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Approach of Changing the Defense Waste Processing Facility Process Antifoam and Performance to Date – 23272

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ABSTRACT

The Defense Waste Processing Facility (DWPF) at the Savannah River Site experiences foaming in process vessels due to high gas generation rates of boiling and chemical reaction off-gassing. Excessive foaming results in carryover events during boiling where the vessel contents foam over through the off-gas lines into the condensate tank. These events are detected by software which interlocks off the steam to the vessels to prevent additional sludge from reaching the condensate tank. Actuation of these interlocks is disruptive to the process and requires boiling conditions to be re-established prior to further material addition. Carryover of sludge into the off-gas system interferes with mercury recovery from the waste and fouls the off-gas system components. Antifoam is added throughout the process to minimize foam production. Historically, DWPF utilized Antifoam 747, but deficiencies had been identified with this antifoam agent. Antifoam 747 generates flammable degradation products that required mitigating controls. It is also the likely source of methyl functional groups for the organo-mercury present in downstream facilities. Antifoam 747 is most effective in a pH of 6-8 and degrades as the pH deviates outside this range. Some stages of the DWPF process operate above a pH of 8 and proved to be particularly susceptible to carryovers even with antifoam usage. The susceptibility to carryovers meant the steam rates had to be limited throughout the whole process. With the startup of the Salt Waste Processing Facility (SWPF) resulting in higher throughput at DWPF, higher steaming rates are required to improve the cycle time. Therefore, in 2017 DWPF requested that Savannah River National Laboratory develop a new antifoam control method for DWPF's Chemical Process Cell (CPC).

SRNL tested both chemical and nonchemical foam controls before focusing on finding a superwetter or commercial antifoam to control foaming. Thirty potential antifoams were tested and Momentive™ Y-17112 (Momentive) was shown to be the most effective at destroying foam and preventing foaming between additions. Momentive was shown to be effective across a pH range of 4 to 13 with no degradation products generated. Momentive was effective in both the nitric-formic acid flowsheet and the new nitric-glycolic acid flowsheet that was recently implemented at DWPF.

DWPF began utilizing Momentive antifoam in June 2021 under the nitric-formic acid flowsheet and has seen great improvements compared to Antifoam 747 usage. Carryover events used to occur regularly in the CPC vessels, particularly when boiling during the high pH stages of the process, but there have been zero carryover events since implementation of Momentive. Antifoam addition frequency has also been reduced incrementally without issue, thereby resulting in fewer processing disruptions and less burden on Operations for antifoam additions, which supports improved cycle times. The lack of flammable degradation products in Momentive allowed for DWPF to remove antifoam controls that required 380 liters of flush material to be added with every addition. This resulted in less wastewater generated and less cycle time used for dewatering. Overall, Momentive™ Y-17112 has been a vast improvement to DWPF processing with no disadvantages identified.

INTRODUCTION

The Defense Waste Processing Facility (DWPF) at the Savannah River Site experiences the generation of foam during the processing of sludge slurry and salt streams from the Salt Waste Processing Facility (SWPF). The occurrence of foam in the vessels is due to a combination of factors that include the rheological properties of the feed, the rate of release of trapped off-gas from the sludge slurry, and the off-gas generation from neutralization reactions at elevated temperatures. Foaming, if not mitigated, during boiling and acid additions can result in carryover events where the vessel contents foam over through the off-gas lines into the condensate tank. These events are detected by software which monitors the pH trend of the condensate tank for carryover indicators and responds by actuating carryover alarms and interlocking off the steam flow and material transfers to the vessels to prevent additional sludge from reaching the condensate tank. Actuation of these interlocks is disruptive to the process and requires a fresh antifoam addition and boiling conditions to be re-established prior to further material addition. Carryover of sludge slurry into the off-gas system interferes with mercury recovery from the sludge slurry, fouls the off-gas system components, and increases the radioactivity of the condensate that returns to the Tank Farm. Large sludge slurry carryover events have the potential to shut down processing for multiple days, due to the required cleanup and recovery of process equipment. The amount of sludge slurry carried over into the off-gas system is determined by observing the iron content of the condensate stream. Iron is selected as a marker for sludge slurry carryover due to its abundance in the sludge slurry and its absence in a typical condensate stream generated from processing.

Antifoam is added to the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) to minimize foam production. Historically, DWPF utilized Antifoam 747, but deficiencies identified over time with this antifoam agent resulted in significant processing constraints. Deficiencies include generation of flammable degradation products, potential production of methyl mercury, and instability under various pH regimes experienced during processing. Further discussion on these topics is provided below.

Antifoam 747 generates flammable degradation products that required mitigating controls. Prior to identification of the degradation products, the antifoam would be diluted in a 20:1 ratio with water and added to the processing vessels as needed. This dilution allowed for controlled addition volumes. Antifoam addition volumes are four liters or less and the pump size and piping size between the antifoam feed tank and processing vessels are too large for accurate transfer volumes of this magnitude. After the degradation products were identified as resulting from antifoam being mixed with water for extended periods, the mitigation action was to add the antifoam to the transfer line via funnel which was then flushed to the process vessels with 380 liters of water directly from the feed tank. This manual addition took longer, required more personnel to perform, and generated additional wastewater, all of which contributed to increased cycle time.

Antifoam 747 is the likely source of methyl functional groups that complex with mercury in downstream facilities. Methyl-mercury is much more soluble and leaches more readily than elemental mercury and challenges regulatory limits.

Antifoam 747 is most effective in a pH of 6-8 and degrades as the pH deviates outside this range. Some stages of the DWPF process operate above a pH of 8 and proved to be particularly susceptible to carryovers even with antifoam usage. The susceptibility to carryovers meant the steam and acid addition rates had to be limited throughout the process. With the startup of the SWPF resulting in higher throughput at DWPF, higher steaming rates were required to improve the cycle time. DWPF adds an SWPF concentrated solids stream (actinides and strontium adsorbed onto monosodium titanate) and an SWPF strip effluent stream (dilute nitric acid with concentrated Cs-137) to each SRAT batch. Any processing upsets at DWPF have the potential for also stopping SWPF processing, so faster cycle time was desired for flexibility.

Due to the above reasons, in 2017 DWPF requested that Savannah River National Laboratory (SRNL) develop a new antifoam control method for DWPF's Chemical Process Cell (CPC).

DISCUSSION

Identification of New Antifoam

SRNL completed testing of both chemical and nonchemical foam controls. Nonchemical foam controls such as water spraying of the liquid surface, ultrasound dispersion, and agitation of the vapor space proved ineffective or impractical. The study soon focused on finding a commercially available chemical for controlling foam. After analyzing thirty potential antifoams for viability through practical testing of each candidate, the commercially available Momentive™ Y-17112 (Momentive) was identified as the most effective option [1].

Momentive was found to be resistant to hydrolysis as demonstrated by its chemical stability across the pH range of 4 to 13 and the lack of degradation products in the off-gas or condensate. It was proven to be effective in both the nitric-formic acid flowsheet and the new nitric-glycolic acid flowsheet that was recently implemented at DWPF.

Not only was the foam destroyed upon addition, but foam was also less persistent between antifoam additions. Less antifoam overall was needed to control foam throughout the batch cycles. The addition rates determined by SRNL were scaled to facility quantities and have been further adjusted through processing experience. The below tables show the total reduction in antifoam additions and associated water volume for typical batches in both the SRAT and the SME.

TABLE I. Reduction in Antifoam Additions in SRAT Batches.

Antifoam 747 Typical SRAT Batch	
Process Step	**Volume**
Before Caustic Boil	4 L
Every 1 h during Caustic Boil	2 L
Before Acid Additions	6 L
After Acid Additions	6 L
Every 12 h During Post-Acid Boiling	1 L
Typical Total Antifoam Volume	45 L
Total Water Volume	7600 L

Momentive Antifoam Typical SRAT Batch	
Process Step	**Volume**
Before Caustic Boil	2 L
Before Acid Additions	2 L
After Acid Additions	8 L
Before Strip Effluent Batches	2 L
Typical Total Antifoam Volume	14 L
Total Water Volume	265 L

TABLE II. Reduction in Antifoam Additions in SME Batches.

Antifoam 747 Typical SME Batch	
Process Step	**Volume**
Before Every Canister Decon	2 L
Before Each Frit Addition	4 L
Every 12 h During Boling	2 L
Typical Total Antifoam Volume	30 L
Total Water Volume	3400 L

Momentive Antifoam Typical SME Batch	
Process Step	**Volume**
Before Every Third Canister Decon	1 L
Before Each Frit Addition	1 L
Typical Total Antifoam Volume	4 L
Total Water Volume	80 L

Implementation Under Formic Acid Flowsheet

DWPF began utilizing Momentive antifoam in June 2021 under the nitric-formic acid flowsheet. Momentive antifoam immediately showed great improvements compared to Antifoam 747 usage. Carryover events used to occur regularly in the CPC vessels, particularly when boiling in the SRAT prior to acid additions. There have been zero carryover events since implementation of Momentive as indicated by processing trends, software carryover alarms, and sampling of the wastewater stream.

One early event proving Momentive antifoam effectiveness at controlling foam happened when the feed pump for the concentrated SWPF solids stream to the SRAT was faulty and troubleshooting took place over multiple days. However, the facility saw no adverse effects even though antifoam was not added during the troubleshooting which involved significant boiling time.

As an example of processing before transition to using Momentive Antifoam, Figure 1 shows the caustic boiling phase of a SRAT batch through preparation and feeding of the SWPF solids stream. The SRAT pressure, SRAT level, SRAT temperature, SRAT steam flow, along with condensate tank level and pH, SWPF solids transfer pump, and antifoam addition valve actuation are plotted on the y axis versus time on the x-axis. Antifoam 747 was added prior to feeding the SWPF solids stream and once every hour when concentrating the SRAT without feeding. This addition frequency prolonged concentration time because the concentration rate is about 1100 liters per hour with 380 liters of flush water being added hourly with each antifoam addition. In this example, the facility added antifoam seven times as indicated by the orange line when concentrating, yet still saw a carryover alarm that stopped processing as indicated by the steam flow (light blue line) dropping to zero. The carryover alarm was actuated by a sudden increase in the pH of the condensate tank (dark blue line), indicating presence of a material other than condensate. The pressure (red line) during this batch was unstable, with a quick building before the carryover event and quick sharp spikes during antifoam additions as foam was dispersed.

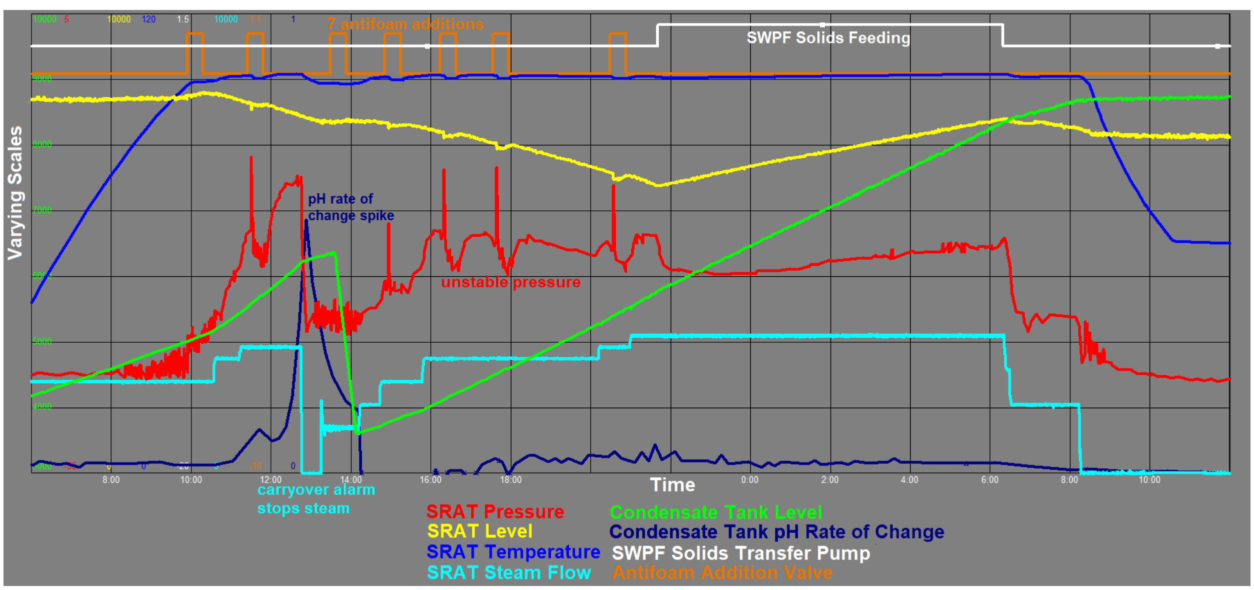

Fig 1. SRAT Processing with Frequent Additions of Antifoam 747 under the Nitric-Formic Flowsheet.

Figure 2 shows the event after implementation of Momentive when pump troubleshooting occurred over the course of a week during the caustic boiling phase when SWPF solids are added. This is the same part of the process as Figure 1 with the same process parameters and colors plotted on the y-axis versus time on the x-axis. Momentive addition frequency during caustic boiling was changed to a single antifoam addition prior to processing and then no subsequent antifoam additions when concentrating or feeding the SWPF solids stream. While troubleshooting the feed pump during this event after Momentive implementation, the SRAT batch was boiled a total of 51 hours after a single antifoam addition with no foaming or carryover indicators occurring. Pressure was more stable, and the pH rate of change carryover alarm showed no increases. The points in this figure where the steam is stopped are unrelated to carryover alarms and done for pump troubleshooting purposes.

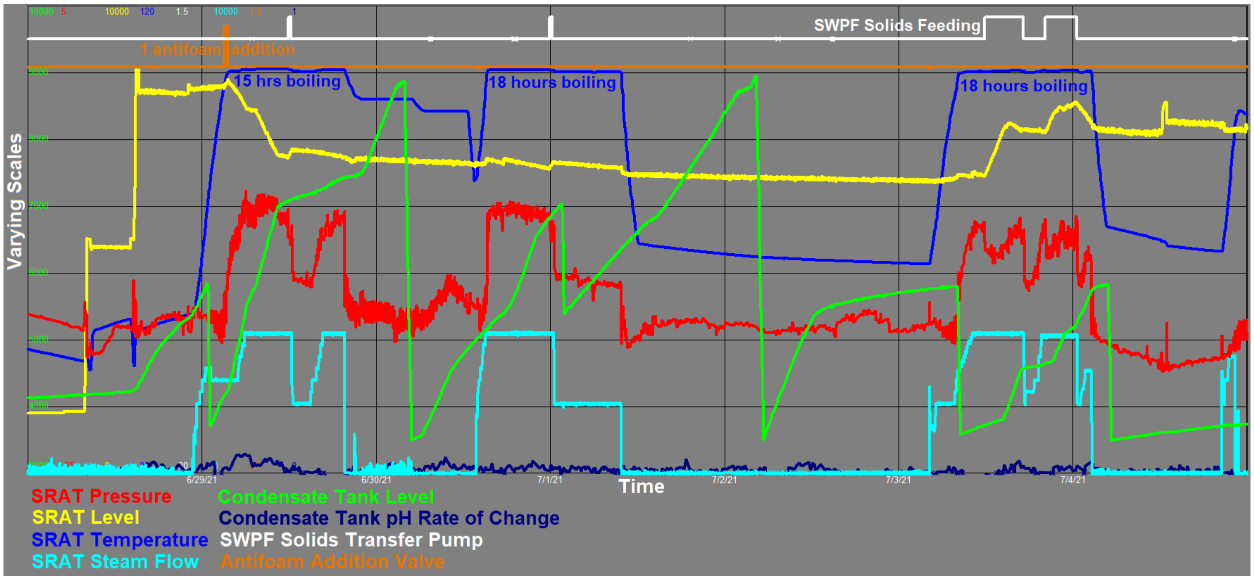

Fig. 2. SRAT Processing with Momentive Antifoam under the Nitric-Formic Flowsheet.

Events such as the one shown in Figure 2 boosted confidence in the Momentive antifoam and subsequently the addition frequency was incrementally decreased. After each removal of an antifoam addition or decrease in antifoam volume, the process was observed for multiple batches for foaming or carryover before additional reductions. Fewer antifoam additions mean less processing disruptions during SRAT and SME processing and thus improved cycle time. For example, the facility previously added antifoam every twelve hours during post-acid boiling. This has been reduced to a single addition prior to each SWPF strip effluent batch. In the SME, rather than adding antifoam every twelve hours during boiling and prior to receipt of material from canister decontamination activities, the facility now only adds antifoam before every third canister decontamination.

Transition to Glycolic Acid Flowsheet

After a year of operation with the new Momentive antifoam, DWPF began transitioning from the nitric-formic acid flowsheet to the nitric-glycolic acid flowsheet in July 2022. The new antifoam continued to perform exceptionally, and additional process improvements were undertaken.

Initial implementation retained the controls for degradation products where each antifoam addition was performed with a full feed tank flush volume. Since there are no flammable degradation products in Momentive, the flushing controls were removed, and antifoam is now added via a 20:1 diluted mixture within the feed tank. This resulted in less wastewater generated and less cycle time used for dewatering, as shown in the total water volumes of Tables 1 and 2. There is also a significant benefit in minimizing operator interaction. With the mitigating flushing controls, a field operator had to manually add antifoam to the transfer line via a funnel for each addition. Antifoam can now be added remotely from the control room. The operators simply need to request an antifoam addition and the software will perform the transfer without further operator involvement.

Figure 3 shows an overall SRAT batch under the current glycolic flowsheet. The same process parameters as Figure 1 and Figure 2 are plotted with the exception of the strip effluent transfer pump shown in black. Antifoam was only added at four points in this week-long process: prior to caustic boiling, prior to acid additions, prior to post-acid boiling, and prior to the second strip effluent batch. DWPF has continued to observe no indications of carryover via the software analysis of trends and the sample results of the wastewater stream. The facility now uses approximately 24% of the total antifoam and 3% of the associated water per batch with Momentive antifoam versus the previous Antifoam 747.

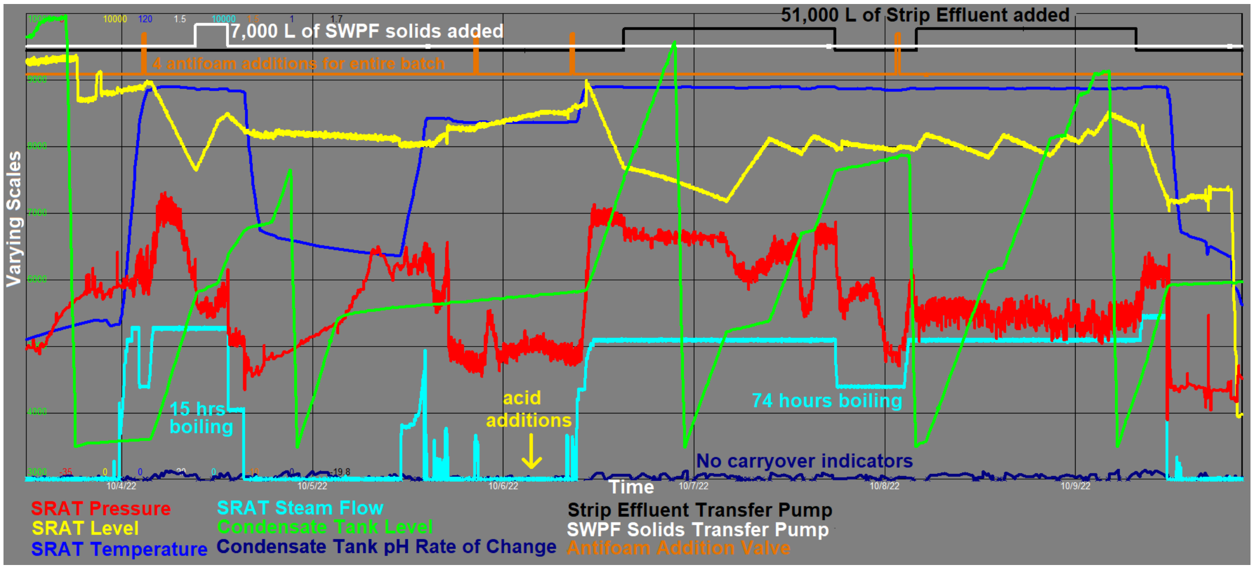

Fig. 3. Processing with Momentive Antifoam under the Nitric-Glycolic Flowsheet.

Reduced Flammability Concerns

Since the flammable antifoam degradation products are no longer a concern and with the lack of hydrogen generation of the glycolic flowsheet, the required purge rates to the facility vessels were reduced. Previously all six nitrogen tanks in the facility were required to be operable while processing. The reduced purge rates now only require that five nitrogen tanks are operable, thus allowing for flexibility in repairs without an extended processing outage.

The reduction in overall antifoam usage helps the facility with regards to melter flammability controls. The melter feed must be maintained within the limits for the lower flammability limit, which includes an upper limit to the concentration of total organic carbon (TOC) present in the melter feed. The limit can be increased but is accompanied by a corresponding decrease in melter feed rate. The glycolic flowsheet is higher in TOC due to the contribution from glycolate and required an increase from 12,750 ppm to 14,000 ppm, which reduced melter feed rate from 5.8 lpm to 4.9 lpm. Antifoam 747 contributed about 2000 ppm to the TOC concentration, whereas Momentive contributes about 275 ppm. The reduction in antifoam volume has allowed the facility to feed the melter at a higher rate than would have been possible with Antifoam 747.

Increased Steam and Acid Addition Rates

After extended facility operation without carryover indications, the facility started increasing the steam rate to process vessels to determine if design basis steam flow rates could be achieved and sustained. Normal operation of the facility involves applying steam into the vessel process coils at a rate of 1500 kg per hour. Through incrementally increasing the steam rate and demonstrating continued effectiveness of Momentive antifoam, the facility is now able to operate at the original facility design basis maximum steam rate of 2250 kg per hour. This change allows for the SRAT and SME to be concentrated 40% faster which significantly decreases overall cycle time.

The maximum steam rate is not currently utilized when feeding the two SWPF streams to the SRAT because the corresponding evaporation rate outpaces the currently possible feed rate. However, the increased steaming capability has allowed the facility to begin evaluating controls and equipment capabilities of the feed pumps. The facility intends to increase the feed rate of the SWPF streams to the SRAT and thereby maximize benefit of the increased steam rate capability. This improvement would reduce the total feeding time of these two streams from 51 to 36 hours. Decreased cycle time provides DWPF with processing flexibility and decreases the likelihood that DWPF outages will impact SWPF. Each SRAT batch has a required amount of steam that must be applied to strip the mercury content. The current batches require 34,000 kg of steam to be applied, which is typically exceeded by the steam needed for strip effluent batch additions. However, future sludge transfers to be sent from the Tank Farm will have a higher mercury content and future SRAT batches may require more than three times as much steam to be applied. When these future high mercury batches are processed, it is crucial the facility be able to steam faster to maintain pace with SWPF. Therefore, the Momentive antifoam is helping the facility prepare for the longer steam stripping times.

A typical SRAT batch involves a glycolic acid addition of 1,200 L. Due to the carryover susceptibility, the acid addition rates were historically limited to 4 lpm and were split into 4 additions with twenty minutes between each addition. The glycolic flowsheet is designed to allow glycolic additions at a rate of up to 16 lpm. An anticipated improvement is implementation of this feed rate in the facility as a single addition, which will significantly decrease the cycle time needed for glycolic additions.

CONCLUSIONS

DWPF has been using Momentive™ Y-17112 antifoam in the CPC since June 2021. This has been a vast improvement to the process with no disadvantages identified. The facility has been able to process more consistently without process upsets caused by carryover events. Rather than fighting constant foaming in the process, the Momentive antifoam eliminates foam and prevents more foaming between additions. The facility now adds much less antifoam than before, which allows for an increased melter feeding rate. The facility can now add acid at faster rates and boil at higher steaming rates which significantly decreases cycle time and allows for faster addition of salt streams generated by SWPF.

These process improvements are great steps towards the Savannah River Mission Completion goal to finish the liquid waste mission within 15 years. Processing upsets and equipment issues at DWPF now have less chance of stopping processing at SWPF. Under the previous antifoam and flowsheet, the DWPF cycle time consistently exceeded the required cycle time to keep pace with SWPF generation of the concentrated solids and strip effluent streams. With Momentive antifoam and the glycolic flowsheet, the facility is able to process with significantly reduced cycle times and increased process flexibility.

REFERENCE

1. Lambert, D. P.; Howe, A. M.; Woodham, W. H.; Williams, M. S.; Hunter, S. C., *Antifoam Development for Eliminating Flammability Hazards and Decreasing Cycle Time in the Defense Waste Processing Facility*, SRNL-STI-2019-00677, Rev. 4., Savannah River National Laboratory: Aiken, SC (2021).