Deployment of Large Tank Monosodium Titanate Strike to Increase Salt Processing at the Savannah River Site – 15115

Aaron V. Staub and W. Pen Mayson
Savannah River Remediation, Aiken, SC 29808

ABSTRACT

The treatment of high level waste (HLW) salt solutions using the Actinide Removal Process (ARP) and Modular Caustic Side Solvent Extraction Unit (MCU) began at Savannah River Site (SRS) in 2008. Since that time, over 6 million gallons of liquid HLW have been treated and the resulting low level waste (LLW) effluent immobilized in cementitious grout at Saltstone. In addition to the continued stabilization of liquid HLW, operating experience from the ARP/MCU facilities has also been valuable in considering the design and construction of the Salt Waste Processing Facility (SWPF) which will utilize similar unit operations on a much larger scale.

ARP removes actinides by contacting waste with monosodium titanate (MST) which is a solid adsorbent for soluble strontium and actinides. Once the sorption reaction is complete, the MST solids are separated from salt solution via ultrafiltration through a crossflow filter. The throughput of initial operations of ARP/MCU was limited by the flowrate through the extraction process. However, after the implementation of a new solvent flowsheet, filtration of MST will be the rate limiting step in salt processing.

For the entirety of ARP/MCU operation, Savannah River Remediation (SRR) has sought to improve process efficiency and performance through optimization and modification of the original facility design. These efforts have resulted in a best-single-year throughput of 4.9 million liters of decontaminated salt solution. In keeping with these practices, SRR recently initiated a project to improve filtration throughput by relocating the MST strike from small batches immediately upstream of the filtration unit to the underground waste tank used to batch and store salt solution feed for ARP/MCU. This process change will allow the bulk of MST solids to decant in the waste tank prior to filtration which should improve both the nominal operational filter flux as well as the achieved utility of filter operation.

INTRODUCTION

Salt waste disposal at the Savannah River Site currently begins within the large, underground storage tanks located in H Tank Farm. Tank 21, an approximately 5 million liter waste tank, is used as a batch preparation and qualification vessel. Waste salt solutions are transferred into Tank 21 from multiple sources until a batch of 3 to 4 million liters has been compiled. Once the waste has been collected and blended, detailed sample analyses are performed to verify the effectiveness of downstream treatment operations and verify the waste will meet facility acceptance criteria requirements. The salt batch is transferred forwards to Tank 49, another large underground tank

used for lag storage and feed, once the qualification process has been completed in Tank 21. The qualified waste stored in Tank 49 is then transferred in smaller 13,000 liter batches to strike tanks located in 241-96H. The strike tanks are used for addition of MST, which sorbs the strontium and actinides, and the salt solution is agitated for a minimum duration to ensure thorough contact and reaction. Once reaction is complete, the reacted slurry is transferred to a separate facility where crossflow filtration separates the actinide solids from the salt solution. Accumulated MST is periodically purged from the filtration system into high level waste (HLW) disposal at the Defense Waste Processing Facility (DWPF), and the clarified salt solution is transferred into one of two receipt tanks at MCU. MCU performs solvent extraction in a semi-continuous process, resulting in a cesium-rich acid strip that is processed at DWPF and a decontaminated salt solution that is turned into low-level waste grout at the Saltstone Production and Disposal Facilities.

The rate-limiting step of the salt treatment process is filtration of MST solids within 512-S, and the structure of the current unit operations present several obstacles toward improving throughput. Based on the current location and process sequencing of the MST strike, the crossflow filter at 512-S is required to separate 100% of all solids introduced into the system by the MST strike. This impacts filter flux, but also affects filter utility as it drives periodic downtime to allow for chemical cleaning of the filter and disposition of the spent cleaning chemicals. Dilute oxalic acid is used to perform this cleaning, but due to the highly alkaline nature of SRS salt solution, large pH changes within the process vessels are unavoidable. This has historically led to difficulty with precipitated salts, with specific species dependent upon the composition of the waste being processed at that time. These precipitates further challenge filter performance and can pose a risk to equipment located within MCU.

DESCRIPTION

Large Tank MST Strike (LTS) Baseline Scope

The LTS Project addresses some of the limitations of the current process by relocating the MST addition from the MST strike tanks in 241-96H to the batch blending and qualification location in Tank 21. Qualification efforts for salt batches generally take 3 months due to the extensive amount of sample preparation and large suite of analyses required to satisfy all downstream facility acceptance requirements. Under the current process, this period is essentially dead-time in which no other value-added activities occur. By relocating the MST addition, the LTS project introduces a unit operation, actinide removal by sorption and settling, without incurring any significant marginal costs to overall batch qualification cycle times. A block flow diagram for the process is shown below in Figure 1.

Much of the infrastructure needed to support LTS is pre-existing and necessary to support current salt batch preparation activities. The tank currently utilizes two mixing pumps, an adjustable-height transfer pump, an active ventilation system, and has available tank-top

penetrations for addition of chemicals. As a result, the LTS project realizes the typical benefits of at-tank/near-tank processing which generally minimizes the capital investment required for infrastructure and utilities associated with the implementation of new treatment processes.

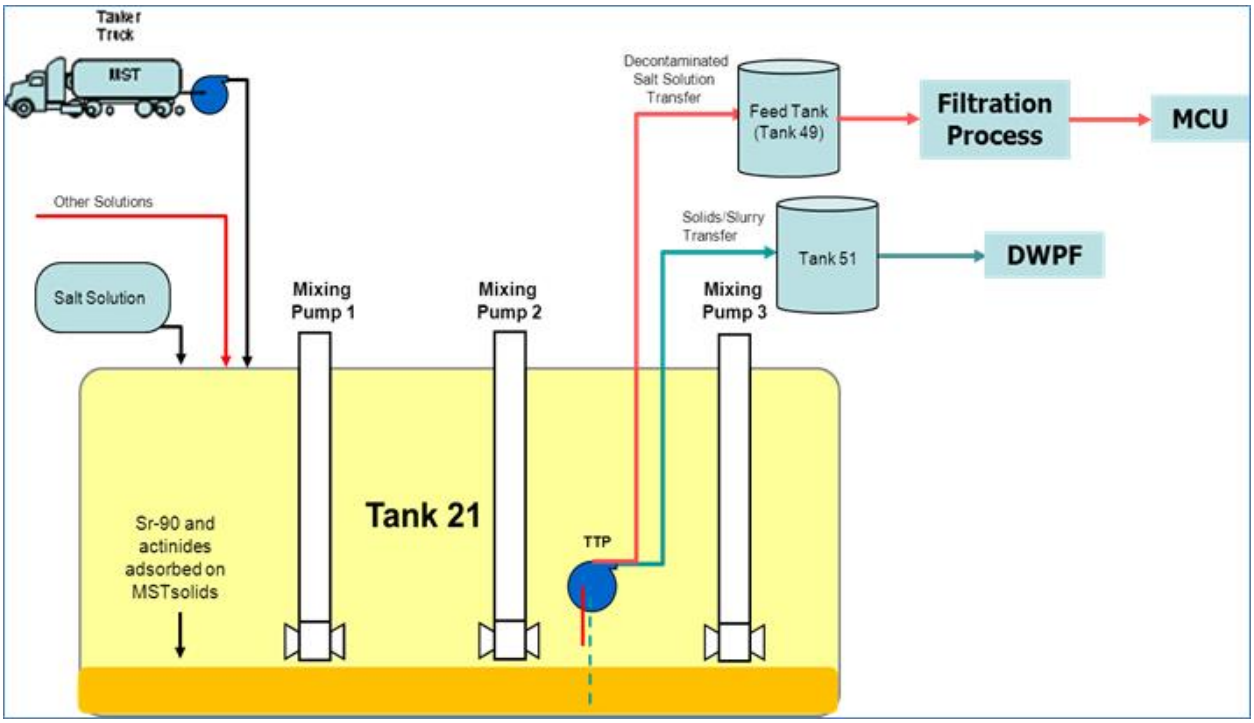

Figure 1: LTS Implementation at Tank 21

Under the LTS process as shown, MST is added to the tank and mixing pumps are used to blend the slurry and keep the solids in suspension. Reaction time and target MST concentrations are consistent with current operations, but the scale is greatly increased from the existing strike tanks. Once the reaction time has been achieved (historically 8-24 hours), the salt qualification sample is taken and the suspended MST particles are allowed to settle for 2-3 months while sample analysis is being performed. Initial settling rate calculations indicate that at least 90-95% removal of the suspended MST mass fraction can be achieved over this duration.

When the current salt treatment processes were commissioned for radioactive operations, total throughput was limited by the solvent extraction operation used to separate soluble cesium. This process was limited to 15 L/min, while filtration operations generally supported operations at close to 20 L/min. In 2013, a new solvent formulation was introduced into MCU which provides more efficient extraction and supports operation at 32 L/min. The extensive solids removal achieved by LTS is expected to result in significant improvements in filter throughput and availability at 512-S which closely align with solvent extraction flowrates. Current filtration operations occur at MST concentrations that regularly approach 5 wt%, and total insoluble solids can be even higher if significant quantities of precipitated solids are present. By nearly eliminating the MST solids

content from incoming salt (see Figure 2 for example of solids removal), nominal filter flux will improve due to reduced cake formation on the filter tubes, and the frequency of filter cleaning operations will be dramatically reduced. The reduction of filter cleaning provides not only an increase in filter availability, but also minimizes the likelihood of undesired solids formation that can result from large pH changes to the salt waste.

Figure 2: 15wt% MST Settling after Suspension (left) and after 24 Hours Settling (right)

While improving overall salt treatment throughput helps to support accelerated waste treatment objectives, the LTS concept also provides opportunities for significant savings in operational costs. The at-tank philosophy not only minimizes total project costs, but those same efficiencies apply once operations commence. Under the current structure, routine operator action is needed to treat each of the “micro-batches” transferred into the strike tanks at 241-96H. By striking the entire “macro-batch” once it is compiled in Tank 21, there is a significant reduction in the labor hours needed to process an equivalent amount of waste. Additionally, by removing the 241-96H facility from salt treatment, there is a corresponding reduction in corrective and preventive maintenance demands associated with all of the other utility systems needed to support use of that facility.

The LTS project has completed design activities along with preliminary hazards and criticality analyses. The project is on schedule to complete field installation and final safety basis development in 2015 and is targeting the initiation of radioactive operations late in the year.

LTS Opportunities

While not part of the initial execution of the LTS project, the concept of MST treatment as envisioned under LTS also contains opportunities that would further enhance the value of the project. Much of the development work for MST has focused on determining appropriate solids concentrations and contact times needed to support a specific level of actinide and strontium removal from the salt waste. This results in a process where MST is separated from salt solution once acceptable waste decontamination has occurred even though additional actinide removal capacity on the MST surface remains. Some accumulation of MST within Tank 21 is inherent in

the LTS process. As fresh MST is added to the mass remaining from previous batch treatments, the potential exists to utilize this excess capacity through optimization of the flowsheet. Under the LTS process, it would be possible to re-use existing MST inventory within the waste tank until mass transport rates at the particle surface become the limiting factor instead of the current batch cycle time limitations. This results in not only a cost savings to actinide removal operation, but also presents a significant simplification when incorporating the actinide-laden MST solids into the HLW disposal processes at DWPF.

Incorporation of salt processing effluents into HLW process is complicated by two primary factors: the physical transfer and processing infrastructure by which the streams are combined, and flowsheet limitations for "coupled" salt/sludge processing. One of the primary physical limitations associated with transferring salt processing effluents into DWPF is the relatively limited amount of lag storage available within the existing infrastructure. Because the ARP/MCU facilities are thus somewhat closely-coupled, continuous parallel operation of the facilities is required to maintain high facility availabilities and throughputs. LTS partially decouples salt processing from HLW processing by accumulating reacted MST within Tank 21, which allows for that material to be added to large sludge batches during preparation in the Tank Farm facilities. At a minimum, this reduces the complexity associated with including MST in HLW sludge, and it may further be possible to re-purpose the tank space used to store reacted MST within DWPF for storage of the cesium-laden acid strip stream from MCU which would further decouple those processes.

Flowsheet limitations are currently driven by process variability, but in the future may depend also on titanium solubility with HLW glasses produced by DWPF. As described above, ARP/MCU operations must coincide with HLW treatment at DWPF. Since MST is collected over multiple filtration micro-batches, this requires periodic transfers of MST solids to DWPF for incorporation into sludge processing. As a result, the DWPF flowsheet must tolerate significant variability associated with the presence (or possibly absence) of MST. Due to the many processing and performance requirements related with HLW glass production, this can frequently result in the selection of glass compositions that favor a broad compositional region rather than targeting more focused goals of melt rate and waste loading within the glass. By adding the MST to sludge batch preparation at a fixed concentration, LTS processing could greatly limit the variability currently associated with the MST stream.

As salt processing throughputs increase at SRS, the total mass of titanium associated with MST that must be included in HLW processing will also rise. Given the current limitations on measured titanium solubility in HLW glasses, a programmatic risk exists that salt processing rates could be limited by the ability to disposition the effluent streams within DWPF. However, the potential for MST re-use in LTS would address this risk by allowing for a total mass reduction in total MST used in salt processing. As a result, realizing this additional actinide sorption capacity would represent not only a direct cost savings to salt processing but also reduce the amount of material that must be disposed into HLW and significantly mitigate a risk associated with the current

flowsheet.

CONCLUSION

The LTS process as presented utilizes “at-tank” waste treatment principles intended to increase total salt processing throughput at SRS while minimizing both project installation and operating costs. The project also attempts to maximize value by providing benefits which cross-cut multiple aspects of waste processing and disposal operations at SRS. The initial deployment of LTS is planned for limited duration within a single waste tank, but should the benefits of the project be fully realized, the potential exists for similar deployments at other salt tanks within the SRS Tank Farms.