Methods for Heel Retrieval for Tanks C-101, C-102, and C-111 at the Hanford Site – 13064

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ABSTRACT

The purpose of this paper is to evaluate the prospects of using bulk waste characteristics to determine the most appropriate heel retrieval technology. If the properties of hard to remove heels can be determined before bulk retrieval, then a heel retrieval technology can be selected before bulk retrieval is complete. This would save substantially on sampling costs and would allow the deployment of the heel retrieval technology immediately after bulk retrieval. The latter would also accelerate the heel removal schedule.

A number of C-farm retrievals have been fully or partially completed at the time of this writing. Thus, there is already substantial information on the success of different technologies and the composition of the heels. There is also substantial information on the waste types in each tank based on historical records. Therefore, this study will correlate the performance of technologies used so far and compare them to the known waste types in the tanks. This will be used to estimate the performance of future C Farm heel retrievals. An initial decision tree is developed and employed on tanks C-101, C-102, and C 111.

An assumption of this study is that no additional characterization information would be available, before or after retrieval. Note that collecting additional information would substantially increase the probability of success. Deploying some in-situ testing technologies, such as a water lance or an in-situ Raman probe, might substantially increase the probability of successfully selecting the process conditions without having to take samples from the tanks for laboratory analysis.

INTRODUCTION

The Hanford tank waste cleanup activities typically involve a bulk waste retrieval followed by a hard to remove heel retrieval. If the properties of hard to remove heels can be determined before bulk retrieval, then a heel retrieval technology can be selected before bulk retrieval is complete. This would save substantially on sampling costs and would allow the deployment of the heel retrieval technology immediately after bulk retrieval. The latter would also accelerate the heel removal schedule.   The purpose of this document is to evaluate the prospects of using bulk waste characteristics to determine the most appropriate heel retrieval technology.

A number of C-farm retrievals have been fully or partially completed at the time of this writing. Thus, there is already substantial information on the success of different technologies and the composition of the heels. There is also substantial information on the waste types in each tank based on historical records. Therefore, this study will correlate the performance of technologies used so far and compare them to the known waste types in the tanks. This will be used to estimate the performance of future C-Farm heel retrievals. An initial decision tree is developed and employed on tanks C-101, C-102, and C-111.

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DESCRIPTION OF THE HEEL RETRIEVAL DECISION PATH

Before a decision path for heel removal can be made, the following preliminaries must be done:

Evaluate Available Waste Characteristics. Samples of C-Farm tanks were taken in the late 1980s through the mid-1990s. Tanks C-101 and C-103 were auger sampled in 1995; Tank C-111 was core sampled in 1994 and auger samples in 1995. The operating experience from the field crew, the sample recovery, and the analytical lab results provide insight as to whether a hard layer exists on the waste surface, how thick that layer might be, and what the characteristics may be for a residual heel layer. For example, C-111 sample recovery was very poor and in C-102 the saltwell screen needed to be shortened because a hard layer was encountered 0.61 m (2 ft.) above the tank bottom. Another example is the retrieval of C-112. This tank was sampled in 1992 using a push mode sampling technique. Indications were of a soft sludge material. However, when modified sluicing began to remove the waste in 2011, there was a hard crust layer.

Define the problem. Based on the review of the Waste Characteristics, determine if a hard-to-remove heel (HTRH) is likely to exist in the single-shell tank (SST) under evaluation. One potential was the retrieval of the material in the C-200 tanks using a vacuum retrieval system. The primary issue with the C-200 vacuum retrieval system was getting the loose material to suck through the screen of the vacuum system. There was also a fair amount of non-waste debris that had to be dealt with, such as chunks of rubber and rocks. Excluding these potential HTRH problems encountered during vacuum retrieval (believed to be primarily an equipment design problem), the expected potential HTRH problems are as follows.
- A solid salt monolith. (S-112) [Note that S-102 has not had an HTRH yet for the currently installed equipment; the whole tank would be an HTRH without the high pressure water agitators].
- An almost solid sludge monolith, i.e., chunks too big to move. (C-111, C-112) It is not certain that retrieval of C-111 may have gone the same way as C-112 if there had been an extended reach sluicer system (ERSS) installed that could have been used to pick holes in the crust.
- Sludge solids that can be partially broken up but are too big to pass through the 9.525 mm (0.375 in.) screen holes on the pumps used. These may be so large that they can only be moved a short distance with the sluicers or they can be mobilized to reach the pump but won't go in it or pass by it. (C-103, C-106, C-108, C-109, C-110)
- Sludge solids that are fine enough to go through the pump but just pass by it when sluiced. (C-103, C-106, C-108, C-109, C-110)

- Sludge solids that may be a mixture of b. through d., which are located in places in the tanks where they cannot be effectively mobilized by the sluicers. (C-103, C-106, C-108, C-109, C-110)

Develop a Process for Bulk Retrieval and HTRH Retrieval. Based on the Bulk Retrieval technology deployed in the SST, develop a best estimate of the HTRH volume and composition that will remain in the tank. For modified sluicing tanks, assume the HTRH volume is >10.194 m^3 (360 ft.^{3}) and an HTRH removal method must be used. This is a conservative assumption and borne out by the fact that an HTRH >10.194 m^3 (360 ft.^{3}) has shown up in five of the six non-saltcake tanks in which modified sluicing has been deployed. For mobile arm retrieval system (MARS) equipped tanks assume the HTRH volume is <10.194 m^3 (360 ft.^{3}) and no other HTRH removal method must be used. This is a justifiable assumption because the MARS contains a minimum of two retrieval technologies built in (supernatant sluicing and high pressure water sprays), plus it has built-in improvements over the modified sluicing processes (see #4 below) where the sluicing nozzles can be directed at the waste from a short distance away, anywhere in the tank, to mobilize it. The pump also has a backstop to catch particles that may otherwise bypass it, and the backstop has pulverizing supernatant and high pressure water sprays built-in. If the MARS is not successful in reducing the residual waste to <10.194 m^3 (360 ft.^{3}), none of the existing or planned in-tank vehicles would be an improvement. If a MARS unit does not get the tank waste to <10.194 m^3 (360 ft.^{3}) the decision process in the attachment below is followed. Estimate what the HTRH composition in a tank may be. It is not possible to know prior to retrieval what the heel volume, chemical composition, or physical composition will be in a tank, but it is possible to predict what they might be. This is being done now and these estimates will be included in the next revision (rev 2) of RPP-40545, *Quantitative Assumptions for Single-Shell Tank Waste Retrieval Planning*. These estimates will be updated as more data are obtained and estimating methods are improved.

Estimate, as part of the retrieval planning process for each tank, what HTRH retrieval method may be best for a tank. It is not possible to predict prior to retrieval what process would be best for a tank, but it is possible to come up with a recommended method based upon the estimated HTRH volume and other factors. The other factors to consider are:
- What are the waste phases? If the tank is all saltcake the only HTRH retrieval category to consider is a high pressure water delivery method. A method to heat the water circulated in the tank would increase dissolution rates and reduce the amount of water required.
- For sludge, what are the best-basis inventory (BBI) phosphate, fluoride, and aluminum content, and what is the tank temperature history? Using this information, and after evaluating the basis for the BBI numbers (whether based upon good core sample data or estimated based upon assumed waste templates), a rough estimate can be made on an HTRH sludge volume and chemical composition based upon comparison to past tanks. Physical composition, i.e., size of waste agglomerates, cannot be predicted with accuracy at this time, but it can be allowed for.
- Double-shell tank (DST) space available for volume generated by either a high pressure water tool or chemical retrieval.
- Riser diameters available on an SST for receipt of high pressure water tools (or future mechanical waste reduction equipment).

Define Generic Categories of HTRH Removal Methods. Provide HTRH retrieval equipment as part of the retrieval design process. This includes both high pressure water tools and chemical retrieval equipment, and provisions for solution recycle from tank back through sluice nozzles. The HTRH retrieval equipment items will not be specific to a single tank; an inventory would be developed and kept until needed. Included are high pressure water vehicles such as the remote water lance (S-112), sand mantis (developed for S-102/S-112 but not used), similar tools developed by TMR Associates but not used, FoldTrak (used in C-109 for a few hours before failure), Mobile Retrieval System (MRS) vehicle (developed for C Farm but not used), and alternate new designs.

Additionally high pressure water arms should be identified. Include the MARS, both sluicing and vacuum, C-107 to receive sluicing system and C-105 planned to receive vacuum system, Articulating Mast System (AMS), designed for MRS retrieval, deployed in C-104 now, and an alternate new high pressure articulating arm.

Chemical retrieval is an alternate method for consideration. Types of chemical treatment include:
- Water, used for sludge compounds like sodium fluoride phosphate ($Na_7F(PO_4)_2 \bullet 19H_2O$) (when known to be present) which are insoluble in the high pH waste solutions normally present in SSTs, but which are somewhat soluble when the sodium, fluoride, phosphate, and free hydroxide are diluted to low levels. This is planned for the C-108 and C-110 HTRHs. Water is also used for HTRH salt heels. Salt dissolution is endothermic. An in-line heater inserted in the recirculation system would speed the retrieval and reduce the amount of water required.
- High molarity (~19$\underline{M}$) caustic. This is used to break up hydrated aluminum hydroxides ($Al_2(OH)_6$), also known as gibbsite, or similar hydrated aluminum oxide compounds. These are formed in the high pH waste solutions normally present in SSTs, but have been shown to break down in 19$\underline{M}$ molar caustic solutions in the lab. This also breaks down sodium bicarbonate and is responsible for the foam and bubbles noted when caustic first contacts HTRH solids.
- Oxalic acid, used for metal oxides in the waste. Oxalic acid (maximum concentration ~1$\underline{M}$) was used to dissolve much of the C-106 heel.
- Other. Other chemical processes aren't developed at this time, but one using $Ca(NO_3)_2$ is undergoing scoping tests in the lab to determine if it will be an improvement over using water for dissolution of sodium fluoride phosphate. This works by sequestering the phosphate, increasing the amount of sodium fluoride phosphate which can be dissolved in a given amount of water. Soaking of the waste using caustic solutions for aluminum dissolution is a viable option. The use of water as a soak for phosphate dissolution has also exhibited beneficial results.

Mechanical retrieval also has other considerations such as the following.
- Some of the in-tank vehicles have blades that can be used to push the waste solids toward the pump inlet and tracks which can run over the waste to crush it. These are both 'aids' to retrieval, not direct mechanical retrieval processes.

- In-tank grinder. Non Entry Systems Limited (NESL) is currently developing a grinder attachment for the in-tank FoldTrak vehicle. There is nothing more robust currently developed or under development at Hanford like this, but Savannah River has deployed a tool that suctions up wastes and directs it to the inlet of an in-tank pump/grinder that reduces the particle size and pumps the slurry from the tank.
- In-tank rotating brush. This is an idea which has been devised by a team of six Washington State University (WSU) students currently working on a class design project. The tool would be equipped with a large wire brush consisting of steel or other cables. The brush would be lowered to the floor and rotated and waste sludge would be directed through the brush to the pump.
- Other. No other processes are currently being evaluated.

Select Retrieval Equipment to Minimize HTRHs. Improve the current modified sluicing design to minimize HTRH volume by the following:

- Provide backstops on pumps like the in-tank attachment designed but not used for S-112, or the MARS backstop, or a similar design to try and catch more of the material that bypasses the pump when forced towards it. The blade of the in-tank vehicle may also work as a backstop, as would a berm constructed behind the pump by the in-tank vehicle.
- Provide a better sluicer design that will reach down to the waste surface as a minimum, and to be articulated to reach other tank locations to the extent practical. The extended reach sluicer is intended to provide such capability.
- Formally develop a reasonable, and effective, process for drilling holes into tank domes and adding new risers to expand sluicer (or other equipment) installations.
- Any additional improvements that can be devised and reasonably implemented.
- A sluicer nozzle, such as that used on the Vertical Reach Sluicing System (VRSS), does not need flow straighteners and is less prone to plugging than the nozzles used on the sluicers now deployed in tanks C-103, C-104, C-108, C-109, C-110, C-111, and C-112. This type of nozzle would provide a more focused sluice stream and subsequently improve waste removal.

When the above preliminaries are done, retrieval can proceed to the point where it is halted due to the presence of an HTRH.

DESCRIPTION OF THE WASTE CHARACTERISTICS

This section covers the waste characteristics of the 100 series tanks in C farm. This study assumes that retrieval experience gained thus far can be applied to other C Farm tanks with known similar waste characteristics and waste types. Note that this assumption holds only to the extent that the waste properties are directly a function of the waste types. This assumption, which appears reasonable, cannot be validated in the present study. A possibility that cannot be excluded is that subtle differences in waste histories have led to substantive differences in waste properties. Table 1 compares the waste types in the 100 series C Farm Tanks prior to any retrieval activities. These inventories were produced from tank characterization reports (RPP-RPT-43028, *2009 Auto-TCR for Tank 241-C-101*, through RPP-RPT-43039, *2009 Auto-TCR for Tank 241-C-112*) and the BBIs for the tanks prior to any retrieval activities.

Table 1 has the waste types listed from the top of the waste to the bottom. As is indicated from this table, the waste in C-111 is similar in nature to C-112; the primary difference is that there is considerably less waste in C-111. The similarity of these two tanks extends to the presence of a surface crust, which was found on the surface of both tanks during the initial attempt at sluicing. Given the larger waste volume, the sluicers were able to get closer to the surface of the C-112 crust, which allowed the operators to mine holes in the crust and remove waste underneath. There is no evidence that this crust is breaking up into small particles in C-112, so the entire crust may end up at the bottom of the tank as large chunks after the softer, underlying waste is removed. Retrieval of C-112 is still on-going at the time of this writing. Thus, the behavior of the crust needs to be monitored and the lessons learned applied to C-111.

Based on the information obtained so far, however, the crust appears to be breakable when the pressure is sufficient. Thus, mechanical methods should be able to remove the crust-heel if a mechanism to deliver high pressure liquid can be applied. The crust on both C-111 and C-112 is on the surface layer, a surface layer that is made up primarily of aluminum based on waste types in Table 1 and compositions in Table 2. The mineralogy of this crust layer has not been determined, but gibbsite is the dominant aluminum-bearing mineral in the cladding waste layer in other C-farm tanks (Table 3). A recent analysis of the aluminum mineralogy of the waste tanks also concluded that gibbsite is the primary aluminum mineral in tanks C-101, C-102, and C-111 (RPP-RPT-47306, *Waste Type Analysis for Aluminum Leachability Estimates of All Non-Retrieved Hanford Tank Waste*). Therefore, it is likely that this crust is largely made up of gibbsite. Gibbsite is readily dissolved in concentrated $NaOH_{(aq)}$ if sufficient surface area is obtained (Letter WRPS-0800062, *Gibbsite Dissolution Rate Tests Results*). It is possible that a large volume addition of concentrated $NaOH_{(aq)}$ would attack enough of the crust to break it apart into more manageable particle sizes, provided good contact between the crust and solution can be maintained.

Historically, Tanks C-102, C-103, and C-104 had organic layers floating on the waste. It is possible, but cannot be confirmed, that the sludge surface absorbed some of this organic material during salt well pumping. It is speculated that the presence of absorbed organic (Tri-butyl Phosphate [TBP], normal paraffin hydrocarbon (NPH), and possible di-2-ethyl hexyl phosphoric acid (D2EHP) from the Plutonium Uranium Extraction (PUREX) Plant and B Plant solvent extraction processes) could have hindered the consolidation of the sludge surface after salt well pumping. In the case of C-103, the organic was deliberately left in the tank during salt well pumping. Separable organic did not show up in the salt well receiver tank or in the sluicing receiver tank during retrieval, supporting the contention that the sludge absorbed the organic like "kitty litter." It is interesting to note that tank C-103 is the only C-100 tank which has been retrieved to <10.194 m^3 (360 ft.^{3}) during modified sluicing so far. It should be noted that the time between when the organic layer was removed from C-103 during saltwell pumping and when retrieval started was very short. This short period may be a contributor to how easy this tank was to sluice since it did not have a significant amount of time to dry out and consolidate a crust.

Per Table 1, tanks C-101 and C-102 are expected to have similar waste types. Given the similarity of waste types, they likely will have similar retrieval performance. Both tanks have

waste surfaces consisting of cladding wastes, like most C-farm wastes. Some tanks with cladding waste on or near the surface have developed crusts (C-111, C-112), whereas others have been easy to infiltrate with sluicers (C-104, C-109). One thing of note is that the surfaces of C-111 and C112 had only cladding waste, whereas the surfaces of C-104 and C-109 were a mixture of cladding waste and other waste types. Thus, the purity of the waste type may play a role in the development of the crust, and it is possible that C-101 and C-102 also have crusts. Table H.3.5-1 in Revision 2 of RPP-40545, *Quantitative Assumptions for Single-Shell Tank Waste Retrieval Planning*, reviews the sampling history of tanks C-101 and C-102. This data indicates that the surface of both tanks was easily penetrated with a rotary mode core (C-102) or auger (C-101) sampling devices more than 15 years ago. Thus, the surfaces were reasonably soft at that time. It is not clear if the surface has dried out and hardened since then. Lancing the surface of these tanks to see if there is a crust may provide insight to the waste behavior prior to the installation of an expensive retrieval technology.

Both Tank C-101 and C-102 have TBP waste below the surface layer. The only other tank in C-farm with TBP waste is C-105, which has also not been retrieved. Thus, there is no experience with retrieving this waste type. The present analysis assumes that TBP waste will be easily removed with the bulk retrieval technology and will not leave the heel in the tank with any waste type not seen previously in C Farm. This assumption could be strengthened if sample data were to come available.

Per the BBI stored on the Tank Waste Information Network System (TWINS) database (TWINS.pnl.gov), each of the three tanks has at least one layer with more than 1000 parts per million (PPM) fluoride concentrations. Per Table 2, there are also large concentrations of phosphate in each of these tanks. High fluoride and high phosphate concentrations are consistent with the conditions conducive to $Na_7F(PO_4)_2.19H_2O$ formation; a phase that frequently has large particle sizes in the waste (PNNL-20646, *Hanford Waste Physical and Rheological Properties: Data and Gaps*). This water soluble fluoride phosphate has been found in the heel of most of the C-Farm tanks emptied so far. Thus, $Na_7F(PO_4)_2.19H_2O$ will also likely be found in the heel of C-101, C-102, and C-111 as well. Consequently, it can be assumed that some of the solids found in the heel of this waste will be water soluble. This phase is soluble in water, but has limited solubility in Hanford supernatant solutions, per 7S110-DLH-05-027 "*Phosphate Solubility Under C farm Retrieval Conditions*". Therefore, $Na_7F(PO_4)_2.19H_2O$ can be dissolved in water, but not supernatant solutions.

Table 1. Comparison of C Farm Waste Types.

Tank ID	241-C-103		241-C-108		241-C-109		241-C-104		241-C-101		241-C-102		241-C-105		241-C-107		241-C-110		241-C-111		241-C-112	
Retrieval History	sluiced, <10.194 m³ HTRH		sluiced, >10.194 m³ HTRH		sluiced, >10.194 m³ HTRH		sluiced, >10.194 m³ HTRH		Not started yet.		Not started yet.		Not started yet.		MRS, good progress so far.		sluiced, >10.194 m³ HTRH		Surface too hard to sluice. Evidence of softer waste below.		Surface too hard to sluice. Retrieving softer waste below.	
	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter	Waste Type	Vol, Liter
Top Layer	AR sludge	109.8	TFeCN and TBP	140.1	CWP and HS	83.3	CWZr, OWW and CWP	424	CWP	208.2	CWZr, CWP, and TH1	1116.7	CWP	450.5	SSR	340.7	TBP and OWW	Removed	CWP and HS	75.7	CWP and HS	64.4
Middle Layer					TFeCN	121.1					TBP	60.6			CWP	90.9			TFeCN	90.9	TFeCN	272.4
Bottom Layer	CWP	162.8	1C	109.8	1C	37.9	TH2, CWP plus Misc.	556.5	TBP	124.9	MW	18.9	TBP	49.2	1C	507.3	1C	670.0	1C	49.2	1C	56.8
Total Waste		272.6		249.8		242.3		980.4		333.1		1196.2		499.7		938.3		670.0		215.8		393.7
Historic Waste Layer or Heel	TBP and 3rd in MW cascade		2nd in 1C cascade		3rd in 1C cascade		1st in MW cascade		1st in MW cascade		2nd in MW cascade		2nd in MW cascade		1st in 1C cascade		1st in 1C cascade		2nd in 1C cascade		3rd in 1C cascade	

Waste Type Definitions and Acronyms

1C	Bismuth Phosphate process 1st cycle decontamination waste
AR Sludge	Water washed PUREX sludge entrained in decants of recovered sludge and solids remaining after acidification.
CWP	PUREX cladding waste (aluminum cladding waste)
CWZr	PUREX zirconium cladding waste
HS	Hot-semi works strontium and rare earths purification waste
HTRH	Hard-to-Remove Heel
Liters	liters
Misc.	Miscellaneous minor waste types
MRS	mobile retrieval system
MW	Bismuth Phosphate process metal waste
OWW	PUREX organic wash waste
SSR	High activity waste from B Plant processing of PUREX acidified sludge and strontium purification waste
TBP	Tributyl phosphate waste (uranium recovery process)
TFeCN	Ferrocyanide sludge from in-farm scavenging of supernatant
TH1	Thoria campaign waste (1966) [including aluminum cladding waste]
TH2	Thoria campaign waste (1970) [included aluminum cladding waste]
vol	volume

Table 2. Bulk Concentrations of Analytes with a Potential to Mineralize or Contribute to Agglomeration.

Tank ID	241-C-103		241-C-108		241-C-109		241-C-104		241-C-101		241-C-102		241-C-105		241-C-107		241-C-110		241-C-111		241-C-112	
	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %	μg/g	Rel. %
Al	124,000	56	52,100	20	67,900	23	54,400	27	134,000	44	138,000	54	200,000	63	40,200	26	14,600	8	93,300	40	19,600	10
Ca	5,340	2	12,700	5	16,500	6	1,800	1	3,470	1	3,290	1	2,550	1	854	1	1,170	1	13,100	6	18,600	9
Na	35,700	16	94,100	37	101,000	35	108,000	53	92,800	31	52,900	21	49,200	16	65,300	42	83,700	46	41,000	18	79,700	39
Si	30,300	14	4,330	2	6,040	2	6,180	3	6,320	2	17,500	7	39,900	13	1,280	1	7,060	4	7,260	3	2,460	1
CO_3	24,800	11	10,500	4	26,900	9	29300	15	12,900	4	37,600	15	16,900	5	7,840	5	10,500	6	21,900	9	23,200	11
PO_4	3,240	1	82,100	32	72,100	25	1,940	1	51,800	17	8,140	3	7,750	2	40,300	26	63,200	35	57,400	25	62,100	30

Rel. % = Relative percent

Table 3. C-Farm Mineralogy from RPP-RPT-46618, *Hanford Waste Mineralogy Reference Report.*

Tank	Minerals	Notes
C-101	Gibbsite, Na3PO4.12H2O Na2U2O7	Surface Layer Information Only
C-103	Gibbsite	Present both before and after sluicing
C-105	Gibbsite, Na2U2O7, and UO3.H2O)	none
C-106	Silver metal, Gibbsite, Boehmite, MnC2O4.H2O, dawsonite, CaC2O4.H2O, Fe2O3, FeOOH,	All Post sluicing
C-107	Gibbsite, Maybe AlPO4, Fe2O3, Na7F(PO4)2.19H2O, Na3PO4.12H2O, Na2U2O7.6H2O	none
C-108	Gibbsite, Fe2O3, $Na_7F(PO_4)_2.19H_2O$, Na2H(CO3)2.H2O, NaSrPO4.9H2O,	All Post Sluicing, gibbsite and $Na_7F(PO_4)_2.19H_2O$ most common. Other trace components found in bulk waste
C-109	Gibbsite, Boehmite, UO3	Prior to retrieval. A draft report indicates Na7F(PO4)2.19H2O is in the heel.
C-112	CaPO4, CaU2O7, amorphous iron hydroxide, SiO2	Prior to retrieval, probably from waste below surface layer

DECISION TREE ANALYSIS FOR TANKS C-101, C-102, AND C-111

This section will evaluate the implications of the information in the last section and use it to make decisions about the method to remove HTRH for the three tanks in question.

The following bullets provide input to the decision tree discussed in the previous section, summarizing the information on the characterization of the tank waste discussed previously.

- Tank C-111 has a hard surface crust of unknown thickness.
- Tanks C-101 and C-102 may also have a surface crust that will still be present as chunks at the end of bulk retrieval.
- The surface crust from any of the three tanks will likely consist of gibbsite, with other minerals entrained in the gibbsite cement.
- Gibbsite may also sufficiently dissolve from the hard crust in concentrated hydroxide to break up the crust. This has not been investigated previously. Water was added to the surface of tank C-111, and no infiltration of this water into the crust was observed even after several days. Thus, it can be assumed that the porosity of the crust is very low (Hillel, 1982).

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In order for this to be successful, the caustic would have to dissolve enough of the material to create sufficient porosity for more caustic to seep into the crust. The likelihood of this is unknown at this point, so this study assumes that it would be ineffective.

- All three tanks may have sand and gravel size material left over that will likely be composed of gibbsite, $Na_7F(PO_4)_2.19H_2O$, or more likely both.
- We know from laboratory investigation that $Na_7F(PO_4)_2.19H_2O$ will dissolve in water if the water is sufficiently hot and if the water is agitated sufficiently to prevent the formation of a diffusion barrier around the surface of the $Na_7F(PO_4)_2.19H_2O$. Prior to this action, residual supernatant should be removed to provide improved contact with the waste material.
- We do know that the gibbsite in the waste can be converted to sodium aluminate in concentrated caustic (WRPS-0800062). Sodium aluminate can be dissolved in water and may be sluiced easier than the gibbsite aggregates. In order for this to be successful, the gibbsite must contact the concentrated caustic for five to 12 days (depending on the temperature) with sufficient agitation to prevent the development of a diffusion barrier around the mineral. The higher the temperature, the less time that is required. Laboratory data indicates that leaving the caustic in contact without any form of agitation may form cemented chunks of solids that are actually larger than the original material (WRPS-0800062). Experience from C-108 would indicate that the contact time is greater than five to 12 days.

From these data, we can now use the decision tree discussed in the previous section to select a retrieval technology for tanks C-101, C-102, and C-111.

Evaluate Available Waste Characteristics. This was performed in the previous section; the relevant information is captured in the bullets above.

Define the Problem. Based on the bullets above, it is believed that tanks C-101, C-102, and C-111 will likely have an HTRH. From these bullets, we can summarize that the heels of tanks C-101, C-102, and C-111 will likely consist of sand and gravel sized particles of $Na_7F(PO_4)_2.19H_2O$ and/or gibbsite, as described in the decision tree section. Tank C-111 will likely also have large chunks of crust material, while it is not yet determinable if C-101 and C-102 will have the crust material. These will be large sludge monoliths of the type described in section 2.b of the decision tree.

Develop Process for Bulk Retrieval and HTRH Retrieval. The $Na_7F(PO_4)_2.19H_2O$ can be dissolved in water and the gibbsite can be dissolved in concentrated NaOH, but both dissolution methods require some sort of mixing to be successful. The crust material appears to be broken up with a large pressure device, a device that could also provide the mixing required for $Na_7F(PO_4)_2.19H_2O$ and gibbsite dissolution in water and caustic. Any high pressure delivery device used to break up the chunks of crust will likely use water to avoid line plugging. Thus, the $Na_7F(PO_4)_2.19H_2O$ dissolution and the breakup of the crust can be performed at the same time successfully. The high pressure device may not be able to mix concentrated NaOH because of the high viscosity of the concentrated NaOH. The high pressure device may be able to disperse enough of the waste prior to adding the caustic that there will be sufficient surface area available for the caustic to attack the gibbsite. This type of high pressure system for dispersion

of NaOH does not currently exist and would require development and testing. Current plans are to use the high pressure water cannons with water only.

From these results, we can conclude that we need some sort of high-pressure delivery system to deliver water and/or caustic for all three tanks. The project is installing high pressure water cannons on the ERSS. This high pressure system will be the second technology deployed for these tanks. The decision on whether a third technology, recommended as a NaOH chemical dissolution is needed will be dependent upon a number of factors including residual quantity of waste, waste form, estimates of residual radiological and non-radiological properties, overall risk profile, and others. We do not yet know where the large chunks will reside physically in the tank. Some sort of in tank vehicle such as the Salt Mantis or the FoldTrac would be the most flexible method of delivering the high pressure water because it can go anywhere in the tank. Issues such as the impact on DST space and riser availability still need to be worked out.

Adequate mixing is required to ensure dissolution of salts and reaction of hydrated aluminum solids with caustic. The sluicers must have open flow passages to pass particles, which will pass through the pump screen. The Retrieval Project has developed and demonstrated nozzles for the VRSS which do not require flow straighteners. It is recommended that any chemical HTRH retrieval system employ a minimum of two such sluicing nozzles to distribute the water or caustic and to agitate the solids. An in-tank vehicle should also be considered for agitating the solids. The vehicle could push the solids back and forth through the water, caustic, or oxalic acid pool in the tank to provide liquid-solid contact and to remove any inert coatings from the surfaces of the particles. Two sluicers may not be enough; one single sluicer will not necessarily perform the job as quickly and efficiently as desired. This was somewhat the case with tank C-108. However, early indications are that the retrieval volume was met with the use of one sluicer. It should be recognized that a two sluicer configuration is the preferred methodology. As noted in a study by (WRPS-0800062), the addition of concentrated NaOH to gibbsite will form an intractable solid mass if there is no mixing.

Any chemical or mechanical HTRH technology will generate fines. Even solids which do not dissolve during HTRH dissolution may break down into sluiceable fines. It is suggested to use a round of recycled supernatant sluicing at the conclusion of the HTRH retrieval process to remove the fines from the SST prior to the final water rinse.

Select retrieval equipment to minimize Hard-to-Remove Heels: It is recommended that sluice nozzles that can pass any solids that can be entrained by the slurry pump be utilized so that retrieval operations are not inhibited from contacting the waste with the sluicer during HTRH retrieval. The new nozzle developed for the VRSS meets this requirement. The effectiveness of the nozzle depends on the momentum transferred to the waste by the sluicing stream, which means fluid velocity. This is the nozzle design and fluid pressure. If the pressure is high enough a water jet should be able to break up the majority of solids that are expected in the HTRH.

Additionally, the capability to heat water or caustic recirculated during HTRH retrieval would prove to be beneficial. The solubility of the material to be dissolved increases as the temperature increases and subsequently the removal effectiveness increases. The heel retrieval tests showed that for C-108 and C-110, most of the solids were dissolved during the dissolution methods

developed. For C-108 it was a water-caustic dissolution and for C-110 it was water alone. Potential increases in dissolution could have been achieved if increased temperatures had been utilized.

Portable valve boxes need to be big enough to insert instruments like Coriolis meters or other process instrumentation (e.g., Raman probe). These types of instrumentation would be beneficial in determining the effectiveness of the dissolution steps as well as the sluicing activities.

CONCLUSION

This report has concluded that tanks C-101, C-102, and C-111 will likely have HTRHs because of their similarity with other C farm tanks. The heels will consist of monolithic chunks made up of the crust in C-111, and possibly in C-101 and C-102. In addition to any monolithic chunks, all three tanks will likely have sand and gravel sized particles containing gibbsite and $Na_7F(PO_4)_2.19H_2O$. From these results, we can conclude that we need some sort of high-pressure delivery system to deliver water and/or caustic for all three tanks. The project is installing high pressure water cannons on the ERSS. This high pressure system will be the second technology deployed for these tanks. Current plans are to use the high pressure water cannons with water only. This study also concluded that a sand Mantis or similar in-tank deployed vehicle can be used to break up the monolithic chunks and also provide mixing for water added to dissolve up $Na_7F(PO_4)_2.19H_2O$. Gibbsite can be destroyed in concentrated sodium hydroxide. The decision on whether a third technology, recommended as a NaOH chemical dissolution is needed will be dependent upon a number of factors including residual quantity of waste, waste form, estimates of residual radiological and non-radiological properties, overall risk profile, and others.

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