directly to the Sludge Solids Receipt Tank (SSRT)

   <u>Description</u>

   The current process of recycling the spent cleaning acid is to adjust the spent acid and add it to the incoming liquid waste from the tank farm. As described above the adjusted spent acid contains precipitates (including Ti). These precipitates carry forward into the Filter Feed Tank

(FFT-A) and are concentrated with the other solids. This increases the solids content that is being processed by the production filters (FLT-102 A/B/C) potentially impacting filtration rate. The additional amount of Ti being recycled and subsequently being presented to the production filters may increase the potential for penetration (as a soluble or colloidal species) and transfer to CSSX.

Alternatively, the adjusted spend acid containing Ti and potentially fines can be sent to the SSRT during the washing cycle. This will allow for more direct disposal of the solids and potential fines to the Defense Waste Processing Facility (DWPF).

<u>Potential Benefit</u>

This minimizes the amount of solids being processed by the production filters (i.e., the precipitates from the adjusted spent cleaning acid are not processed through the production filters). Since the precipitates in the adjusted spent cleaning acid may contain fines, they could impact CFF production. Moving concentration / filtration of this material to the washing filter removes any effect they may have on the production filter and allows evaluation of potential performance improvements on filtration. In addition, this minimizes the amount of Ti being presented to the production filters thereby decreasing the potential for penetration of Ti (as soluble or colloidal species) and transfer into CSSX. The increased amount of Ti is presented to the Washing Filter which undergoes some chemistry changes as the solids are washed which can allow precipitation of any soluble or colloidal Ti species or the material is held in the Wash Water Hold Tank which could allow for delayed precipitation of soluble Ti species.

<u>Status</u>

This improvement initiative has been successfully implemented. Overall, this has been very successful in improving showing approximately a 45% increase in overall filtration rate. In addition, there has been a decrease in the transmembrane pressure (TMP) to achieve the increase in filtration rate which would indicate that even further increases in filtration rate should be possible.

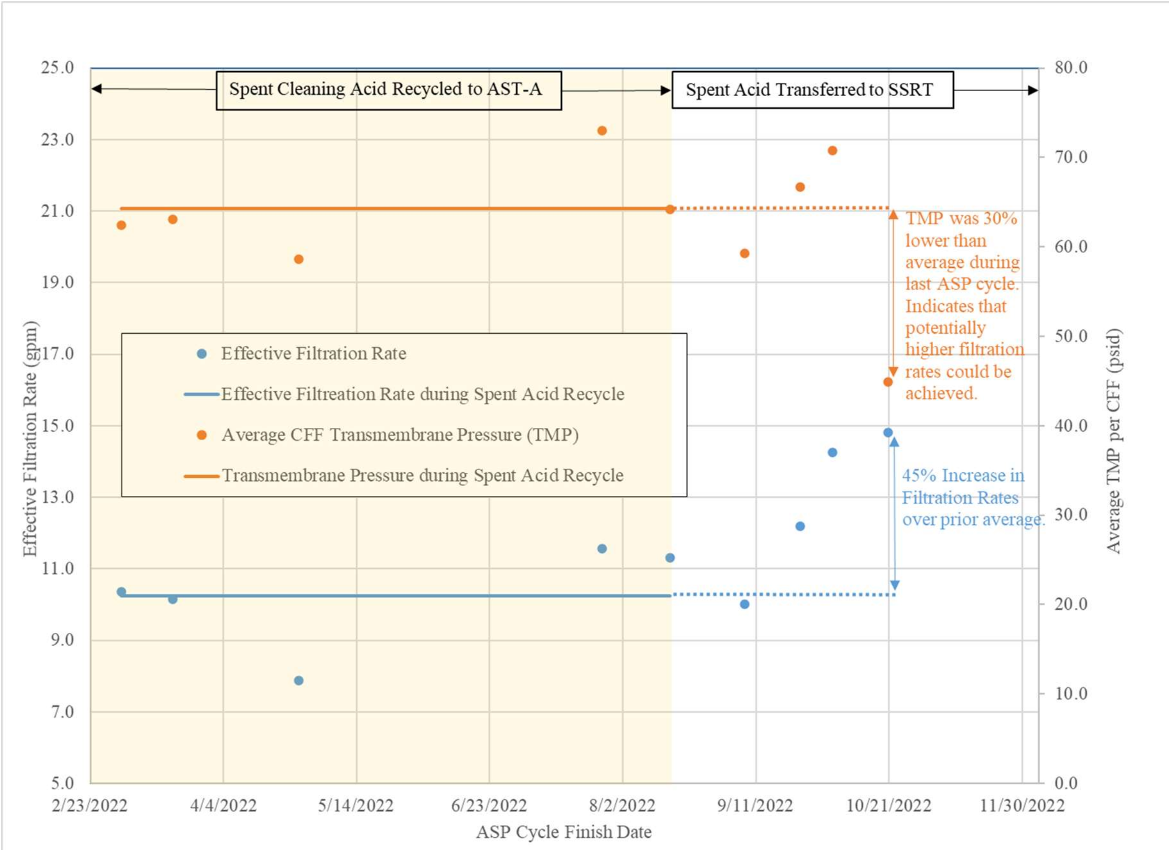

Figure 2. Effective Filtration Rate for Change in Disposition of Spent Cleaning Acid

2) Addition of Filter Aid

Description

The current feed solution to the crossflow filters consists of transfers from Tank 49 that have typically settled for a period of time that allows undissolved solids to drop out of suspension. This process may allow for sedimentation separation of the remaining solids with a preferential retention of fines suspended in the solution. Filter aid is a standard method for improving filtration of a stream that contains fine particulate. Addition of a filter aid provides the fine solids active sites for agglomeration to enhance the solid particle development and efficiency for MST/sludge solid filtering. Sludge simulant was used during the CC period and has well understood and good filtration performance. Therefore, utilizing sludge simulant to demonstrate a filter aid provides controlled and known material (chemical and physical) characteristics and eliminates totally new condition characteristics (the material has been processed in the LW system previously), reduces downstream uncertainty and impact evaluation requirements, and uses resources (simulant) previously and easily available.

Benefit

Currently filtration is limiting SWPF operations to 0.00048 – 0.00060 m^3/s (4-5Mgal/yr). Enhancing CFF throughput (e.g., through addition of a filter aid) could allow restoration of filtration to 0.0011+ m^3/s (9+ Mgal/yr) through reduced fines fouling of the filters and improved cleaning efficiency between filter backwash evolutions.

Status

At the time of submission of this paper this improvement initiative has not yet been implemented. However, the initiative is task ready and is expected to be implemented in the next few weeks.

3) Reducing the Amount of MST

Description

Fouling of CSSX process components has been shown to contain a Ti bearing solids that presumably passes through the CFFs in as a soluble or colloidal species. Since, MST is the only significant source of Ti in SWPF, the reduction of MST effectively reduces the amount of Ti being processed within SWPF. Reducing MST may reduce the amount of Ti being transferred to CSSX and the attendant subsequent fouling.

In addition, reducing the amount of MST will also reduce the rate of buildup of Titanium solids in the CFF and could improve CFF throughput and potentially reduce the CFF cleaning frequency.

Benefit

Currently filtration is the overall rate limiting step in SWPF however, once filtration performance is improved fouling in CSSX will limit overall throughput through SWPF. Reducing the amount of MST should both decrease the amount of Ti transferred to CSSX and subsequent fouling of CSSX process equipment and improve filtration through reducing the amount of solids being processed by the ASP CFFs.

Status

At the time of submission of this paper this improvement initiative has not yet been implemented. However, the required Documented Safety Analysis (DSA) and Technical Safety requirements (TSR) changes have been submitted to the Department of Energy (DOE) for approval. Approval of the DSA and TSR are expected in the fourth quarter of 2022 with implementation to follow shortly thereafter.

4) Reducing the Amount of MST plus addition of a filter aid

Description

Similar to reducing the amount of MST above and the addition of a filter aid this combines the two. This may have additive or synergistic benefits from the combination of the two items.

Benefit

Currently filtration is the overall rate limiting step in SWPF however, once filtration performance is improved fouling in CSSX will limit overall throughput through SWPF. Reducing the amount of MST should both decrease the amount of Ti transferred to CSSX and subsequent fouling of

CSSX process equipment and improve filtration through reducing the amount of solids being processed by the ASP CFFs.

Status

At the time of submission of this paper this improvement initiative has not yet been implemented. However, following implementation of Item 2 and 3 above and analysis of the results this will be ready for testing.

5) MST Strike in the Alpha Finishing Facility (AFF) vs ASP (reduced MST in ASP + full MST in AFF)

Description

Reducing the amount of MST in ASP may not allow for sufficient removal of Pu and Sr-90. Therefore, to achieve the benefits of reducing the amount of MST described above while achieving sufficient removal of Pu and Sr-90 may require an additional strike with MST in AFF. Thus, reduced fouling in CSSX and increased filter performance in ASP can be realized and the second strike in AFF post CSSX will ensure that sufficient removal Pu and Sr-90. It will also allow comparison of filtration performance at the full MST concentration (in AFF) but with feed that has already been filtered to remove fines.

Benefit

The benefits of this will be essentially the same as reducing the amount of MST in ASP described above but will allow for additional removal of Pu and Sr-90, if needed, and allow comparison of filtration performance of salt solution that has already been filtered once

Status

At the time of submission of this paper this improvement initiative has not yet been implemented. Implementation of this initiative requires a Reediness Assessment (RA) for the AFF. Initial preparations for the RA are underway and the RA is expected to be completed in first quarter 2023. Following the successful completion of the RA then this initiative will be tested.

6) Reduced MST Strike in the ASP with Reduced MST Strike in AFF

Description

Operate the reduced MST Strike ASP flowsheet and CSSX process with additional filtration in AFF with reduced MST in AFF. This will demonstrate a combined ASP and AFF flowsheet with filtration rates achievable based on reduced MST contributions.

Benefit

This will allow evaluation of the optimized filtering with minimized MST additions.

Status

At the time of submission of this paper this improvement initiative has not yet been implemented. Implementation of this initiative requires a Reediness Assessment (RA) for the AFF and will follow Item #5 above.

In addition, Savannah River National Laboratory (SRNL) is completing radiation damage studies on MST. Previous testing has been done on radiation stability, but this was primarily evaluating retention of Pu and Sr-90 (and was shown effective). However, testing has not been completed on release of Ti from MST from radiation damage. SRMC is working with SRNL to complete the following testing to evaluate release of Ti from radiation damage.

- Contact simulant salt solution (no radioactive material) with MST. Filter salt solution and complete analysis of Ti in the salt solution. This will establish a baseline amount of Ti that could pass through the CFFs.
- Contact simulant salt solution with MST spiked with sufficient Pu to achieve doses of 0.5 MRad and 5 MRad. Filter salt solution and complete analysis of Ti in the salt solution.
- Contact simulant salt solution with MST spiked with sufficient Sr-90 to achieve doses of 0.5 MRad and 5 MRad. Filter salt solution and complete analysis of Ti in the salt solution.
- Contact simulant salt solution with MST spiked with sufficient Cs-137 to achieve doses of 0.5 MRad and 5 MRad. Filter salt solution and complete analysis of Ti in the salt solution.
- Contact real salt solution with MST to achieve doses of 0.5 MRad and 0.5 MRad. Filter salt solution and complete analysis of TI in the salt solution.

This will relatively easily show if radiation damage can release soluble or colloidal species of Ti that can pass through the CFFs.

Furthermore, there is a potential for some specific chemical component of the tank waste to interact with MST in a manner that results in fines that can negatively impact filtration and/or MST interaction (e.g., complexation, spalling, etc). SRMC is working with SRNL to evaluate the options for further studies for specific known or observed chemical species in waste feed solutions (e.g. mercury) that may impact filtration or have an interaction with MST.

CONCLUSION

The proposed runs above provide a controlled set of test cases to help elucidate the influence of the mechanisms above on SWPF throughput. After collecting the information then additional mitigative actions can be put into place to maximize throughput through SWPF. The first initiative has been shown to be very effective and increased filtration performance by 45%.