Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-09SR22505 with the U.S. Department of Energy (DOE) National Nuclear Security Administration (NA).

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Salt Waste Processing Facility (SWPF) Transition into the Liquid Waste Program at Savannah River Site (SRS) and Implementation of Next Generation Solvent (NGS) - 22433

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Abstract

Savannah River Remediation LLC (SRR) manages and operates the liquid waste facilities at Savannah River Site (SRS) for the Department of Energy (DOE). Liquid waste at SRS is currently stored in aging underground storage tanks. This waste is a complex mixture of insoluble solids (sludge) and soluble salts in an alkaline solution. To treat waste streams to remove Cs-137, Sr-90, and actinides, SRS initially developed the small-scale Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Extraction (CSSX) Unit (MCU). ARP-MCU was in operation from April 2008 to June 2019 and processed approximately 28 million liters (7.4 million gallons) of waste. ARP-MCU was recently replaced with a full-scale operation in the Salt Waste Processing Facility (SWPF), which was designed, constructed, tested, and initially operated by the Parsons Corporation. The SWPF began hot operations in January 2021. The SWPF has the capability of processing up to approximately 32 million liters (9 million gallons) of salt waste per year after the implementation of Next Generation Solvent (NGS) which is scheduled to occur in FY2023. The SWPF contains three major processes: Alpha Strike Process (ASP), CSSX, and Alpha Finishing Process (AFP).

The newly commissioned SWPF will be transitioned to the Liquid Waste (LW) contractor after one year of operation and transition is scheduled to be completed in March 2022. Nuclear facility transitions from one contractor to another typically bring challenges from transitioning personnel and negotiating contracts to adopting policies and procedures. In addition to the typical challenges, this transition will involve additional challenges such as existing Information Technology (IT) infrastructure not being connected to the government site network prior to the transition, and policies and procedures not being consistent with the current LW contractor policies and procedures. To minimize cost and disruption to operation of the facility, the contract transition will take a novel approach where the LW contractor will accept the facility "as-is" and continue processing under the existing policies and procedures. During the first year of LW contractor operations, the LW contractor will perform an evaluation process to determine what changes need to be made and will develop plans to implement the needed changes. SWPF transition activities are scheduled to begin in January 2022 and finalize in March 2022, at which point the LW contractor will begin their first year of operation of the SWPF.

After one year of operation by the LW contractor, a new type of solvent will replace the current customized solvent at the SWPF. The current customized solvent being used in the CSSX process is known as BOBCalix. The BOBCalix solvent contains four major constituents: Isopar®L, BOBCalixC6 extractant, Cs-7SB modifier, and Tri-octylamine (TOA) suppressor. The plan is to replace the BOBCalix with a solvent known as NGS or MAXCalix. The NGS also contains four major constituents: Isopar®L, MAXCalix extractant, Cs-7SB modifier, and TiDG suppressor. NGS was implemented and used successfully in the ARP-MCU process and has demonstrated better efficiency and capability than the BOBCalix. In addition, boric acid will replace nitric acid in the stripping and concentrating stage of CSSX in the implementation of NGS.

This paper describes the planned transition of the SWPF into the liquid waste program and the implementation of NGS after one year of LW contractor operation. It is expected to be of interest to other liquid waste treatment facilities as it discusses initiatives of a major salt processing facility for the removal of radioactive strontium, actinides, and cesium.

INTRODUCTION

SRR safely manages and operates the liquid waste facilities at the SRS for the DOE. The SRS liquid waste system consists of 51 waste storage tanks, waste evaporators, treatment facilities, Defense Waste Processing Facility (DWPF) vitrification plant, and Saltstone Production and Disposal Facilities (SPF and SDF). Waste processed through the latter is being disposed of onsite in Saltstone Disposal Units and DWPF vitrified waste is destined for a federal repository. Eight of the 51 waste storage tanks have been operationally closed and filled with grout. As liquid waste treatment and disposal continues, the remaining storage tanks and ancillary infrastructure will be closed in the coming years. Radioactive waste at SRS was generated from the chemical separation facilities. The waste is a complex mixture of insoluble solids (sludge) and soluble salts in an alkaline solution. Continued long-term storage of these radioactive wastes poses an environmental risk.

SRS initially deployed the small-scale ARP-MCU system to remove radioactive strontium, actinides, and cesium from salt waste and enable disposal at the SPF. ARP-MCU was in operation from April 2008 to June 2019 and processed approximately 28 million liters (7.4 million gallons) of waste. ARP-MCU was recently replaced with a full-scale operation in the SWPF, which was designed, constructed, tested, and initially operated by the Parsons Corporation. The SWPF began hot operation in January 2021. The newly commissioned SWPF will be transitioned to the LW contractor after one year of operation and transition is scheduled to be completed in March 2022.

Nuclear facility transitions from one contractor to another typically bring challenges from transitioning personnel and negotiating contracts to adopting policies and procedures. To minimize cost and disruption to operation of the facility, the contract transition will take a novel approach where the LW contractor will accept the facility “as-is” and continue processing under the existing policies and procedures. During the first year of LW contractor operations, the LW contractor will perform an evaluation process to determine what changes need to be made and will develop plans to implement the needed changes. SWPF transition activities are scheduled to begin in January 2022 and finalize in March 2022, at which point the LW contractor will begin their first year of operation of the SWPF.

The SWPF consists of three major basic unit operations: ASP, CSSX, and AFP. Dissolved salt solution from the H-Area Tank Farm is sent to the ASP in the SWPF. In the process, a monosodium titanate (MST) strike is performed on the salt solution to sorb strontium and select actinides. After MST contact, the resulting slurry is filtered to remove the MST and entrained sludge. The filtrate is transferred to the CSSX process for further treatment to remove cesium and the solid particulates removed by the filters are washed and transferred to the DWPF for vitrification. The CSSX process extracts the cesium from the radioactive waste using solvent to produce Decontaminated Salt Solution (DSS). The DSS is then sent to the Saltstone Facilities following the AFP to be incorporated in grout, and the cesium enriched strip effluent is sent to DWPF for vitrification. The AFP appears after the CSSX process but follows the same operation as the ASP. It allows for an additional MST strike to occur if the final DSS still contains high levels of strontium or actinides. However, the AFP has not been through an operational readiness review and has not been placed into service. The flow path of solution through the three main unit operations is shown below in Figure 1. The CSSX process will have much of the focus for this paper because it is the system that employs the customized solvent.

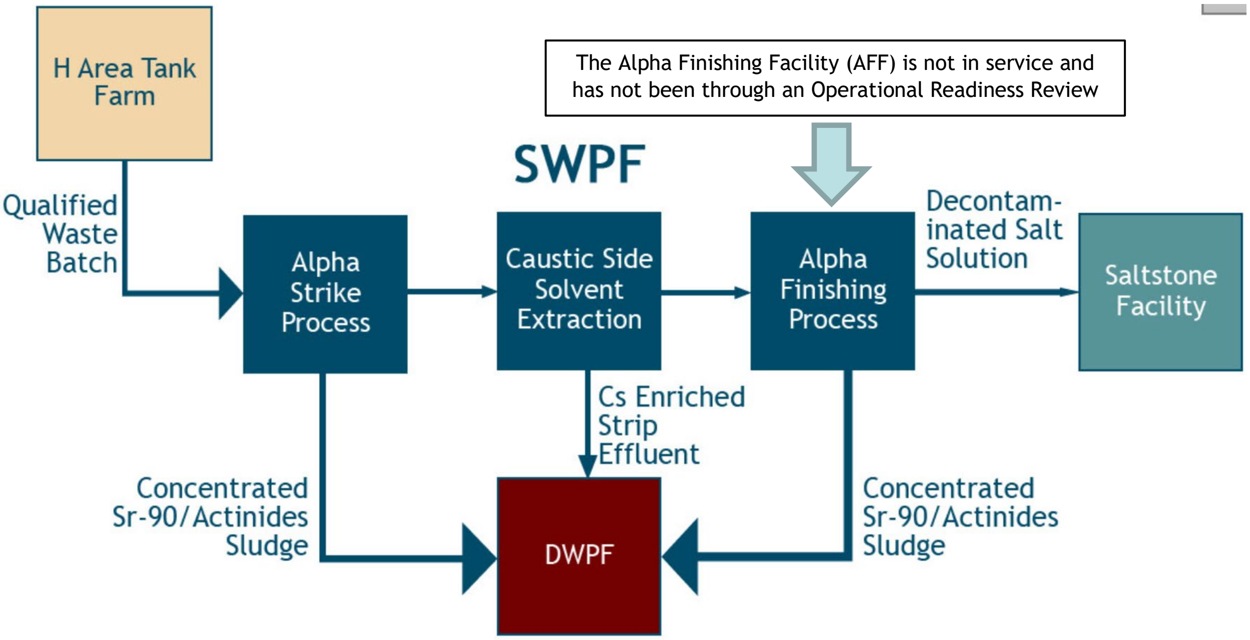

Fig. 1. SWPF Basic Unit Operations Process Flow Diagram.

The customized solvent currently being used is known as BOBCalix solvent. The solvent replacing BOBCalix at the SWPF in FY2023 is NGS. NGS will bring better radioactive cesium removal efficiency and has the potential to increase throughput at the SWPF. In fact, the SWPF has the capability of processing up to approximately 32 million liters (9 million gallons) of salt waste per year after the NGS is implemented. This is not the first time NGS has been implemented at SRS. NGS was also implemented and showed success in the ARP-MCU system. This paper will discuss the specific solvent mixture for BOBCalix and NGS, NGS supply and production status, BOBCalix and NGS CSSX process, the benefits of the new boric acid strip and sodium hydroxide scrub with the implementation of NGS, the new NGS building infrastructure, and Savannah River National Laboratory (SRNL) NGS implementation testing and research.

NGS IMPLEMENTATION DISCUSSION

BOBCalix Versus NGS Mixture

BOBCalix and NGS have minor differences in composition that make a huge impact in solvent extraction efficiency. The unique solvent matrix of BOBCalix is an organic chemical composite that is made up of four components. The first chemical in the BOBCalix mixture is Isopar®L. Isopar®L makes up most of the solvent at 69.14% by mass and is the carrier of the other three solvent components. Isopar®L provides good stability and promotes good hydraulics due to its low density and viscosity. The next component is Calix[4]arene-bis(tert-octylbenzo-crown-6), or BOBCalixC6 extractant. It is a white powdery substance and can be seen in Figure 2. BOBCalixC6 makes up 0.94% of the solvent by mass and has a molarity of 0.007 M. It is the specially developed component of the CSSX solvent that is designed to extract the cesium from the clarified salt solution and is why the solvent is called BOBCalix. The third component is 1-(2,2,3,3-tetrafluropropoxy)-3-(4-sec-butylphenoxy)-2-propanol, or Cs-7SB modifier. It is yellowish-clear, syrupy liquid and can be seen in Figure 3. Cs-7SB makes up 29.8% of the solvent by mass and has a molarity of 0.75 M. It is the constituent of the solvent that functions to prevent the BOBCalixC6 extractant from separating out of the solvent. The modifier is not soluble in water but is soluble in the solvent and it will dissolve the extractant. In other words, the modifier is added to the solvent to dissolve the extractant and hold it in the solvent. The last component is Tri-n-octylamine or TOA suppressor. TOA makes up 0.12% of the solvent by mass and has a molarity of 0.003 M. TOA is a component of the solvent that increases stripping efficiency by suppressing the effect of impurities on the stripping process.

Fig. 2. BOBCalixC6.

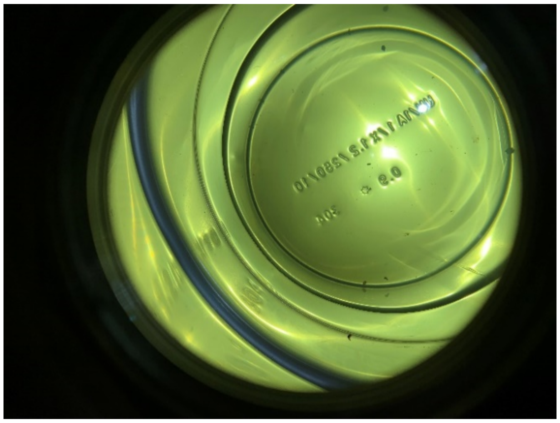

Fig. 3. Cs-7SB.

Like BOBCalix, NGS is also a unique solvent matrix with an organic chemical composite that is made up of four components. However, NGS differs from the BOBCalix mixture in two of the four components. The Isopar®L and Cs-7SB modifier are the same as in the BOBCalix, but the extractant and suppressor are changed for NGS. The new extractant is 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arene-benzocrown-6, or MAXCalix. It is a white powdery substance. The MAXCalix functions like the BOBCalixC6 and is the specially developed component of the CSSX Solvent that is designed to extract the cesium from the clarified salt solution. The molecular structural differences between BOBCalixC6 and MAXCalix can be seen in Figure 4. The new suppressor is *N*,*N*',*N*''-tris(3,7-dimethyloctyl)guanidine, or TiDG. TiDG is a white solid particle substance and can be seen in the drying process in Figure 5. The TiDG suppressor functions similar to the TOA and is a component of the solvent increasing stripping efficiency by suppressing the effect of impurities on the stripping process. This guanidine type suppressor works best with the boric acid strip solution which will be described in the BOBCalix Versus NGS CSSX Process section below. The Isopar®L and Cs-7SB modifier will function and serve the same purpose with the NGS as in the BOBCalix. The exact composition of NGS is to be determined based on results of future SRNL testing which will be discussed in the SRNL NGS Implementation Testing and Research section.

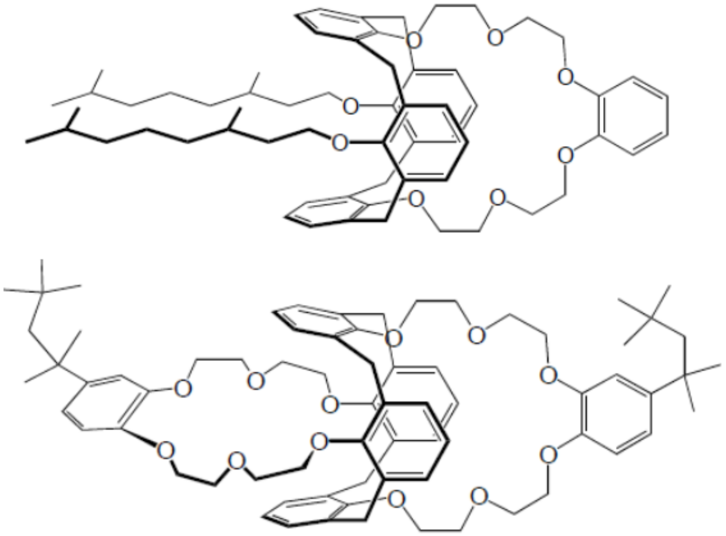

Fig. 4. Molecular structure of MAXCalix (Top) and BOBCalixC6 (Bottom).

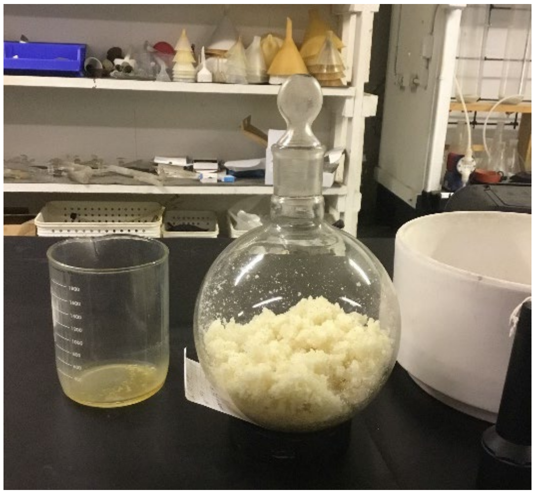

Fig. 5. TiDG in Drying Process.

NGS Supply and Production Status

The NGS initial fill and first trim chemicals have been ordered. The NGS initial fill chemicals have been received, and the trim chemicals are in production. Due to not having an exact composition for NGS being implemented at the SWPF, the NGS chemicals were conservatively estimated and purchased based on past ARP-MCU processing solvent composition and past literature reviews on NGS composition. The estimated concentration for each component was 0.003 M TiDG suppressor, 0.64 M Cs-7SB modifier, 0.05 M MAXCalix, and diluent Isopar®L. Based on preliminary results from SRNL testing, the NGS composition is not expected to be significantly different than the estimated concentration, and the purchased supply is expected to be sufficient for SWPF processing.

BOBCalix Versus NGS CSSX Process

The CSSX process using NGS will be different than the current process using BOBCalix. There are four major stages in the CSSX process: Extraction, Scrub, Strip, and Wash. The first stage has to do with cesium extraction and the other three have to do with solvent recovery. Each stage has contactors which mix two liquids and then use the dissimilar densities of the liquids to separate. This is all done through the spinning of a rotor. The solvent has a much lower density than the other chemicals used in CSSX allowing for the separation.

The BOBCalix CSSX process can be seen in Figure 6. In the BOBCalix extraction stage, the Clarified Salt Solution (CSS) from the ASP comes in contact with the BOBCalix solvent, and the solvent removes the cesium. The DSS is then sent to a storage tank and eventually to Saltstone via a hold tank. The solvent also removes some impurities like K^+ and Na^+ which is the reason for the scrub stage. The scrub stage contacts the solvent with 0.05 M nitric acid (HNO_3). The low pH (acidic) environment causes the impurities to form soluble salts with nitrate ions like potassium nitrate (KNO_3) and remove them from the solvent. However, the cesium remains in the solvent. Next, the cesium-laden solvent is contacted with 0.001 M nitric acid in the stripping stage. The 0.001 M nitric acid introduced during the stripping stage has a comparatively lower concentration of nitrate ions. Since chemical concentrations naturally seek equilibrium, there is a natural tendency for the solvent nitrate ions to migrate to the acid solution in the contactors. This is called nitrate-swing and as a result causes the removal of the cesium from the solvent. As mentioned, the strip effluent is sent to DWPF for vitrification through a hold tank. Lastly, a caustic wash with 0.01 M sodium hydroxide (NaOH) is contacted with the solvent. The suppressor and modifier contained in the solvent degrade over time and form impurities and pick up nitrates that change the pH and hinder solvent performance. Caustic wash removes these impurities and neutralizes the solvent. The solvent is then sent back to the hold tank for reuse.

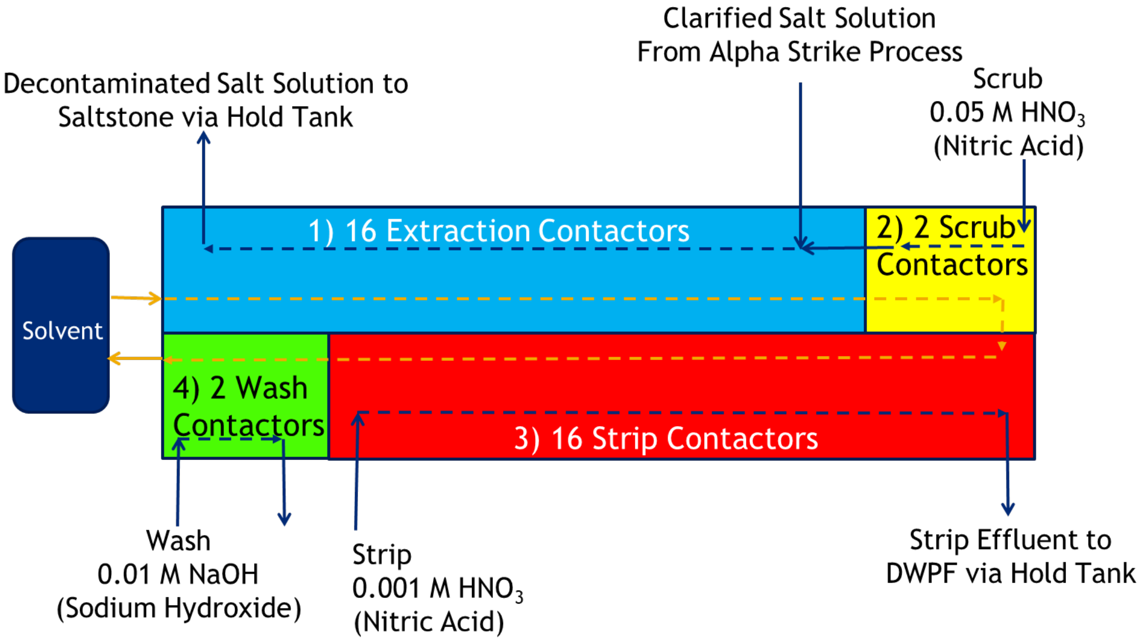

Fig. 6. BOBCalix CSSX Process Flow Diagram.

The NGS CSSX process can be seen in Figure 7. The stages have remained the same from the BOBCalix CSSX process but some of the chemicals that interact with the solvent have changed. In fact, the extraction and wash stages are the same. The difference with NGS solvent implementation involves the scrub and strip stages. Instead of nitric acid scrub as with the BOBCalix system, the NGS system will use a 0.025 M sodium hydroxide scrub. The sodium hydroxide interaction will be similar to the nitric acid interaction with the environment causing the impurities to form soluble salts, but instead of with nitrate ions, with hydroxide ions like potassium hydroxide (KOH). They are then removed from the solvent and the cesium remains as with the BOBCalix scrub. The switch to an alkaline scrub was necessary with the implementation of NGS so that not only will potassium be additionally removed, but the nitrate in the solvent will also be replaced by hydroxide equivalents. The hydroxide equivalents can then react with boric acid in the strip solution to make inextractable cesium borate, effecting super-efficient stripping [1]. Therefore, the NGS system uses a 0.01 M boric acid (H_3BO_3) for the stripping stage. Similar to the nitric acid stripping in the BOBCalix system, since chemical concentrations naturally seek equilibrium, there is a natural tendency for the basic hydroxide ions to migrate to the acidic solution in the contactors. This is called pH-swing instead of nitrate-swing and causes the removal of the cesium from the solvent. The benefits of NGS, boric acid strip and NaOH scrub in the CSSX process are described in the next section.

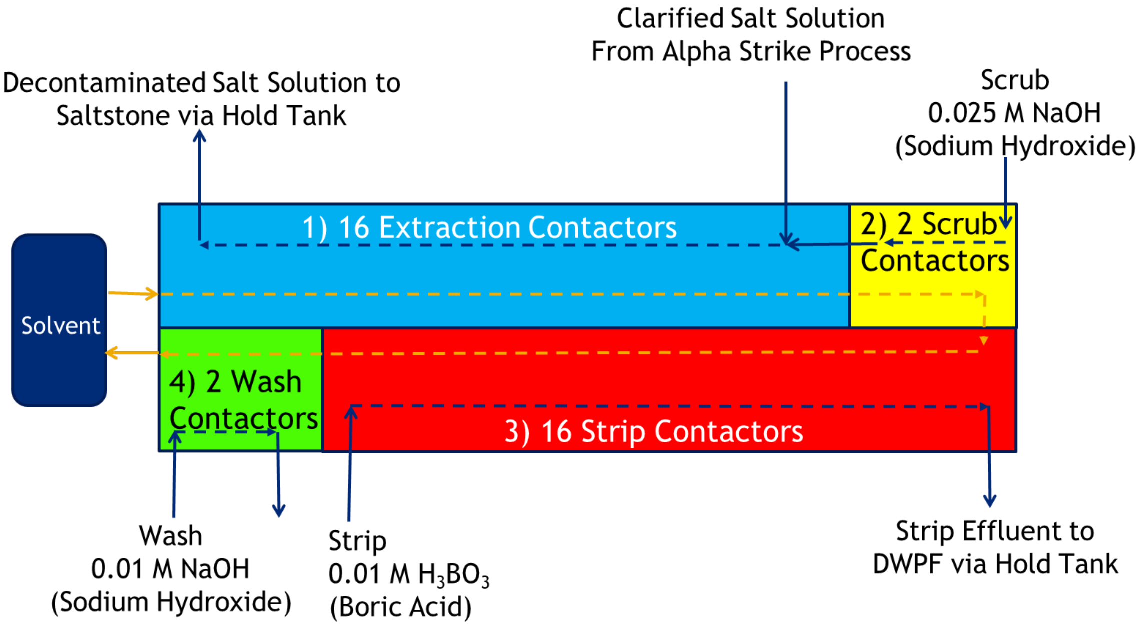

Fig. 7. NGS CSSX Process Flow Diagram.

Benefits of NGS, Boric Acid Strip, and NaOH Scrub

The implementation of NGS, boric acid strip, and NaOH scrub will have many benefits to the SWPF. One benefit is boric acid is a vitrification-friendly acid which is important for the strip effluent going to DWPF. In addition, the boric acid strip and NaOH scrub combination create a sharp decrease in cesium distribution ratio (D_{Cs}) on stripping going from a nitrate-swing to a much more effective pH-swing cycle [1]. In other words, they allow for more efficient removal of cesium from the solvent during stripping. The NaOH scrub also allows for better compatibility with the alkaline conditions of extraction, eliminating one possible source of particulate solids and its attendant difficulties due to aqueous carryover into scrubbing and scrub solution mixing with waste feed in the first extraction stage. Consequently, aluminate precipitation upon neutralization of drops of waste feed is avoided. This is important when it comes to reducing crud formation and the clogging of the coalescers, which are a separate part of solvent recovery [1]. Furthermore, without the new strip/scrub chemistry, the increased calixarene concentration in the solvent would simply increase the stripping D_{Cs} by the same factor as extraction [1]. In other words, the boric acid strip and NaOH scrub help eliminate impurity build up with the NGS solvent. Lastly and most importantly, the implementation of NGS has the benefits of providing a higher cesium decontamination factor (DF) or removal of cesium and the potential to increase throughput in the SWPF by 5-20% [1]. As a result, the implementation of NGS, boric acid strip, and NaOH scrub will provide a better and more efficient SWPF.

NGS Building Infrastructure

Additional infrastructure was built for the implementation of NGS with the boric acid strip and NaOH scrub. More specifically, an entirely new building was constructed for NGS implementation. The arrow in Figure 8 points to the NGS Building in relation to the entire SWPF. This building houses the Boric Acid Strip Receipt Tank, Boric Acid Strip Feed Tank, and Caustic Scrub Feed Tank, as seen in the drawing in Figure 9. NGS will be stored in the same Solvent Hold Tank that currently holds the BOBCalix. The NGS Building, infrastructure, and systems will be ready for operation in FY2023 following a system check on the equipment which has been installed but not operated.

Fig. 8. NGS Building Location.

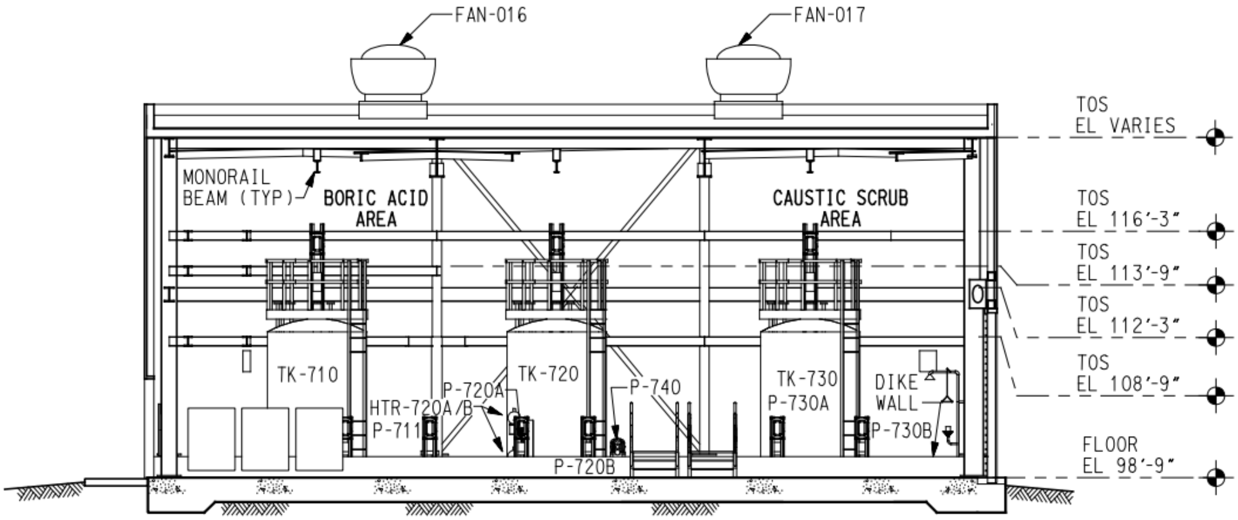

Fig. 9. NGS Building Drawing.

SRNL NGS Implementation Testing and Research

The contactors used in SWPF are larger and have a higher flowrate than the MCU contactors where NGS was used. This size and flowrate difference resulted in knowledge gaps for the conversion to NGS in

SWPF. Targeted testing at SRNL is needed to close those knowledge gaps. The most important gap is determining the correct ratios of components in the NGS solvent to match the physical properties of the BOBCalix. This laboratory testing at SRNL is determining density, surface tension, interfacial tension, viscosity, and third phase formation to create the correct NGS ratios. The risk of not having similar physical properties could result in the need to adjust the contaminated SWPF contactor weirs for the extraction bank contactors and strip bank contactors. Improper weir sizes could create operational issues due to hydraulic instability stemming from excessive aqueous carryover downstream. SRNL is also performing literature reviews on NGS thermolytic hydrogen generation rate (HGR), radiolytic G-value, vapor-pressure curve, and partitioning ratio to address potential flammability in SWPF. The flammability information will be used in the development of the SWPF Safety Basis for NGS implementation. Lastly, SRNL is performing NGS guanidine suppressor degradation analysis which involves identifying and testing the potential impact of guanidine degradation products on the SWPF process. Degradation of the NGS suppressor creates the risk of accumulation of an impurity and detracts from solvent performance, reducing DF and other potential issues and increasing frequency of trimming. Presently the testing and research from SRNL has been going well, and there have been no impacts to NGS implementation at the SWPF.

CONCLUSION

NGS is on track to be implemented at the SWPF in FY2023. The benefits of implementing NGS in the SWPF lie in the potential faster processing rate and a higher cesium DF. NGS initial fill and first trim chemicals have been ordered. The NGS initial fill chemicals have been received, and the trim chemicals are in production. The remaining work for implementation of NGS are to complete the SRNL testing, update and implement the SWPF Safety Basis for NGS, and perform a system check on the NGS equipment previously installed but not operated.

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