Implementation of Glycolic Acid Flowsheet in the Defense Waste Processing Facility (DWPF) – 17348

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ABSTRACT

The disposition of high level waste (HLW) into canistered waste forms began at Savannah River Site (SRS) in 1996. For its entire processing history, DWPF has added formic acid as a pretreatment step in producing acceptable melter feed from incoming waste sludges sent from the HLW Tank Farms. While this process has been used to successfully produce more than 4,000 radioactive canisters, the addition of formic acid and its tendency to catalytically decompose in the presence of trace quantities of noble metals adds substantial process complexity in order to safely accommodate hydrogen generation and pH shifting during batch operations. Research efforts have been in progress for several years to identify a chemical surrogate for formic acid which performs the essential process functions without the associated negative consequences. The final analytical work to demonstrate the effectiveness of glycolic acid in the DWPF is nearly complete and a project team has been created to safely integrate the new acid into the chemical process.

The project team is currently executing an implementation schedule which addresses safety basis development, revision to operations procedures and training, facility modifications, chemical procurement, and updated process monitoring. Introduction of glycolic acid into DWPF is currently scheduled to take place in early 2017, beginning with a blended flowsheet of glycolic and formic acid and ultimately transitioning to glycolic-only processing.

This paper provides an overview of planned glycolic acid flowsheet implementation in the DWPF. This paper discusses several issues related to implementing such a significant change to the chemical process including:

1) Process chemistry differences between the two flowsheets with quantitative comparison for several properties of interest;
2) Technical approach to hazards analysis and safety basis development strategy;
3) Status of project execution for major deliverables; and
4) Path forward for facility modifications related to legacy formic acid support equipment.

INTRODUCTION

Acidification of incoming waste sludges has been a fundamental aspect of every batch processed at DWPF. Wastes stored in the HLW Tank Farms are maintained highly alkaline as a corrosion control, but must be neutralized as the presence of silicon glass-formers in DWPF can lead to scale formation during vessel boiling and de-watering. Since facility startup, acidification has been accomplished using a blend of formic and nitric acids. The relative ratio of the two acids allows for good control of the redox potential of the final melter feed. This is of particular importance to optimum melter operation [Ref 1]. An overly reducing feed creates the potential for deposition of elemental metals in the melter pot, which can create short circuits for the electrodes and lead to melter failure. A completely oxidized feed can result in significant gaseous oxygen release in the cold cap, creating an insulating foam layer which lowers melt rate and decreases throughput. The presence of a reducing acid is also important in the pretreatment operations of the DWPF Chemical Process Cell (CPC). Mercury oxides are reduced to elemental mercury in the CPC and then steam stripped from the waste [Ref 2]. This prevents accumulation of mercury deposits in the melter off-gas system and provides a mercury purge for the overall SRS Liquid Waste (LW) system.

While this flowsheet has been used successfully for more than twenty years, the use of formic acid as the primary reductant brings some complications. Trace quantities of noble metals are present in most of the sludges stored in the Tank Farms and the surfaces of these metals become activated shortly after the completion of acid addition in DWPF. Once the noble metals are activated, a portion of the free formic acid will catalytically decompose [Ref 3]. Gaseous hydrogen is among the off-gas by-products of the reaction, and it is evolved in sufficient quantities to require continuous monitoring of vapor composition by safety-credited gas chromatographs during operation. Additionally, this acid decomposition results in significant pH variation over the course of batch processing. Incoming waste transitions from essentially pH 14 down as low as 4-5 and then trending back towards neutral or slightly alkaline. Instability of pH during steam stripping of mercury has occasionally led to processing issues during steam stripping. It should also be noted that formic acid, which is received as a 90 wt% solution and stored in an outdoor chemical receipt facility, represents the single largest chemical hazard at DWPF.

To address some of the compromises created by the use of formic acid, a project was initiated in 2010 to identify if there were any alternative chemical reductants which could perform the same essential functions of formic acid without the attendant issues associated with catalytic decomposition. The primary stated goals of the Alternate Reductant Project are to:

- Identify and develop a reductant system that will reduce hydrogen generation consistently below the lower flammability limit (LFL) and eliminate the requirement to have gas chromatographs as safety significant
- Improve the safety and operability of the (CPC) to allow design boil-up rates and throughput while concentrating sludge and salt processing feeds and while stripping mercury
- Minimize downstream impacts and integration issues
- Incorporate ease of implementation in the reductant system design

After consideration of more than twenty alternative reductants, the project team downselected glycolic acid as the preferred option for full technical development. Given the scope of development work needed to justify a major flowsheet change to a HLW processing facility, a comprehensive overview of the research effort associated with the project is beyond the scope of this paper. However, experimentation performed by the Savannah River National Lab (SRNL) demonstrated that the primary project objectives would be achieved via a glycolic acid flowsheet. Figure 1 shows the impact on hydrogen generation between the formic flowsheet and an 80/20 blend of glycolic and formic acid [Ref. 8]. While it was ultimately determined to use a 100% glycolic acid flowsheet, the same behavior is exhibited there as well.

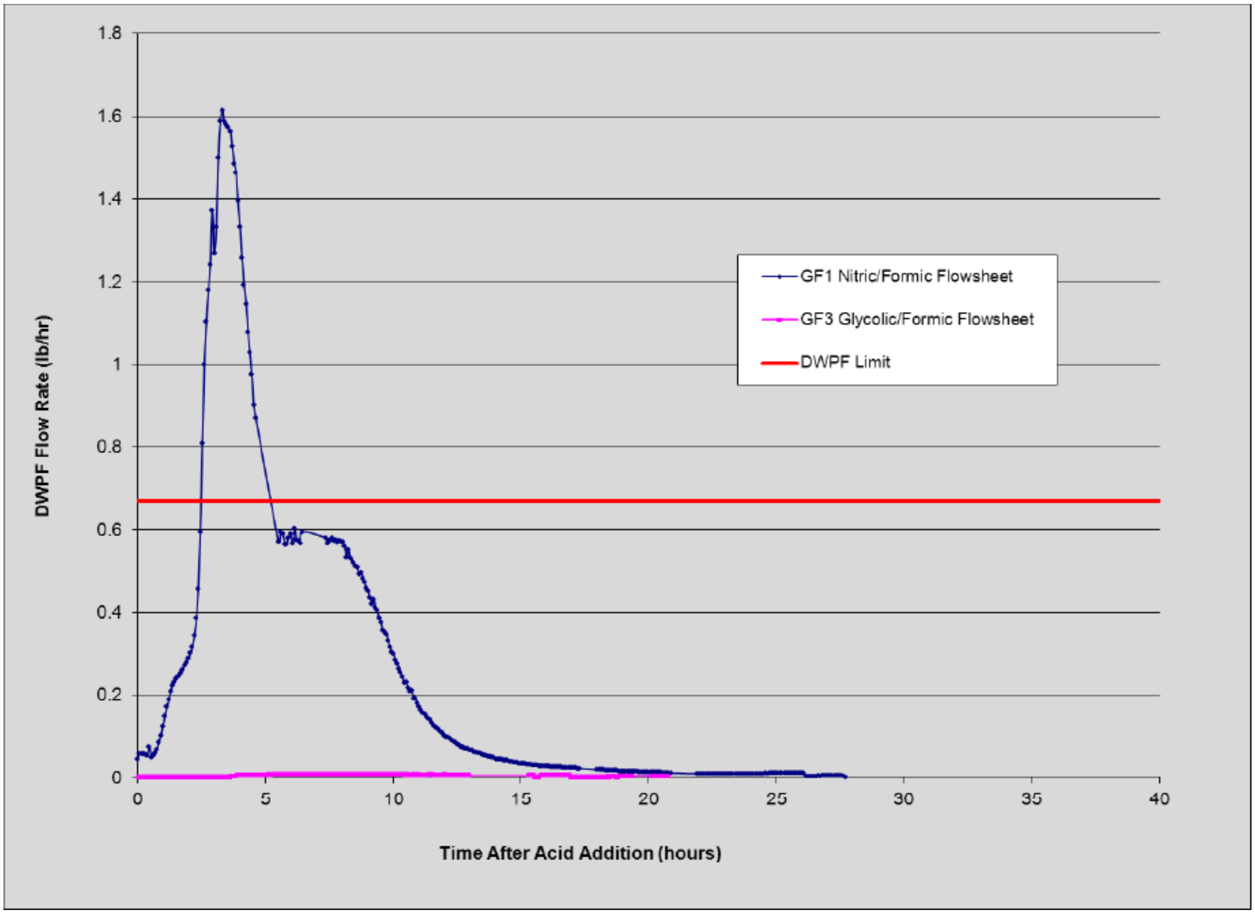

Figure 1: Hydrogen Generation Comparison between Formic Flowsheet and 80/20 Glycolic/Formic Blend

The greater stability of glycolic acid is also evident in Figure 2 which shows how the pH of the batch changes over the course of the reaction cycle [Ref. 8]. In the formic acid runs, the decomposition of the formic acid leads to a rebound in the pH curve and ultimately results in an alkaline product. However in the blended flowsheet containing 80% glycolic acid, the pH remains steady throughout the batch. Melter feed batches processed by the glycolic flowsheet have also had much lower yield stresses than equivalent formic batches [Ref. 8]. This allows for greater de-watering and higher solids concentrations to be transferred using the existing transfer pumps and improves overall process efficiency.

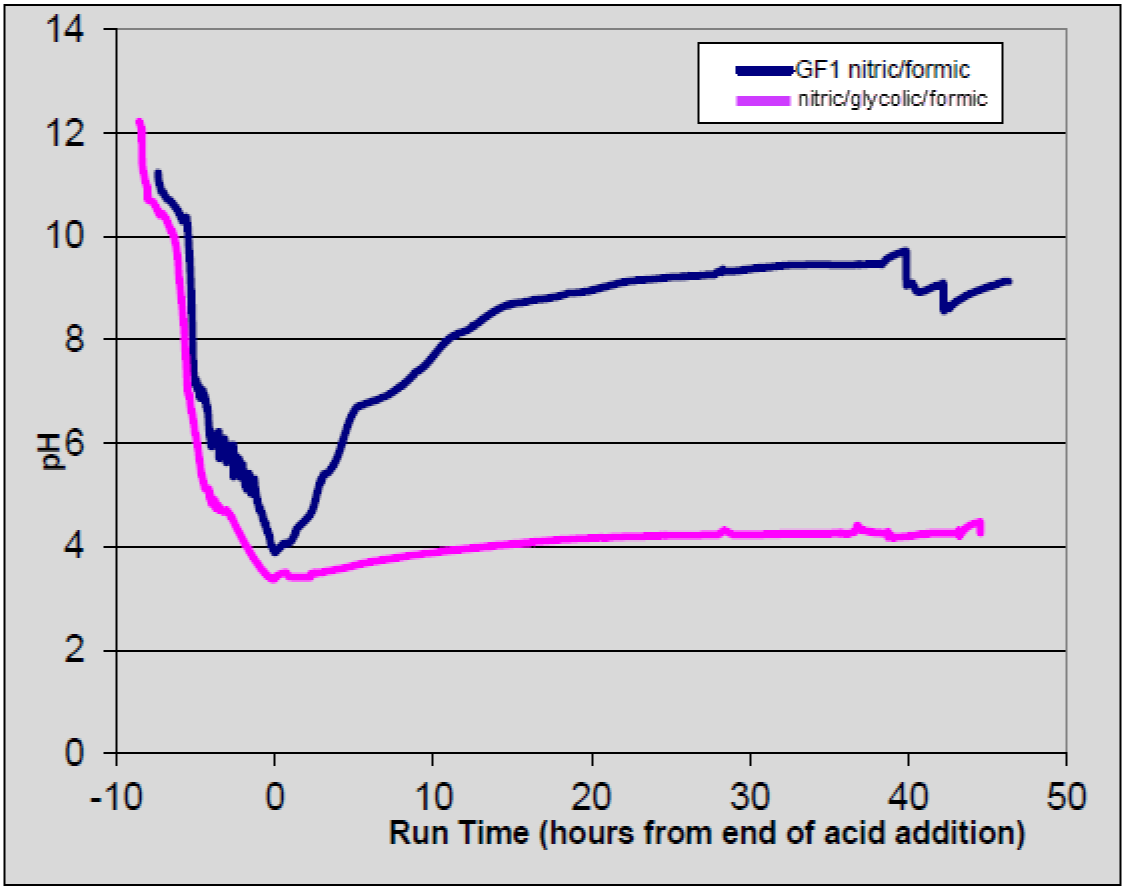

Figure 2: pH Trends between Formic and 80/20 Glycolic/Formic Blend

TECHNICAL APPROACH TO HAZARDS ANALYSIS

Safe implementation of glycolic acid receipt, storage, and use in DWPF is necessary in order to realize the benefits of the new flowsheet. Due to the extensive impacts on many different facility aspects, the project team developed a Safety Basis Strategy (SBS) to provide a common understanding of the management expectations, scope, roles and responsibilities, strategy and methods to be used for Alternate Reductant Project safety basis considerations. The SBS summarizes the methodology for hazard categorization and controls identification as well as identifies key process inputs and assumptions [Ref. 6]. The SBS then highlights the documentation and analysis that will be developed to support final implementation.

The SBS states that two separate revisions to the existing documented safety analysis (DSA) are planned to support the use of glycolic acid at DWPF. The first DSA submittal considers an interim configuration in which both formic and glycolic acids may be present within DWPF. A Consolidated Hazards Analysis Process (CHAP) has been performed to document the controls needed for the safe handling and use of glycolic acid. This process includes not only operation at DWPF but also downstream facilities as the potential exists for some amount of dissolved glycolate to be present in waste effluent streams from DWPF. As the hazard controls for formic acid generally bound the controls needed for glycolic acid, the interim submittal does not significantly impact the facility design or operation.

Any residual formic acid present in process vessels and piping systems will be flushed once operations utilizing glycolic acid have commenced. After any residual formic acid has been removed from the facility, DWPF will implement a final DSA change that considers only glycolic acid as the primary chemical reductant and excludes the receipt and storage of formic acid. This will include a modified control set that is specific to glycolic-only operation. Purge requirements for numerous process vessels will be reduced (due to the significant reduction in hydrogen generation) and continuous off-gas monitoring of the primary treatment tanks will no longer be required.

ALTERNATE REDUCTANT PROJECT STATUS

Much of the effort in the first years of the Alternate Reductant Project was focused on downselection of the preferred flowsheet and research needed to improve the technical maturity of the process. A roadmap for technology development was created early in the project life-cycle to define the scope of work needed to support eventual facility implementation [Ref. 7]. As the project is approaching its final months, an updated Technology Maturation Plan has been drafted to provide the current status against Technology Readiness Level (TRL) 6. All experimental work to achieve TRL-6 has been concluded and the project team is now awaiting only completion of the final output reports.

Despite the resource intensive research program, there is a relatively small amount of physical work within the facility that is necessary to support glycolic acid use. A spare formic acid storage tank will be converted for use as a receipt location of 70 wt% glycolic acid. This modification includes: changes to temperature control setpoints (as 70 wt% glycolic acid solutions begin to freeze at approximately 10 ^{o}C), refurbished level indication using radar-based instrumentation, new labeling for affected valves and process vessels, updates to existing pressure relief valve verification records, and updates to procedures and control system graphics on the distributed control system. The scope of the necessary modifications and applicable codes and standards has been documented in a Task Requirements and Criteria document [Ref. 8] and the necessary design changes and procurements are currently in progress.

The approach to the safety basis has been previously described. Hazards Analysis meetings have been conducted with personnel from the project team, facility design authority, operations, and nuclear safety. Applicable controls have been identified for both the interim and final safety basis change packages. Several input deliverables that support the safety basis changes have been completed, including updated purge calculations accounting for the beneficial impact of glycolic acid. However, some additional analysis inputs (notably those used for flammability control in the melter off-gas system) are awaiting final reports from the technology maturation work. Once these results are received, safety basis development efforts will proceed to conclusion.

Much of the work scope necessary to implement the alternate reductant flowsheet at DWPF has either been completed or is in its final stages. Currently the project is on track to introduce glycolic acid in the early part of 2017.

PATH FORWARD POST-IMPLEMENTATION

Once the facility has transitioned into full-glycolic operations, there will be additional opportunities that can be realized. For example, the reduction in required vessel purge flow will reduce the total vapor flow into the ventilation system, which will allow faster boil-up rates at current vessel vacuum levels. This leads to faster processing, particularly in mercury steam stripping where the process step duration is directly related to the content of mercury in the feed and the total mass of steam flow supplied through the heating coil.

Similarly, removing the requirement to continuously monitor major process vessel off-gasses will inherently increase overall facility availability as it eliminates down-time associated with corrective maintenance when the equipment is required to be operable. However, it should also be noted that there is a significant amount of mechanical complexity within the remote process cells in order to provide a filtered vapor sample to the gas monitors located outside of the process cells. Once the monitoring function is no longer needed, much of the remote piping can be removed as well. This allows for significant simplification of a subset of the remote components in the vessel ventilation system. That in turn affords shorter maintenance intervals by requiring fewer manipulations of interfering components to reach failed equipment.

Maximizing the benefits associated with the new flowsheet will require additional facility modification as well as sufficient operational experience post-implementation to optimize the process. However, the project team is working now with representatives from facility Engineering, Operations and Maintenance organizations to develop the scope of work expected to have the most immediate return on investment. Design development is expected to continue into 2017 and implementation of some of these designs may push into 2018 based on planned outages next year.

CONCLUSION

The Alternate Reductant Project represents the most significant change to DWPF operation since the integration of salt processing effluents from the Actinide Removal Project and Modular Caustic Side Solvent Extraction processes. Changing the form of the chemical reductant has the potential for significant impacts to facility safety, waste form compliance, emergency preparedness, remote process cell design, and total throughput. The project team has been steadily maturing the flowsheet over the past several years, and this effort is now culminating in some of the final project deliverables needed to implement the new flowsheet into the facility. This change is expected to occur in early 2017, although the full benefits may not be realized until 2018 or beyond.

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