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Savannah River Salt Processing Options Study

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EXECUTIVE SUMMARY

The Department of Energy's Savannah River (DOE-SR) Field office requested the Savannah River National Laboratory (SRNL) to develop alternative salt processing options/strategies that could be deployed in SRS Salt Processing facilities, mainly the Actinide Removal Process (ARP) -Modular Caustic Side Solvent Extraction Unit (MCU) with a change in operating philosophy to a technology demonstration approach. The goal of these optional strategies is to reduce the overall risks to the Savannah River Site (SRS) salt processing program for the remainder of the operational life cycle. This can be accomplished in a number of different ways. For example, strategies that increase the long-term throughput and operating envelope for ARP-MCU would reduce the risks and ensure a swift and successful startup of the Salt Waste Processing Facility (SWPF) or developing an alternative approach which accomplished alpha and strontium removal in a novel manner.

SRNL formed a team with broad HLW processing experience to brainstorm ideas that would fit within the defined assumptions for the study. There were four key assumptions that were foundations of this study:

- nominally four million gallons of salt waste would be processed,
- strategies would be deployed and tested within a four-year operating window,
- Salt Batch 7 was assumed to be processed prior to implementing any new strategies,
- the study was not limited to the current High Level Waste System Plan.

The ideas were documented and rankings of the benefits and probability of success of these ideas were judged by the team. An averaged benefit and probability score was used to develop a listing of the highest ranked ideas. With the stated assumption that the ARP-MCU will be operated in a demonstration-oriented philosophy, SRNL recommends that DOE-SR consider the three highest ranked ideas for deployment:

1. Demonstrate the ARP and the caustic-side solvent extraction (CSSX) processes with wastes containing higher sodium concentrations to reduce the overall volume of salt to be processed.
2. Demonstrate the rotary microfilter (RMF) technology under radiological conditions in the 512-S filtration process to increase throughput in ARP-MCU for the remaining operational window and to demonstrate this technology for other potential deployments across the DOE complex.
3. Demonstrate Saltstone performance with higher sodium and aluminum containing wastes as well as higher waste to premix ratios to reduce the overall volume of grout produced over the life cycle of the SRS salt waste program.

A second, slightly lower ranked set of ideas showed both benefit and probability for reducing the risks in the SRS salt waste program and SRNL recommends that these be considered as well. Of this second set, the idea of processing wastes containing higher alpha (principally $^{238,239,240}Pu$), ^{237}Np and ^{90}Sr activities ranked the highest. Processing this material would demonstrate the performance of the alpha removal process that will be necessary when the SWPF is operational which would be highly beneficial. The wastes that have been processed to date in ARP have not required any strontium or alpha removal to meet the Saltstone Waste Acceptance Criteria (WAC) limits. Therefore, the alpha-removal process has not been challenged at the radiological pilot scale as much as the solvent extraction technology has been exercised.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
CF	Concentration Factor
CSSX	Caustic-Side Solvent Extraction
DOE-SR	Department of Energy Savannah River
DSS	Decontaminated Salt Solution
DWPF	Defense Waste Processing Facility
ESS	Extraction-Scrub-Strip
ISDP	Interim Salt Disposition Process
LAW	Low Activity Waste
MCU	Modular CSSX Unit
mMST	Modified Monosodium Titanate
MST	Monosodium Titanate
NGS	Next Generation Solvent
PSD	Particle Size Distribution
RMF	Rotary Microfilter
SCIX	Small Column Ion Exchange
SDU	Saltstone Disposal Unit
SE	Strip Effluent
SFT	Salt Feed Tank
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation, LLC
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
WAC	Waste Acceptance Criteria
WTP	Waste Treatment and Immobilization Plant

1.0 Introduction

The High Level Waste that is stored at the Savannah River Site (SRS) is a mixture of sludge, evaporated saltcake, and supernatant liquids created from pH-adjusted chemical residues from nuclear materials production. The sludge has been retrieved on a batch basis since 1996 and immobilized in borosilicate glass in the Defense Waste Processing Facility (DWPF). The saltcake is retrieved through the addition of conditioned water and this material along with the supernatant liquids will eventually be processed in the Salt Waste Processing Facility (SWPF) that is currently under construction.

The Interim Salt Disposition Process (ISDP) was placed into operation during the spring of 2008 and consists of two processes developed to remove strontium (Sr), actinides, and cesium (Cs) from alkaline waste: the Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Extraction Unit (MCU). The ARP process involves two agitated strike tanks where monosodium titanate (MST) is added to the salt solution in the 241-96H Tank Farm facility with a nominal contact time of 6 to 12 hours. The MST is added to remove the majority of the soluble Sr and actinides from the salt solution. After filtration to remove the MST solids, the solution is transferred to one of three feed tanks in MCU where it is processed through a solvent extraction process to remove cesium. The byproducts of the MCU process are a concentrated cesium stream called strip effluent (SE) and a decontaminated salt solution (DSS). The DSS is sent to the Saltstone Production Facility (SPF) via Tank 50H for final disposition in a state permitted landfill. The MST solids and SE are transferred to DWPF for incorporation into the final glass product. Since 2008, the ISDP has processed over 4.2 million gallons of retrieved and diluted salt waste. Figure 1 shows photographs of the current Savannah River salt processing facilities.

ARP **MCU** **Saltstone**

Figure 1. Photographs of the Savannah River Salt Processing Facilities

While more than 99% of the activity from the dissolved saltcake and supernate goes to DWPF, more than 90% of the volume goes to the Saltstone facilities (Production and Disposal) where the waste is mixed with fly ash, blast furnace slag, and Portland cement to produce a cementitious wasteform that is disposed of in engineered vaults referred to as Saltstone Disposition Units (SDUs). Two different SDU designs have been used at SRS. The first, shown with the other designs in Figure 2, was a rectangular design containing a number of disposal cells. The second design, which allowed for more Saltstone to be contained in a given watertight unit, is the cylindrical SDU. These cylindrical SDUs will hold nominally 3 Mgal of grout, which is enough for more than a million gallons of salt waste. In the future, Savannah River Remediation (SRR) has proposed the use of a mega-SDU concept that would hold approximately 30 million gallons of grout as shown in Figure 2.

Figure 2. Various Types of SDUs

Budgetary restrictions may prescribe the construction rate of the mega-SDUs for the grouted waste potentially for several years. There is space in the four remaining circular SDUs for waste disposition on the order of ~4 million gallons of DSS. Therefore, DOE-SR has requested the Savannah River National Laboratory (SRNL) to conduct an options study[1] that examines the salt processing strategies with the goal to reduce the overall SRS salt processing program risk. ARP-MCU has the potential to provide significant risk reduction for the start-up and early operation of the SWPF by executing strategies that will reduce the risk and increase the probability that SWPF will start-up successfully. SRNL was asked to provide an option study that examines these potential strategies that include the following:

- Determine optimal feeds to process through ARP-MCU to provide better technical understanding for future operations;
- Document what will be learned and benefits to the overall salt processing program; and
- Determine whether testing is needed to support the proposed processing options.

Depending on the operating assumptions and target for risk reduction the relative benefits of ideas can change fairly dramatically. As defined below, the SRNL technical team evaluated a series of process strategies that could lead to an overall reduction in programmatic risk for the SRS salt program.

[1] July 2013 Financial Plan.

2.0 Team Approach

Over a period of several weeks, the SRNL team members met to discuss various concepts and ideas. The team discussed four major assumptions for this study. These key assumptions included: 1) nominally 4 Mgal of salt waste could be processed in the existing Saltstone SDUs; 2) the operating window is for the near term nominally four years; 3) Salt Batch 7 would be processed and will not be available to support these efforts; and 4) the team was not constrained by the current System Plan 18 waste processing strategies.[2] All of the ideas that were developed were binned into one of four general categories:*

- Enhance Confidence in SWPF Startup (4 ideas)
  These ideas would reduce the risk of startup related issues to ensure the maximum amount of waste is processed during the first year of operation.
- Demonstrate New Technology Deployments (11 ideas)
  These ideas would deploy new technologies that would improve process operations by replacing outdated technologies.
- Increase Range of Performance in Radiological Environments (4 ideas)
  These ideas would expand operating windows to reduce the overall risk and theoretically reduce the amount of waste needed to be treated.
- Demonstrate Improved Strategies to Increase Throughput (10 ideas)
  These are ideas that would increase the amount of salt waste that could be processed through ARP for its life cycle and/or SWPF for the remainder of the mission.

*It should be noted that ideas could fit in one or more bins. The exact bin was not used as a differentiating factor.

Once a list of applicable ideas was generated, later sessions were used to evaluate each of the ideas in terms of benefit and probability. The benefit was defined as the relative degree of beneficial results to reduce the overall salt processing risks, while the probability was the relative likelihood of being able to implement the idea and whether the result would be conclusive whether positive or negative. For benefit, a high ranking was given to those ideas that would provide information that greatly reduces the risk for the salt program, increases confidence in SWPF startup and operation, or reduces salt mission duration and cost. A medium ranking was given to those ideas that would likely lead to an increased salt throughput or slight reduction in life cycle costs. Lastly, a low ranking was given to those ideas that will provide some information to reduce risk in the salt program but, alone, will not mitigate risk. The idea may provide some immediate benefit but not for the long term. Several factors were assimilated under the benefit definition including risk reduction, life cycle cost reduction, increased throughput, reduced volume of waste forms, increased confidence in flowsheet, improved confidence in successful startup, and cost of implementation versus return on investment. Appendix A contains a tabular version of the individual idea descriptions.

[2] D. P. Chew and B. A. Hamm, “Liquid Waste System Plan Revision 18,” SRR-LWP-2009-00001, Rev. 18, June 24, 2013.

For the probability definition, the rankings were similar. A high ranking was given to those ideas that could be completed within the four year processing window (which includes technology maturation, deployment and operational time to assess the outcome) and the outcome would be very likely to be successful. A medium ranking was given to those ideas that are likely to be completed within the four year processing window and were likely to provide a successful outcome. A low ranking was given to those ideas that would be very difficult to implement or that required lengthy predecessor work that would not likely be complete prior to the end of the processing window. The factors under the probability definition included technical maturity, regulatory acceptance, and authorization basis changes.

Once the list of ideas was established, the team members independently reviewed each idea (from all 4 categories) and rated it in terms of benefit and probability. After rating the ideas, the team collectively went through the ratings and discussed the pros and cons. In some cases, team members researched and provided additional information about a particular idea. With the additional information, team members were allowed to change their rating. The ratings were converted into number values (Low=1, Medium=2, High=3). The multiple benefit and probability ratings for each idea were averaged. A single rating value was derived as the product of the average benefit and probability scores. See Table 1 for the list of ideas. Appendix B contains the individual grades for probability and benefit for each of the ideas.

Table 1. List of Ideas

1.0	**Enhance Confidence in SWPF Startup**
1.1	Obtain radiological performance data for the Parsons V-10 centrifugal contactor design by installing in MCU
1.2	Test the removal of temperature control on the CSSX system with Next Generation Solvent to reduce design, construction and operational costs for SWPF
1.3	Demonstrate performance of SWPF coalesce/contactor materials with actual waste in MCU
1.4	Demonstrate Concentration Factor (CF) increases to reduce water load to DWPF
2.0	**Demonstrate New Technology Deployments**
2.1	Demonstrate mMST at the radioactive pilot scale
2.2	Demonstrate large tank MST strike
2.3	Increase ARP throughput by removing alpha/Tc/I by using a tea bag approach to radionuclide removal
2.4	Decontaminate cesium from the Strip Effluent stream using an inorganic ion exchange material to avoid sending the volume to DWPF
2.5	Test RMF as a parallel filter train in ARP
2.6	Demonstrate an on-line organic monitor
2.7	Demonstrate other on-line monitoring capabilities, e.g., Cs, gamma monitor, solvent composition
2.8	Demonstrate Saltstone performance with high Al salt, high waste to premix ratio, and higher Na
2.9	Demonstrate an alternative disposition pathway for Drain Water Return System
2.10	Demonstrate TcO4- Removal using the Current Solvent Extraction System
2.11	Demonstrate Salt-Only Glass Production at DWPF
3.0	**Increase Range of Performance in Radiological Environments**
3.1	Process salt at higher sodium concentrations
3.2	Process higher alpha- (Pu-238 such as T39 and/or Np in T33/34) and strontium-containing wastes to test the MST radionuclide removal process
3.3	Increase Temperature across ARP-MCU to increase throughput
3.4	Increase cesium concentration to demonstrate solvent radiolytic stability
4.0	**Demonstrate Improved Strategies to Increase Throughput**
4.1	Lower the amount of sodium hydroxide needed to keep Al in solution
4.2	Develop an operational model of ARP-MCU by developing a better understanding of the relationship between lab and facility decontamination factors
4.3	Demonstrate a containerized grout and store pour containers till Saltstone vault is available
4.4	Divert Caustic Wash solutions to reduce overall volume of Decontaminated Salt Solution (DSS)
4.5	Investigate whether one could store DSS in a “ready to close” waste tank as Low Level Waste and process through Saltstone once vaults are available
4.6	Demonstrate a larger and narrower Particle Size Distribution for MST to increase filter flux
4.7	Demonstrate an optimized MST addition strategy rather than a purely batch addition approach
4.8	Demonstrate Nitric Acid cleaning versus Oxalic Acid in 512-S
4.9	Validate Scaling Factor Approach to reduce Salt Qualification durations
4.10	Eliminate washing of MST concentrate in ARP process

3.0 Results and Discussion

As discussed in the Team Approach section, the group developed ranking scores for each of the ideas, in terms of Benefit and Probability. Scores for each term were either high (3), medium (2), or low (1), with higher values being better. The individual rankings for each term were then averaged, generating average Benefit and Probability scores of 1-3 for each idea. Then, for each idea, a final score was mathematically generated from the Benefit and Probability scores in the following fashion:

$$\text{Final Rating} = 0.5\times\text{Benefit} + 0.5\times\text{Probability}$$

This generated a Final Rating for each idea that ranged from 1-3 points.

This list of ideas was reviewed and Table 2 contains the list of ideas with final ratings of 2.4 or higher (80% of the maximum possible of 3), in descending order.

Three ideas have the highest values. There is then a break in the values and four other ideas form a natural second grouping. Additionally, a sensitivity analysis was conducted whereby the weighting factors were changed from 0.5 to 0.25 and 0.75 for each of the benefit and probability and then reversed.

Table 2. Ideas with a Final Rating of 2.4 and Higher

Idea	Final Rating
3.1 Process salt at higher sodium concentrations	2.83
2.5 Test the Rotary Microfilter (RMF) as a parallel filter train in ARP	2.67
2.8 Demonstrate Saltstone performance with high Al salt, high water to premix ratio, and higher Na	2.67
3.2 Process higher alpha- (Pu-238 such as T39 and/or Np in T33/34) and strontium-containing wastes to test the MST radionuclide removal process	2.50
2.2 Demonstrate large tank MST strike	2.50
4.7 Demonstrate an optimized MST addition strategy rather than a purely batch addition approach	2.42
4.8 Demonstrate nitric acid cleaning versus oxalic acid of the crossflow filter in 512-S	2.42

3.1 Discussion of Highest Ranked Ideas

The highest ranked idea is to demonstrate alpha removal, filtration to remove MST and insoluble solids, and CSSX processes on salt waste with a higher sodium concentration on the order of 7 to 9 M sodium. The Next Generation Solvent (NGS) system that is being incorporated into the

MCU flowsheet has many advantages including higher Cs decontamination, higher extractant concentration, and perhaps better organic carryover behavior. Additionally, recent experimental results indicate that the NGS system is capable of decontaminating salt solution with higher sodium concentrations; perhaps as high as 8M Na.[3] The benefit of processing at higher sodium concentrations is two-fold. There is a possible reduction in the overall volume of salt waste that would need to be treated and a concomitant reduction in the amount of SDU space that would be required for disposal. Moreover, there is a secondary benefit to processing higher sodium-bearing feed and that is that the cesium concentration would be higher and would be processed into an immobilized form in a more timely fashion. This would reduce the risk of cesium being stored in the tank farm. One promising aspect to this idea is that the level of sodium can be raised incrementally. For example, MCU has already operated with sodium values above 6.4 M in the feed solution. The Saltstone WAC allows sodium concentrations as high as 7 M without a deviation. The feed sodium concentration could be raised by reducing the dilution of feed batches, until the effective practical limit is reached for ARP/MCU.

The baseline sodium concentration for SWPF is 6.44 M. This was based on a composited average of all the wastes in the tank farms. The dilutions that occur across the processing unit operations bring the concentration down to 5.6 M. Adjusting to ~8 M would not solubilize some low solubility salts like phosphate, sulfate, and oxalate. Solubilizing these salts would result in a solution composite that would be fairly low in sodium concentration. A more detailed modeling exercise is needed to determine a realistic volumetric reduction in total waste volume being sent to Saltstone.

Processing at higher sodium concentration includes risks associated with higher viscosity of the salt solution being processed and increased probability of solids formation, e.g., sodium aluminosilicate, across the ARP-MCU facilities that will need to be addressed. Additionally, the hydraulic performance of the centrifugal contactor at this feed density would need to be demonstrated. Thus, there is a significant benefit to demonstrate processing at higher sodium concentration in the ARP-MCU before SWPF starts processing. One concern about demonstrating this idea in ARP-MCU is whether there is available feed that would have high sodium concentration while meeting the feed specification for ARP-MCU of 1.1 Ci/gal.[4] Recent work by Martino and Coleman[5] indicate that Tank 38H has an average sodium concentration of 7.9 M, and a recent memorandum by Martino[6] showed the radiocesium level to be very low and on the order of 0.2 Ci.

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[3] B. A. Moyer, J. F. Birdwell, Jr., L. H. Delmau, N. C. Duncan, D. D. Ensor, T. G. Hill, D. L. Lee, B. D. Roach, F. V. Sloop, E. L. Stoner, and N. J. Williams, "Next Generation Solvent Development for Caustic-Side Solvent Extraction of Cesium," ORNL/TM-2013/224, Rev. 1, June 2013.

[4] Waste Solidification Engineering, "Waste Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility (U)," X-SD-Z-00001, Rev. 10, March 2011.

[5] C. J. Martino and C. J. Coleman, "Evaporator Feed Qualification Analysis of Tank 38H and Tank 43H: January 2010 through April 2013," SRNL-STI-2012-00464, Rev. 0, August 2013.

[6] C. J. Martino, SRNL-L3100-2013-00068, April 2013.

Two other ideas had rankings above 2.4. The first of these two ideas was to install a rotary microfilter in a parallel mode to the crossflow filtration process within 512-S. Installation of the RMF will increase ARP throughput by increasing filtration capacity and allowing for filtration of feed while the crossflow filter is being chemically cleaned. Deployment would demonstrate the DOE-developed technology at a technology readiness level that would make other deployments such as small-column ion exchange (SCIX) at Savannah River or Hanford or continuous sludge washing possible. A Technology Readiness Assessment of SCIX[7] indicated that the RMF was ready for deployment needing only an integrated test for coupling with ion-exchange equipment. The second idea of these two ideas that was fairly highly rated was to operate the SPF under higher sodium concentrations. Additionally, included in this idea was to expand and optimize the operating window to allow for higher aluminum content in the waste and optimizing the waste to premix ratio to enhance waste loading.

The idea for SPF deployment of higher sodium/aluminum-containing wastes would couple well with other ideas such as demonstrating alpha removal. It was, however, kept separate because other technologies e.g., at-tank evaporation[8] could be utilized to increase the sodium concentration in the Saltstone feed prior to transferring from Tank 50H without having to operate the pretreatment facilities at the high sodium concentration. The SRS SPF typically processes DSS from Tank 50H at a sodium concentration of around 5 M. A recent SRNL study in support of Hanford has demonstrated the ability to fabricate cementitious waste forms with DSS at sodium concentrations up to 10 M.[9] Concentrating the DSS has a substantial impact on the volume of the cementitious wasteform needed to immobilize a given amount of waste, as depicted in Figure 3. For example, an increase in DSS sodium molarity from 5 M to 8 M would result in about a 40% reduction in the volume of grout produced (at the current SPF water to premix ratio of 0.60). This would provide a substantial cost savings and reduce the number of SDUs needed to complete the SRS mission. Increasing the DSS to dry blend ratio (typically described as water to premix ratio) also reduces the necessary volume of grout, although the effect is less pronounced.

[7] H. Harmon, et al., “Small Column Ion Exchange Technology at Savannah River Site Technology Readiness Assessment Report,” November 2011.
[8] A. R. Tedeshi, J. E. Corbett, R. A. Wilson, and J. Larkin, “Full Scale Technology Maturation of a Thin Film Evaporator for High-Level Liquid Waste Management at Hanford,” WRPS-51528-FP, Rev. 0, January 25, 2012.
[9] K. M. Fox, K. A. Roberts, and T. B. Edwards, “Cast Stone Formulation at Higher Sodium Concentrations,” SRNL-STI-2013-00499, Rev. 1.

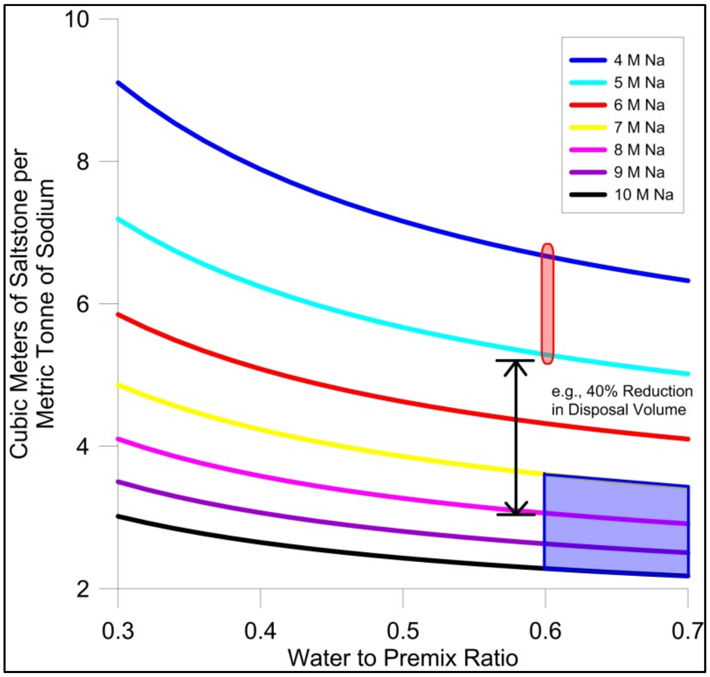

Figure 3. Estimated volume of grout needed to immobilize a given mass of sodium as a function of sodium molarity and water to premix ratio. (from ref. 9)

Red shaded area approximates region of recent SPF operation. Blue Shaded area approximates region investigated in recent high sodium Cast Stone study.

The second grouping of ranked ideas (highlighted in yellow in Table 2) contains four ideas which are to process higher alpha and strontium-containing wastes through ARP (3.2), demonstrate a large tank MST strike (2.2), demonstrate an optimized MST addition strategy (4.7), and demonstrate nitric acid filter cleaning (4.8). Since startup in 2008, the feed solutions processed in the ARP facility have had alpha, ^{237}Np, and ^{90}Sr activities that are below the current Saltstone Waste Acceptance Criteria (WAC) limits.[4] Consequently, the performance of MST to remove Pu, Np, and Sr has not been challenged. The low alpha, ^{237}Np, and ^{90}Sr activities have allowed the facility to reduce the quantity of MST added from 0.4 g/L to 0.2 g/L and the contact time from 24 hours to as low as 6 hours in the strike tanks to increase throughput.[10]

The SWPF will process feed solutions that can have much higher alpha, ^{237}Np, and ^{90}Sr activities than those planned for processing in the ARP facility. Currently, SWPF will perform additional strikes with MST if the alpha, ^{237}Np, and ^{90}Sr activities are not reduced sufficiently to meet the Saltstone WAC limits. Even with additional MST strikes, there is a risk that sufficient removal of the alpha, ^{237}Np, and ^{90}Sr will occur at the current flowsheet conditions in SWPF. Testing feed solutions in ARP that have higher alpha, ^{237}Np, and ^{90}Sr activities will determine whether MST

[10] D. T. Hobbs, D. T. Herman, M. R. Poirier, "Decontamination Factors and Filtration Flux Impact to ARP at Reduced MST Concentration", SRNL-STI-2012-00299, rev. 0, June 2012.

performance is sufficient at the current baseline flowsheet for SWPF and is highly recommended by the team as a salt program risk reduction activity.

A large tank MST strike would add MST directly to the large tanks in the tank farm as was planned as part of the SCIX project.[7] The MST would be mixed with the tank contents. After mixing for some period of time, the mixing would be stopped and the MST allowed to gravity settle. The supernatant would then be decanted off of the settled solids, polished filtered if required and transferred to the solvent extraction process. The MST solids used in the large-tank treatment operation would eventually be processed in combination with the sludge solids. In addition to demonstrating MST performance in a large-tank mode as planned for the suspended SCIX project, this activity would be expected to increase throughput in MCU. Since the bulk of the MST solids would have gravity settled, the solids content sent to the crossflow filters in 512-S (or a deployed RMF) would be much smaller resulting in higher filtration fluxes. Furthermore, the contact time between the MST solids and the supernatant would be decoupled from that in the current ARP operation. Consequently, the throughput to the MCU operation would be increased compared to the current operation. It should be noted that MST has been directly added into an SRS waste tank before as part of the In-Tank Precipitation process and remains safely stored in Tank 48H. The specific of the deployment is not exactly the same as this idea, but the background work could be leveraged.

For the optimized MST addition strategy, the ARP and SWPF flowsheets use a fixed quantity of MST and contact time in the alpha-strike tanks to remove ^{90}Sr and alpha-emitting radionuclides. The concentrations of the radioisotopes change in each macrobatch of salt feed solution. More efficient usage of MST and reduced contact times in the alpha-strike tank could be realized by developing a detailed MST performance model that predicts the quantity and contact time needed to successfully remove ^{90}Sr and alpha-emitting radionuclides at varying feed concentrations.

The last strategy is to demonstrate filter cleaning with nitric acid. One of the predicaments facing ARP is the cause of filter fouling is not known, i.e., what chemical species is blinding the pores. Oxalic acid cleaning, the baseline technology for ARP, is very useful if the fouling is caused by iron- and titanium-based fouling agents. However, cleaning with oxalic acid can produce sodium oxalate solids upon pH-adjustment with sodium hydroxide, which can have adverse impacts on downstream operations including MCU and DWPF. Previous testing has established that 4.0 M nitric acid is also an effective filter cleaning agent for crossflow filters particularly for aluminosilicates.[11]

A significant benefit of using nitric acid for cleaning is that it offers the potential for reducing the formation of solids that require processing compared to solids produced using oxalic acid. This benefit was the key driver that led the SWPF to change from oxalic acid to nitric cleaning of their

[11] M. R. Poirier and S.D. Fink, "Investigation of Alternative Cleaning Solutions for Mott Porous Metal Filters," WSRC-TR-2002-00526, Rev. 0, November 12, 2002.

crossflow filters.[12] Note also, the Hanford Tank Waste Treatment and Immobilization Plant (WTP) also specifies nitric acid as the cleaning agent for crossflow filters, although the composition of the largely iron-based sludge solids at the WTP will be different than the titanium-based MST solids at ARP and SWPF.

Implementation of this idea at ARP would provide operating experience with actual waste in advance of SWPF startup. It would also determine if nitric acid cleaning will provide improved removal of filter fouling agents, allow for higher filter fluxes, and result in longer operating periods between cleaning cycles. Before this idea is implemented, the downstream impact to DWPF needs to be considered since the use of nitric acid in place of oxalic acid will increase nitrate sent to and, possibly, alter the reductant demand in the Chemical Processing Cell of the DWPF.

While the initial ratings lead to what appears to be a reasonable set of rankings, SRNL performed two additional rankings in an effort to ensure that differences in the Benefit and Probability weightings did not overly influence the rankings. With the weighting shifted toward benefit, the same three ideas (3.1, 2.5, and 2.8) showed as the highest ranking. There was a natural break following the next four ideas, which were the same four ideas (2.2, 3.2, 4.7 and 4.8) from the equal weighting analysis in only a slightly differing order. When the weighting was shifted toward probability, all seven ideas were included with the top three ideas being the same. However, two new ideas were included in the lower tiered ranking. The highest ranking in the second tier was the idea of demonstrating the Modified Monosodium Titanate (mMST) technology (2.1).

The mMST technology has shown faster kinetics of removing strontium and the actinides with the added benefit of low affinity for sorption of uranium.[13] Also, the quantity of mMST needed to achieve Sr and Pu decontamination factors equivalent to that measured with MST ranges from a factor of 2 to 4 times lower than that for MST.[13] Consequently, this technology could increase the throughput across the SRS salt processing facilities and the SWPF by shortening the batch contact time and increasing filter flux as a result of the reduced solids concentration. There are a number of technical issues that would require resolution prior to deployment in SWPF including the current criticality-related issues. Prior to introducing mMST into the HLW system, testing needs to determine the impact, if any, that mMST has on hydrogen production in the Slurry Receipt and Adjustment Tank within the Chemical Processing Cell of the DWPF.

The other idea in the second tier of the probability-based ranking is the concept of testing the Parsons full-scale contactors in MCU to gain radiological performance data prior to SWPF startup. There are several known design features that are different between the MCU and SWPF

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[2] N. DesRocher, "Mass Balance Model Calculations as a Result of Nitric Acid Replacing Oxalic Acid", M-CLC-J-00143, Parsons Corporation, August 24, 2011.

[13] D. T. Hobbs, M. D. Nyman, T. B. Peters, M. R. Poirier, M. J. Barnes, M. E. Thompson, S. D. Fink, "Tailoring Inorganic Sorbents for SRS Strontium and Actinide Separations: Optimized Monosodium Titanate Phase II Final Report," WSRC-STI-2007-00082, June 2007.

contactors with differing views as to their impacts on processing actual salt waste. Actual operation of the SWPF contactor in the MCU radiological environment would reduce the risk of startup-related issues at the SWPF.

3.2 Additional Development Activities to Support Deployment

For the three ideas that consistently appeared at the top of the rankings, SRNL developed a description of the research and development activities that would be required for deployment. An overview of the perceived scale of experimental work for each idea is given below.

3.2.1 *Process Salt at Higher Concentrations through ARP and MCU (3.1)*

Higher concentrations of salt (higher sodium concentrations) in the SWPF system would potentially decrease the overall volume of salt waste processed, and would more rapidly send the bulk of the cesium to be immobilized at DWPF. Broadly speaking, it is expected that moderate increases in the sodium concentration would not disrupt the system performance as the sodium concentration in MCU has risen to greater than 6 M. However, technology maturation would be necessary in the following areas to allow for a demonstration in ARP in advance of a potential SWPF deployment. The areas include:

- Determine acceptable MST and NGS performance over a range of sodium concentrations from 7 to 10 M. The approach would be to conduct batch tests examining the removal efficiency for both processes and determine the kinetic parameters for the MST testing. All of which would be used to develop an operating window that optimizes throughput for various salt compositions.
- Examine the physical characteristics of the salt solution (density, viscosity, dispersion) to determine impacts on filtration and contactor performance along with the propensity to precipitate solids throughout the process unit operations. The goal is to increase the sodium concentration but establish parameters that keep the volumetric flowrate as close to the maximum. Additionally, solution stability with respect to solids precipitation will be examined.
- Confirm that the higher sodium feeds have acceptable hydraulic properties in the full scale contactors (V-5/10). The goal would be to optimize the contactor performance at the higher sodium concentration at the maximum waste flowrate while minimizing organic carryover to downstream facilities.
- Perform a parametric modeling analysis to better project the reduction in volume of waste that would be disposed in Saltstone.

3.2.2 *Test RMF as a Parallel Filter Train at ARP (2.5)*

SRR currently has 4 rotary filter units in storage. These units were purchased under the SCIX project as field deployable units. SRNL proposes installing two of the units in parallel in a test stand with a cross flow filter. The purpose of the testing would be to develop the implementation operational strategy. No fundamental research is required. Testing would be designed to develop the necessary control automation, develop operational procedures, select and test deployment instrumentation, and train personnel on equipment operations. The major advantage of using the new units is to gain experience with the design changes from the full-scale laboratory units to the production units. Most noticeably is the change from an air seal to a water seal in the production units.

While the procedures and controls are being developed in an integrated demonstration, the layout of the RMFs in the filtration cell will be completed. The layout drawing will include the layout of all connections and utility requirements. This information will then be used for the design and eventual fabrication of the necessary jumpers to deploy the filter units.

3.2.3 *Demonstrate Saltstone Performance with High Aluminum, Salt, High Waste to Premix Ratio and Higher Sodium (2.8)*

The SRS SPF typically processes DSS from Tank 50H at a sodium concentration of around 5 M. A recent SRNL study in support of Hanford has demonstrated the ability to fabricate cementitious waste forms with DSS at sodium concentrations up to 10 M.[14] Thus, it appears reasonable that DSS can be immobilized at a much higher sodium concentration resulting in a significantly reduced volume of grout. For example, an increase in DSS sodium molarity from 5 M to 8 M would result in about a 40% reduction in the volume of cementitious waste form produced (at the current SPF water to premix ratio of 0.60). Various other approaches could be taken to concentrate the DSS feed to the SPF, such as increasing the sodium concentration in ARP/MCU processing, concentration at Tank 50H with a skid mounted evaporator, or adding an evaporator/skid to the SPF. These evaporative processes would lead to the formation of undissolved solids in the Saltstone feed which would need to be evaluated. The Saltstone WAC does allow for the presence of solids in the feed. The operability impacts would need to be addressed.

Development work is needed to implement this approach including:

- Further define the operating window for SPF to map acceptable solution compositional ranges for possible SRS waste feeds.
- Expand the understanding of operating the SPF process with DSS containing undissolved solids (i.e., salts above their solubility limit in solution) in terms of operability (e.g., solid deposition in lines) and waste form performance (e.g., compressive strength, leaching behavior, etc.).
- Characterize the hydraulic properties of grout formulated with concentrated DSS over a range of simulated waste compositions.
- Measure and model the contaminant retention and release from grout formulated with concentrated DSS. Leaching results for Hanford cementitious waste forms formulated at sodium concentrations (simulated DSS) are promising.

[14] K. M. Fox, K. A. Roberts, and T. B. Edwards, "Cast Stone Formulation at Higher Sodium Concentrations," SRNL-STI-2013-00499, Rev. 2.

3.2.4 *Process higher alpha- and strontium-containing wastes to test the MST radionuclide removal process (3.2)*

As previously described, a second tier of activities was evident when reviewing the ranking scores. Of those ideas, the team believed one idea was critical to reducing the overall SRS salt processing program risk. This idea was the concept of performing a demonstration in ARP of decontaminating a feed that is high in alpha and strontium including processing a stream that is high in neptunium content. The rationale is these types of waste will be very challenging for SWPF to process from a throughput perspective as the contact time may be excessive and is compounded by the fact that ARP has not treated a feed that provided a challenge to the alpha removal process. As described above, feed could be made available. In order for this material to be processed in ARP, the following activities would need to be accomplished:

- Complete a sampling of the potential tanks and complete analysis to confirm the high alpha and strontium contents.
- Determine mass:liquid ratios necessary for ARP to reach SWPF release criteria for strontium and actinide concentrations as a function of starting radionuclide concentration.
- Ensure the kinetics of the radionuclide removal over the expected compositional ranges is sufficiently rapid to allow for deployment in SWPF.

3.3 Categorical Review of SRNL Rankings

Another approach to evaluating the ideas is to examine the ranking of each idea within the category into which the ideas were binned. This approach allows one to see the highest ranked ideas within each category and select appropriate ideas to implement if only one category was deemed to be important. For example, if starting up SWPF is the most important category, then examining those ideas would be of highest priority. The four categories used in this evaluation included (1) Enhance Confidence in SWPF Startup, (2) Demonstrate New Technologies, (3) Increase Range of Performance in Radiological Environments, and (4) Demonstrate Improved Strategies to Increase throughput. Summarized below is a discussion for each of these areas.

3.3.1 *Enhance Confidence in SWPF Startup (Category 1)*

Aside from the radiological testing of the Parsons centrifugal contactor design, which only showed in the probability-weighted ranking, there were only three other ideas binned solely in this category. Two of these ideas had a ranking higher than that of the Parsons centrifugal contactor testing. These ideas were demonstrating performance of SWPF coalescer/contactor materials with actual waste in MCU (1.3) and using the Next Generation Solvent technology to increase the concentration factor (CF, the ratio between the volumes of salt feed divided by the volume of strip effluent) across MCU (1.4) to reduce water load to DWPF. The SWPF coalescer is fabricated out of stainless steel mesh; whereas, the MCU coalescer material is a polymeric material. The ARP experience has been high pressure drop across the coalescer from some form of fouling. Therefore, demonstrating the SWPF coalescer/contactor materials with actual waste in MCU has the potential to reduce the salt processing program risks in two ways. The first would be to establish that the coalescer plugging problems experienced in ARP occur at a lower frequency with the SWPF coalescer material and actual waste to better establish performance expectation for SWPF. The second way would be in the SWPF coalescer media does perform better than the downtime for ARP due to the coalescer would be reduced for the remaining processing window. The other idea, Next Generation Solvent technology to increase the CF across MCU, would reduce water load to DWPF, which should increase the throughput in the DWPF by reducing the time required to evaporate the water. If this could be implemented in SWPF, there would be a substantial improvement in the coupled operations of SWPF and DWPF.

3.3.2 *Demonstrate New Technologies (Category 2)*

A number of the ideas that the team has recommended are in this category including the rotary microfilter, the deployment of mMST, and large tank MST strike. Discussion of those ideas can be seen in Section 3.1. There are two other ideas that the team would like to highlight. The first is to demonstrate an alternative disposition pathway for Drain Water Return System (2.9). The SDUs at SRS contain drain water return systems that send excess flush water and bleed water back to the Salt Feed Tank (SFT) at the SPF. This liquid is added to the decontaminated salt solution in the SFT and recycled through the SPF process. The volume of the return liquid can be significant relative to the amount of salt solution processed (on the order of 5% or 10% of the grouted space). Developing and demonstrating an alternative to disposing of this volume to other SRS facilities such as the Effluent Treatment Facility may warrant consideration. The idea scored low on probability due to the team's perception that modifying the facility design to route the drain water to another location would be extremely difficult. The team was unsure whether or not there were systems in place to transfer the liquid to an alternative disposition pathway like a diversion box or transferring the liquid to a trailer for disposal at the Effluent Treatment Facility. The second idea is to increase ARP throughput by augmenting alpha removal by using an in-tank tea-bag approach to radionuclide removal. In this concept, a tea bag containing one or more sorbents is introduced into waste tanks prior to retrieving the waste for processing. This effectively utilizes the time until the waste is retrieved as an opportunity to deploy separations technologies. Furthermore, materials that are effective for other radionuclides such as ^{99}Tc and ^{129}I could be used. The idea was scored low based on its low level of maturity, degree to which mass transfer issues can be overcome, and degree of operational and regulatory approval.

3.3.3 *Increase Range of Performance in Radiological Environments (Category 3)*

The goal of this category is to increase the operating range of a particular unit operation to allow either increases in operating efficiency or throughput. Four ideas were binned in this category and two have already been discussed. Those two were processing higher sodium concentrations (3.1) and processing higher alpha and strontium concentrations through ARP (3.2) to lower the risk of handling these types of solutions in SWPF. However, one idea is worth mentioning in this portion of the report and that is to increase the operating temperature across ARP-MCU to increase throughput (3.3). The idea is that operating ARP-MCU at higher temperatures lowers the viscosity of the salt solution, which would allow for higher filtration rates in the throughput rate limiting step. It is recognized that a higher temperature in the extraction bank of MCU would reduce the decontamination levels. However, with the high DFs using the Next Generation

Solvent, this reduction may still be acceptable and may be worthy of further study. Other aspects that would require study include effects of higher temperatures on the kinetics of solids formation and the increased dissolution of titanium from MST.

3.3.4 *Demonstrate Improved Strategies to Increase Throughput (Category 4)*

There were 10 ideas that were binned in this category with two ideas previously having been discussed. Those ideas were to demonstrate an optimized MST addition strategy rather than a purely batch addition approach (4.7) and demonstrate nitric acid cleaning in 512-S (4.8). Two other ideas rated fairly high, demonstrate a larger and a narrower particle size distribution for MST to increase filter flux (4.6) and validate a scaling factor approach to reduce Salt Qualification durations (4.9).

There are two aspects of implementing a new particle size distribution (PSD) requirement for MST that are contained in this idea. The first is that the PSD for procured MST[15] is typically a bimodal distribution with one peak centered slightly less than 1 µm and the second around 7.5 µm. The second aspect is the recently reported[11] increased amount of fines in the ARP material than that included in historical laboratory and pilot testing. The goal of this idea is to work with the supplier and "size" the MST such that ARP only receives the particles comprising the PSD centered at 7.5 µm to affect an increase in filter flux and potentially limit filter fouling by the finest of the MST particles. SRNL believes the tank farm contractor is pursuing the removal of the fines.

The idea of using scaling factors in salt batch qualification would attempt to couple the data from the previous salt batch analysis and known radionuclide scaling techniques to reduce the number of radionuclides that require quantification. This could reduce the duration and cost of the Macrobatch qualification sampling which will be demanding with the large volumes of waste to be treated in SWPF.

4.0 Conclusions

The DOE-SR requested the SRNL to develop alternative salt processing options that could be deployed in ARP-MCU if the mission of the facility changed to a more demonstration oriented philosophy. The goal of these optional strategies is to reduce the overall risks to the Savannah River salt processing program for the remainder of the operational life cycle. This can be accomplished in a number of different ways. For example, strategies that increase the throughput for ARP-MCU would reduce the risks as would strategies that ensure a swift and successful startup of SWPF. Likewise, technologies that eliminate the bottlenecks for salt processing throughput would be included.

[15] D. T. Hobbs, "Comparison of Particle Size Results of Monosodium Titanate Samples Measured by Microtrac® S3000 and S3500 Instruments," WSRC-TR-2008-00015, Rev. 0, January, 2008.

SRNL formed an experienced, technical team to identify and evaluate ideas that would fit within this conceptual model. There were four key assumptions that were established for this study: nominally four million gallons of salt waste would be processed in this study, the study would examine a four-year operating window, Salt Batch 7 was assumed to be processed, and the study was not limited to the current Savannah River System Plans. These ideas were documented and rankings of the benefits and probability of success of these ideas were judged by the team. An averaged benefit and probability score was used to develop a ranking of the highest scoring ideas. Assuming ARP/MCU adopts a demonstration philosophy, SRNL recommends that DOE-SR consider the three highest-ranked ideas for demonstration:

- Demonstrate the alpha removal process and the CSSX process with wastes containing higher sodium concentrations in ARP-MCU to reduce the overall volume of salt to be processed,
- Demonstrate the RMF technology under radiological conditions in the 512-S filtration process to increase throughput in ARP-MCU for the remaining operational window and to demonstrate that technology for other potential other deployments across the DOE complex, and
- Demonstrate Saltstone performance with higher sodium and aluminum containing wastes as well as higher waste to premix ratios to reduce the overall volume of grout produced over the life cycle of the SRS salt waste program.

A second grouping of ideas showed both benefit and probability for reducing the risks in the SRS salt waste program, and SRNL recommends that these be considered as well. Of this grouping, the idea of processing wastes containing higher alpha, Np, and Sr concentrations ranked the highest. Processing this material would confirm operational performance of MST with waste solutions containing challenging alpha, ^{237}Np, and ^{90}Sr activities.

Appendix A. Ideas Summaries

All of the generated ideas were binned into one of 4 categories. The ideas are listed here in those categories. For each idea, the title, idea description, the mitigated risk or benefit, and the success criteria are described.

6.1.1 Enhance Confidence in SWPF Startup

Title: **Obtain radiological performance data for the Parsons V-10 centrifugal contactor design by installing in MCU**
Description: The design of the centrifugal contactors that are installed in the MCU facility and those contactors designed for use in the Salt Waste Processing facility are not precisely equivalent (different weir configuration, etc.). The concept would be to remove the extraction bank of contactors currently installed at MCU and replace them with the full scale contactors that are in Parsons' possession and start-up the Parsons units with actual radioactive waste.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The risk that is mitigated is that the Parsons design has not been demonstrated under full scale radiological service. It has been tested at the full scale with simulated wastes. Testing with radioactive samples has only been performed on the small scale without prototypic contactor design. The benefit to DOE-SR is successful completion of this demonstration in MCU would help assure a smoother SWPF startup.
Describe the success criteria used to judge the performance of this idea: The success criteria would be a direct comparison of the Parsons contactor performance to that of the MCU contactor with the same waste feed.

Title: **Test the removal of temperature control on the CSSX system with Next Generation Solvent to reduce design, construction and operational costs for SWPF**
Description: There are two aspects: 1) Change operational temperature parameters to improve Cs removal performance. Some improvement in performance can be gained by lowering the extraction temperatures below 23 °C and raising the strip steps to above 33 °C. To avoid disruption due to changes in solubility chemistry with changing temperatures, only small changes should be examined. 2) Removing temperature controls to reduce costs. Removing temperature controls will likely have a large impact on strip performance, but with SWPF already predicting Cs DF in excess of requirements, the drop in DF will not impact the waste form.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: 1) Altering the operating temperatures will increase cesium removal 2) Removing temperature controls will decrease building and operating costs for a small cost in cesium removal performance
Describe the success criteria used to judge the performance of this idea: Monitor cesium removal and weigh the increase against the operating costs (#1) or determine if the decline in cesium removal for #2 is outweighed by the benefit in reducing the build and operating costs associated with active temperature controls.

Title: **Demonstrate performance of SWPF coalescer/contactor materials with actual waste in MCU**
Description: This task would involve evaluating the performance of a SWPF acquired coalescer and contactor, not only in terms of cesium removal performance, but also in terms of chemical compatibility.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Using an actual SWPF contactor and coalescer will enable SRNL to examine performance with real waste and allow for the experimentation in changing some of the operating parameters, such as Organic:Aqueous (O:A) ratios. Furthermore, any materials of construction in the SWPF contactor and coalescer can be tested for chemical compatibility against samples of real waste.
Describe the success criteria used to judge the performance of this idea: Some of the positive information gained would be to test the high activity waste with the actual contactors and coalescers to be utilized at SWPF upon start-up. This would alleviate a number of issues with determining flow rates, O:A solvent ratios for realistic D-values, residence times and mixing velocities to avoid emulsion formation.

Title: **Demonstrate Concentration Factor (CF) increases to reduce water load to DWPF**
Description: Investigate changes in the O:A ratio in the strip steps (to higher O:A ratios) to determine if decreasing the volume of strip acid sent to DWPF while retaining acceptable cesium removal performance.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Reducing the volume of strip acid sent to DWPF will improve DWPF throughput.
Describe the success criteria used to judge the performance of this idea: ESS and V-5/10 testing using new O:A strip ratios will give adequate indication of cesium removal.

6.1.2 Demonstrate New Technology Deployments

Title: **Demonstrate mMST at the radioactive pilot scale**
Description: An improved form of MST, referred to as peroxide-modified MST or mMST, has been shown to exhibit faster removal of Pu and Sr, resulting in significantly higher effective removal of Pu and Sr than the baseline MST material in a batch contact process. For example, similar decontamination factors for Pu and Sr are achieved with mMST at about one-fourth the concentration and contact time of that for MST.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The use of mMST can reduce the quantity and contact time needed to achieve alpha, ^{237}Np and ^{90}Sr removal in SRS feed solutions. Reduced titanate solids and contact times will allow increased throughput in SWPF. Also, the use of mMST will reduce the risk that MST cannot achieve the required removal factors needed for high alpha and ^{90}Sr feed solutions and eliminate the need to operate the Alpha Finishing Plant in the SWPF. The reduced quantity of titanate solids used in SWPF will minimize the impacts of titanium in the DWPF.
Describe the success criteria used to judge the performance of this idea: Compare alpha and ^{90}Sr removal performance of mMST in comparison to that of MST to confirm bench-scale

measurements. Additional success measures could include higher cross flow filter flux rates.

Title: **Demonstrate Large Tank MST strike**
Description: Add MST directly to the large tanks in the tank farm. The MST is mixed with the tank contents. The material is allowed to settle and is decanted. The decanted liquid can then be polish filtered to feed to the solvent extraction process. The MST would be processed with sludge solids.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Large Tank MST strikes reduce the bottleneck at ARP. It is anticipated the SWPF will have similar filtration issues. Performing the strike in the tank farm will also remove the need for a second strike in ARP.
Describe the success criteria used to judge the performance of this idea: Success would be achieved by increasing the amount of available feed for the solvent extraction process. The Sr/Alpha strike would no longer be a choke point in production. Success will be based on adequate Sr/actinide removal such that material is not leached back out of sludge in tanks (i.e. new solubility equilibrium is not leachable).

Title: **Increase ARP throughput by removing alpha/Tc/I by using a tea bag approach to radionuclide removal**
Description: Implement a self-contained drop-in treatment unit for the removal/concentration of select species. Units can be deployed directly in the tank farm with long soak times. Units would target specific troublesome species (alpha, Tc, I, Sr, etc.). Process can take advantage of long contact time in tanks. Disposition of the tea bags would need to be developed but could be envisioned as an addition to the sludge preparation tanks.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Selected troublesome species can be removed without the use of new facilities. Based on material balance, certain high Sr tanks could be targeted to reduce Sr levels to potentially eliminate the second strike in ARP.
Describe the success criteria used to judge the performance of this idea: Success is measured by the ability to remove the targeted species in a cost effective manner. The "tea bag" must be of sufficient size to make appreciable progress in treatment.

Title: **Decontaminate cesium from the Strip Effluent stream using an inorganic ion exchange material to avoid sending the volume to DWPF**
Description: Utilize a sorbent such as crystalline silicotitanate (CST/SCIX) to strip the Cs from the SE stream. A column could be installed in an unused cell. There was a route to get organic directly out of the facility that is not in use. This path may have been disconnected but should be able to reactivate. Loaded resin would be ground and sent to DWPF to be vitrified.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: A more concentrated (Cs) stream can be added to DWPF reducing the water load. Less water addition will reduce SRAT/SME process time. DWPF production could be decoupled from Salt processing

allowing better attainment for both facilities.
Describe the success criteria used to judge the performance of this idea: End result should be shorter SRAT/SME processing times.

Title: **Test RMF as a parallel filter train in ARP**
Description: Incorporate RMF as a parallel filter in ARP. Install and operate RMF in parallel to current crossflow filter. The use of the RMF will increase filtrate production.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Reduce ARP filter time. Would relieve current filtration bottle neck. Deployment would demonstrate the DOE developed technology. Operation in parallel minimizes implementation risk (if it breaks you do not lose your current production capability).
Describe the success criteria used to judge the performance of this idea: Document increased filtration rate. Operation in parallel should have minimal effect on current production (not interfering or replacing current technology). Demonstrate performance and attainment of RMFs.

Title: **Demonstrate an on-line organic monitor**
Description: Add an in-line organic monitor for Isopar L.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: An online monitor on the SEHT stream will provide instant reading of Isopar L carryover.
Describe the success criteria used to judge the performance of this idea: This will reduce the number of SE samples that have to be pulled and sent to F/H lab for analysis.

Title: **Demonstrate other on-line monitoring capabilities Cs, gamma monitor Solvent Composition**
Description: Install an online monitor on the SHT stream.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: This instrument would give immediate readings on the Cs loading in the solvent.
Describe the success criteria used to judge the performance of this idea: Having instantaneous Cs readings in the SHT would give immediate notice of poor stripping.

Title: **Demonstrate Saltstone performance with high Al salt, high water to premix ratio, and higher Na**
Description: Increasing the waste loading of Saltstone can significantly reduce the volume required for the immobilization of LAW at SRS. Waste loading can be increased by concentrating the decontaminated salt solution and by increasing the ratio of salt solution to cementitious dry feeds.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Minimizing the volume of Saltstone produced will maximize the value of existing Saltstone disposal units and minimize the costs of construction of additional units.

Describe the success criteria used to judge the performance of this idea: SRNL has recently demonstrated the formulation of Hanford cementitous waste forms with simulated 10 M sodium salt solutions at water to premix ratios 15% higher than the current Saltstone baseline with promising results. Further work is needed to demonstrate the performance of this material formulated at high LAW concentrations.

Title: **Demonstrate an alternative disposition pathway for Drain Water Return System**
Description: The Saltstone Disposal Units (SDUs) at SRS contain drain water return systems that send excess flush water, bleed water, and in leakage back to the Salt Feed Tank (SFT) at the Saltstone Production Facility (SPF). This liquid is added to the decontaminated salt solution in the SFT and recycled through the SPF process. The volume of the return liquid can be significant relative to the amount of salt solution processed (on the order of 5%). When processing with admixtures, a portion of the admixture is also returned to the process, in effect increasing the admix dose.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Drain water returned to the SFT increases the volume of Saltstone that must be produced and dispositioned. Valuable SDU volume could be saved if a different method were available for the disposition of drain water returns. Alternatively, the elimination of the SDU sheet drain system would alleviate this issue as well as significantly reduce SDU construction costs and complexity.
Describe the success criteria used to judge the performance of this idea: The composition of drain water would have to be evaluated to determine whether other disposition options are available. Other methods, such as improved flushing strategies and formulation with less bleed water could be employed to minimize drain water returns if an alternate disposition option is not possible.

Title: **Demonstrate TcO_4^- removal using the current solvent extraction system**
Description: Determine a drop-in addition to the current solvent system that will remove TcO_4^-. Must be compatible with the current extraction, scrub and strip regime.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Less Tc to Saltstone for long-term disposition in South Carolina (any decline is good).
Describe the success criteria used to judge the performance of this idea: Monitor ^{99}Tc activity on the DS output of test to confirm, and ensure Cs removal does not suffer.

Title: **Demonstrate Salt Only Glass Production**
Description: The volume of salt cake in the SRS tank farm is much greater than the volume of HLW sludge. This is likely to result in a scenario where DWPF completes the HLW immobilization mission far ahead of the LAW mission. DWPF will then have to transition to processing only the waste resulting from the decontamination of salt feed.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: DWPF has not demonstrated the ability to transition to, or process, a salt-only feed. The planned reduction in DWPF production for FY14 presents a unique opportunity to demonstrate frit

development and actual vitrification of a SRAT batch containing only feed from ARP/MCU. This demonstration would allow for the identification and remediation of any potential issues before the inventory of HLW sludge is exhausted and would provide valuable data to guide waste retrieval planning.

Describe the success criteria used to judge the performance of this idea: Success criteria would include the ability to select a frit composition that can be used to vitrify salt-only waste at a desirable waste loading, the ability of a vendor to prepare that frit, the ability to appropriately prepare a salt-only batch in the DWPF SRAT and SME, demonstrating melter and off-gas system operation with this feed, and demonstrating the ability of the facility to make the transition from a sludge feed to a salt-only feed.

6.1.3 Increase Range of Performance in Radiological Environments

Title:
Process salt at higher sodium concentrations

Description: The Next Generation Solvent system that is being incorporated into the MCU flowsheet has many advantages including higher Cs decontamination, higher extractant concentration and perhaps better organic carryover behavior. Additionally, experimental results indicate that the solvent system is capable of decontaminating salt solution with higher sodium concentrations.

Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The risk that is reduced is the ability to meet regulatory milestones in the out years for closing SRS HLW tanks. The benefit is that at 7.5M Na, there is nearly a 30% reduction in the overall volume of salt waste that would need to be treated and a 30% reduction in the amount of SDU space that would be required to be built. There are risks associated with the higher viscosity of these more concentrated solutions and possible solids formation that will also have to be studied.

Describe the success criteria used to judge the performance of this idea: This would require a salt batch (nominally 250 kgal) at the higher sodium concentration and operate ARP-MCU under these conditions and measuring facility performance along with downstream facility issues and comparing those results against similar salt batches at lower sodium concentrations. Additionally, laboratory data would need to show acceptable ^{99}Tc and ^{129}I leach indices at the higher sodium levels.

Title:
Process higher alpha- (^{238}Pu such as T39 and/or ^{237}Np in T33/34) and ^{90}Sr-containing wastes to test the MST radionuclide removal process

Description: Since startup in 2008, the feed solutions processed in the ARP facility have had alpha (principally ^{238,239,240}Pu), ^{237}Np, and ^{90}Sr activities that are below the current Saltstone WAC limits. Consequently, the performance of MST to remove Pu, Np and Sr has not been challenged. Furthermore, the facility has reduced the quantity of MST added from 0.4 g/L to 0.2 g/L and the contact time from 24 hours to as low as 6 hours in the strike tanks to increase throughput.

Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The SWPF will process feed solutions that have much higher alpha, ^{237}Np and ^{90}Sr activities than that planned for processing in the ARP facility. Currently, SWPF will perform additional strikes with MST if the alpha, ^{237}Np and ^{90}Sr activities are not reduced sufficiently to meet the Saltstone WAC

limits. There is a risk that the MST may not achieve sufficient removal of the alpha, Np-237 and Sr-90 at the current flowsheet conditions in SWPF. Testing feed solutions in ARP that have higher alpha, ^{237}Np and ^{90}Sr activities will determine if MST performance is sufficient at the current baseline flowsheet for SWPF.
Describe the success criteria used to judge the performance of this idea: Assemble and process feed solutions having elevated alpha, ^{237}Np and ^{90}Sr activities in ARP at the SWPF baseline flowsheet conditions. Sufficient quantities of waste need to be processed so that steady-state conditions are achieved at ARP. Additionally, samples from the DSS Hold tank would confirm acceptable Sr and actinides levels.

Title: **Increase Temperature across ARP-MCU to increase throughput**
Description: Control temperature in the ARP/MCU process in order to increase production. Increased temperature in ARP will increase filtration rate (reduced viscosity) as long as attention is paid to component solubility.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Reduction in viscosity due to temperature increases can increase the filtration throughput in ARP. It is assumed that SWPF will face the same filtration throughput issues that are being realized in ARP.
Describe the success criteria used to judge the performance of this idea: Document improvements in facility production rates without precipitation of solids downstream.

Title: **Increase cesium concentration to demonstrate solvent radiolytic stability**
Description: To date, ARP-MCU has processed a number of batches of aqueous salt solution with successful decontamination. However, the concentration of cesium has been relatively low compared to the maximum cesium concentration that will be processed through SWPF. It would be beneficial for MCU to process a salt batch with a cesium concentration nears it safety basis limit of 1.1 Ci/gallon.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Implementation of the Next Generation Solvent technology in conjunction with the current generation CSSX solvent presents a new risk to the processing of salt through ARP-MCU. R&D has been performed to reduce this risk. Information regarding the radiolytic stability of the NGS solvent components under a higher radiation environment could reduce the risk for SWPF when it switches from the current to the next generation of solvent technology.
Describe the success criteria used to judge the performance of this idea: Success would be determined through sampling of the solvent components and comparison to the expected radiation stability documented from studies using cobalt-60 irradiation.

6.1.4 Demonstrate Improved Strategies to Increase Throughput

Title: **Lower the amount of sodium hydroxide need to keep Al in solution**
Description: The tank farms has established minimum hydroxide levels to ensure that when the scrub acid mixes with the waste in the in-line mixer that the aluminum will not precipitate out in

the extraction contactor. This phenomenon has been observed and causes vibration concerns. Recent efforts at improving the thermodynamic modeling associated with salt batch planning may be able to better predict what hydroxide level are needed. This would reduce the overall volume of waste generated and treated. Additionally, the Next Generation Solvent which is being introduced into MCU will operate with a caustic scrub feed, which reduces the tendency to precipitate solids when the waste and spent scrub solutions are mixed.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The benefit to DOE-SR in demonstrating this idea in ARP-MCU is a slight reduction in the total inventory of salt waste over the life of the salt mission at SRS. Additionally, this demonstration could result in a cost savings resulting from reduction of caustic purchases.
Describe the success criteria used to judge the performance of this idea: Vibration data is routinely collected during operation of the centrifugal contactors and comparisons can be made relating the vibration behavior to the quantities of waste processed. Additionally, plant data should indicate the magnitude of overall salt production and processing.

Title: **Develop an operational model of ARP-MCU by developing a better understanding of the relationship between lab and facility decontamination factors**
Description: Lab scale testing always provides decontamination factors at ARP and MCU that are less than what the actual facilities generate. This is due to a poorly or unknown understanding of the factors present in the scale up from the lab to the facility.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: A better ability to use the lab scale data to predict the actual facility performance would give more accurate estimates for planning.
Describe the success criteria used to judge the performance of this idea: An improved model would be used to compare to the actual facility performance.

Title: **Demonstrate a containerized Saltstone Waste Form**
Description: Construction of additional SDUs at SRS may be delayed by budgetary issues. Alternative methods of Saltstone disposition would allow for immobilization of LAW waste to continue in the interim. One potential is to pour Saltstone into relatively small, transportable containers, such as the ubiquitous intermodal shipping container. The containers would be stored on site until new SDUs can be constructed. Permanent disposal of the containers may involve a new type of SDU, grouting in place, or shipment to an off-site disposal facility.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: This idea would allow for LAW immobilization to continue at SRS while SDU construction is paused. The disposal of decontaminated salt solution is essential to the continued operation of the entire SRS radiochemical processing and liquid waste system.
Describe the success criteria used to judge the performance of this idea: A demonstration of the performance of containerized Saltstone would be needed to ensure that regulatory disposal requirements continue to be met. Containerized Saltstone for eventual disposition to an engineered disposal unit may provide an additional barrier to radionuclide release, allowing for higher salt concentration and therefore less Saltstone volume needed to immobilize SRS LAW.

Title: **Divert Scrub and Caustic Wash solutions to reduce overall volume of Decontaminated Salt Solution (DSS)**
Description: Wash and Scrub are folded back into the DS stream. If the Wash and Scrub are low enough activity, these might have a route out through ETF.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Reduce volume to Saltstone.
Describe the success criteria used to judge the performance of this idea: Examine Wash and Scrub streams for radionuclide content. Consider use of CST as a polish if needed.

Title: **Investigate whether one could store DSS in a "ready to close" waste tank as Low Level Waste and process through Saltstone once SDUs are available**
Description: The concept captured in this idea is to store decontaminated salt solution processed through ARP-MCU and awaiting disposition in Saltstone in an emptied waste tank once retrieval has met the performance requirements for operationally closing the tank.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The risk that is reduced is the ability to meet regulatory milestones for closing the SRS HLW tanks. Salt will need to be processed to meet these milestones, and if the Saltstone SDU space in SDUs 3A, 3B and 5A, 5B has been consumed, then salt processing is shut down. Interim storage options such as this idea would allow for additional ARP-MCU operations.
Describe the success criteria used to judge the performance of this idea: The success criteria would center on regulatory acceptance of the emptied tank not containing HLW and the storage of decontaminated salt as Low Level Waste in these tanks.

Title: **Demonstrate a larger and more narrower Particle Size Distribution for MST to increase filter flux**
Description: MST is an inorganic ion-exchange material that has a spherical shape with a particle size ranging from about 0.5 to 35 microns. Increasing the particle size with a narrower particle size distribution should lead to higher filter fluxes in crossflow filtration systems at ARP and SWPF.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Crossflow filtration equipment that is used to separate MST from supernatant liquids typically uses stainless steel sintered metal filters having a nominal pore size of 0.1 – 0.5 microns. Since the particle size of the MST contains particles that are similar to the pore size of the filter element and exhibit a somewhat wide range of particle sizes, MST solids can accumulate in densely packed layers that reduce filter flux through the membrane elements. Modifying the production of MST to produce larger particles with a narrower particle size distribution should reduce packing density resulting in increased filtration rates. In addition to higher filtration fluxes, the time interval between filter cleaning should be increased leading to increased facility throughput. (This idea could also apply to mMST)
Describe the success criteria used to judge the performance of this idea: Modify synthesis of MST and or clarification of fines to produce larger particles and narrow particle size distribution. Particle size will be measured using the Microtrac S3500 instrument, which is currently used in

the qualification of vendor-produced material. Materials having larger particle size and narrower particle size distribution will be tested for crossflow filter and ion-exchange performance.

Title:

Demonstrate an optimized MST addition strategy rather than a purely batch addition approach

- **Time based**
- **Process model**

Description: The ARP and SWPF flowsheets use a fixed quantity of MST and contact time in the alpha-strike tanks to remove ^{90}Sr and alpha-emitting radionuclides. The concentrations of the radioisotopes changes in each macrobatch of salt feed solution. More efficient usage of MST and reduced contact times in the alpha-strike tank could be realized by developing a detailed MST performance model that predicts the quantity and contact time needed to successfully remove Sr-90 and alpha-emitting radionuclides.

Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: Having a MST performance model will minimize quantity of MST used in ARP and SWPF and increase confidence that the process will successfully remove ^{90}Sr and alpha-emitting radionuclides to the meet the Saltstone WAC limits. Reduced usage of MST in SWPF will also minimize/eliminate adverse impacts of titanium in the DWPF melter.

Describe the success criteria used to judge the performance of this idea: A detailed flowsheet model of the ARP flowsheet will be developed using MST performance from bench-scale ion-exchange tests and operating data from the ARP facility. This model will be validated by comparing predicted MST performance versus that measured in the ARP facility since startup of the facility in 2008. If good agreement is observed, the model will be used to predict future performance and periodically checked against actual performance to confirm model accuracy.

Title:

Demonstrate Nitric Acid cleaning versus Oxalic Acid

Description: Fouling of the cross flow filter in ARP and the associated chemical cleaning using oxalic acid reduces the facility availability and when neutralized produces sodium oxalate solids, which must be processed through DWPF and MCU. Switching to nitric acid for cleaning would reduce the formation of solids that require processing. However, nitric acid burden in DWPF must be evaluated to ensure viability of this flowsheet change.

Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The benefit of the switch to nitric acid is two-fold. First, when neutralized with sodium hydroxide, solids will not be formed as in the case of neutralizing oxalic acid with sodium hydroxide. These newly formed solids increase the concentration of insoluble solids, which results in a lower filter flux. Secondly, the nitric acid could possibly dissolve the solids that blind the filter and reduce its performance. Nitric will dissolve different species and may result in a better cleaning.

Describe the success criteria used to judge the performance of this idea: The measure of success is an increase in filter flux on average and instantaneously following chemical cleaning.

Title: **Validate Scaling Factor Approach to reduce Salt Qualification durations**
Description: The qualification process for the Salt Batch requires quantification of a number of isotopes and analytes that are either important to the performance assessment or permit. The analyses are very expensive. Similar approaches in the solid waste arena have lowered characterization costs by relating one isotope concentration to another (for example, the ratio of 137Cs to 226Ra) in order to minimize the number of analytes.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The benefit is a reduction in the cost associated with each salt batch qualification.
Describe the success criteria used to judge the performance of this idea: The approach to scaling factors is welcomed by the NRC.

Title: **Eliminate washing of MST concentrate in ARP process**
Description: Currently at the end of each cycle in ARP, the contents of the Late Wash Precipitate Tank are washed with water to remove sodium salts. The end point of washing is a fixed point and is 0.5M sodium concentration. The step in the process occupies at least one operational shift. If the step can be eliminated for ARP and SWPF, additional throughput would be realized.
Describe the risk that will be reduced/mitigated or the benefit this idea has to DOE-SR: The benefit is increased throughput by eliminating the process step but also the water added eventually is disposed in Saltstone as the cementitious waste form.
Describe the success criteria used to judge the performance of this idea: The un-washed product from ARP is demonstrated that it can be successfully treated in DWPF.

Appendix B. Idea Ranking Sheet

Bin	Idea	Benefit						Probabilty					
Enhance Confidence in SWPF Startup		WRW	Herman	Fox	Washington	Hobbs	Peters	WRW	Herman	Fox	Washington	Hobbs	Peters
	Obtain radiological performance data for the Parsons V-10 centrifugal contactor design by installing in MCU	L	M	M	M	L	L	H	M	H	M	H	H
	Test the removal of temperature control on the CSSX system with Next Generation Solvent to reduce design, construction and operational costs for SWPF	L	M	L	M	L	M	L	M	M	H	M	M
	Demonstrate performance of SWPF coalesce/contactor materials with actual waste in MCU	M	H	M	H	M	M	H	M	M	M	M	H
	Demonstrate Concentration Factor (CF) increases to reduce water load to DWPF	M	H	M	M	M	M	M	M	M	M	M	M
Demonstrate New Technology Deployments													
	Demonstrate mMST at the radioactive pilot scale	M	H	L	M	M	M	H	H	H	H	M	M
	Demonstrate large tank MST strike	H	H	H	M	H	M	H	M	H	M	M	M
	Increase ARP throughput by removing alpha/Tc/I by using a tea bag approach to radionuclide removal	M	H	M	H	H	M	L	M	L	L	L	M
	Decontaminate cesium from the Strip Effluent stream using an inorganic ion exchange material to avoid sending the volume to DWPF	M	H	H	H	H	M	L	L	L	L	L	L
	Test RMF as a parallel filter train in ARP	H	H	H	H	M	H	M	M	H	M	H	H
	Demonstrate an on-line organic monitor	L	L	L	M	L	L	M	M	M	L	M	M
	Demonstrate other on-line monitoring capabilities, e.g., Cs, gamma monitor, solvent composition	L	M	L	M	L	L	M	M	M	L	L	M
	Demonstrate Saltstone performance with high Al salt, high water to premix ratio, and higher Na	H	H	H	H	H	M	H	M	H	M	M	H
	Demonstrate an alternative disposition pathway for Drain Water Return System	M	H	M	M	M	M	M	M	M	M	M	M
	Demonstrate TcO4- Removal using the Current Solvent Extraction System	L	M	M	H	L	M	L	L	M	M	L	M
	Demonstrate Salt-Only Glass Production at DWPF	L	M	H	H	H	H	L	L	L	L	M	L
Increase Range of Performance in Radiological Environments													
	Process salt at higher sodium concentrations	H	H	H	H	H	H	H	M	M	H	H	H
	Process higher alpha- (Pu-238 such as T39 and/or Np in T33/34) and strontium-containing wastes to test the MST radionuclide removal process	H	M	M	H	H	M	H	L	H	H	M	H
	Increase Temperature across ARP-MCU to increase throughput	M	M	M	H	M	M	M	M	M	H	L	M
	Increase cesium concentration to demonstrate solvent radiolytic stability	L	M	L	M	L	M	H	M	H	M	M	H
Demonstrate Improved Strategies to Increase Throughput													
	Lower the amount of sodium hydroxide need to keep Al in solution	L	H	L	M	M	L	H	M	M	H	H	M
	Develop an operational model of ARP-MCU by developing a better understanding of the relationship between lab and facility decontamination factors	L	M	M	M	M	M	L	M	M	H	H	H
	Demonstrate a containerized grout and store pour containers till Saltstone vault is available	H	H	M	M	H	M	L	L	L	L	L	L
	Divert Scrub and Caustic Wash solutions to reduce overall volume of Decontaminated Salt Solution (DSS)	L	M	H	H	L	M	L	M	M	L	M	M
	Investigate whether one could store DSS in a “ready to close” waste tank as Low Level Waste and process through Saltstone once vaults are available	M	H	H	H	M	M	L	L	M	L	L	L
	Demonstrate a larger and more narrower Particle Size Distribution for MST to increase filter flux	M	H	M	M	M	M	M	H	H	M	H	M
	Demonstrate an optimized MST addition strategy rather than a purely batch addition approach	M	H	M	H	M	M	M	M	M	H	M	H
	Demonstrate Nitric Acid cleaning versus Oxalic Acid	H	M	H	H	M	M	M	M	H	M	M	H
	Validate Scaling Factor Approach to reduce Salt Qualification durations	M	M	H	M	H	M	M	M	H	M	L	H
	Eliminate washing of MST concentrate in ARP process	L	M	M	M	M	M	L	L	H	H	L	M