Freeze Technology Applications for the Nuclear Industry, Applicable to VLLW, LLW, ILW as well as in ER and the NORM Industry - 14594

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ABSTRACT

The use of freeze technology for moving and removing sludges and other water containing materials under water has been used for over 10 years outside the nuclear industry.

During the last ten years underwater applications of freeze technologies have been explored in Sweden. The technology can, and has been, used in many different steps in a remediation action. Freeze Sampling where undisturbed samples are removed in both soft and hard sediment/sludge, Freeze Dredging; retrieval of sediment with good precision and minimal redistribution, and Freeze Drying; volume reduction of contaminated sludge/sediment.

Another application is object rescue and the most spectacular example is the retrieval of the Swedish aircraft of the type DC:3 was shot down by the Soviet Union in 1952. The plane was found in the Baltic Sea and was taken up in 2003-2004. After rescuing the DC:3 Freeze-Dredging was performed in order to retrieve small objects embedded in the sediments spread around in the area close to the aircraft. The water depth was 128 m and the depth of the sediments frozen was 20 cm.

The use of freeze technology has been investigated by the UK's National Nuclear Laboratory (NNL) for the recovery of nuclear waste. The application involves freezing the waste on a cold surface, which does not have to be flat, and then retrieving it as a single mass which can then be treated or stabilized as necessary.

The application of freeze technology for the recovery of waste from US underground storage tanks is being explored through a USDOE International Technology Transfer and Demonstration programme. A sample deployment being considered involves the recovery of residual mounds of sludge material from waste storage tanks at Savannah River. Operational constraints and success criteria were agreed prior to the completion of a process down selection exercise which specified the preferred configuration of the cryohead and supporting plant. Subsequent process modeling identified retrieval rates and temperature gradients through the waste and tank infrastructure.

INTRODUCTION

The technology for the recovery of waste by the freezing of liquid associated with the waste are denoted in many different ways e.g. freeze dredging [1] and cryograb. The frozen liquid forms part of the 'grab' and is therefore a flexible, versatile and efficient method for recovering solids that might otherwise prove difficult to recover.

Freezing of the liquid is achieved by cooling a surface which is placed in contact with the waste, or liquor surrounding the waste. As water transforms to ice, a continuous barrier for contaminant confinement and immobilization is formed. The confinement results in minimal spreading of sediment/sludge during handling and transport which can otherwise make retrieval of small amounts of solids difficult.

A variety of designs exist for the plates which are tailored to the specific requirements of the deployment. These range from flat plates for large scale recovery of waste, to 'fingers', or collections of fingers for sampling/recovery from difficult locations or even direct injection of refrigerant into waste. A range of options for cooling of the grab surface exist and are selected based on the operational requirements and deployment limitations. Refrigerant options include liquids, gases and electrical cooling.

Once the waste has frozen, the ice-block of waste is moved, attached to the plate, to the required destination. The waste is detached by ceasing cooling and awaiting thaw. The thaw may be accelerated by heating the grab.

PROJECT AT SAVANNAH RIVER SITE (SRS)

The Savannah River Site has 51 underground tanks that are used for storing 138,000 cubic meters (36.4 million gallons) of hazardous and radioactive waste. Four different designs have been used and are called Type-I to Type-IV tanks. All but the Type IV tanks contain dense networks of vertical and horizontal cooling pipes, referred to as cooling coils, which can circulate cooling water. Access to the interior of the tanks is attained through access portals, called risers, which rise from the top of the tank through the ground cover to the land surface. The waste tank bottom is 13.7-15.2 m (45 -50 feet) below ground level. The majority of the risers are less than 0.6 m (2 feet) in diameter. The area above a tank is typically congested with supporting infrastructure.

The tanks contain waste resulting from reprocessing operations. Because the waste tanks are made of carbon steel, the acidic reprocessing waste stream is neutralized with sodium hydroxide and corrosion inhibited with sodium nitrite in the separation facilities before being sent to the tank farms. The neutralization reaction creates salts and precipitates solids [2].

The composition of the sludge solids depends primarily on the original separations process. Significant progress has been made to date with some of the tanks Waste has been recovered by mechanical agitation and pumping. The recovered sludge is vitrified. Where residual solids have remained an additional process of oxalic acid based chemical cleaning has been developed and in combination with hydraulic recovery has proved very effective in removing material from tanks.

Due to the complex geometry of certain tanks dead-spots have been encountered where hydraulic recovery becomes challenging and time-consuming. The dead spots result in 'mounds' of material ranging from 2.5-5 cm (1-2 inches) deep and wide e.g. [3] but in some instances accumulations are up to 0.3-0.6 m (1-2 feet) deep and wide (Figure 4). It is necessary to remove such material in order to comply with agreed standards for tank closure.

Freeze technology has therefore been assessed to support the chemical cleaning phase of the tank closure.

Programme

Phase 1 of the programme provided a conceptual analysis of the application of freeze technology to the retrieval of residual material supported by theoretical calculation and conceptual modeling [2]. A specific constraint associated with certain tanks requires that the tank wall temperature to be maintained at above 21ºC (to prevent embrittlement). This requirement placed emphasis on the ability to predict the temperature gradient through the freezing waste. The study concluded that Freeze technoology could successfully meet the success criteria and operate within the identified constraints.

Phase II has provided bench scale validation of the theoretical modeling. The work included:

- Characterisation of the physical and thermal properties of a waste simulant for Savannah River Site tank sludge,
- Evaluating the sludge rheological and particle size properties, before and after the free-thaw cycle,
- Measurement of the freezing rate and temperature gradient of the waste simulant using a bench-scale test rig,
- Comparison of freezing trial results with a thermal model to allow validation/refinement of the model,
- Initial investigation of the potential cooling of the steel tank wall by the cryohead by performing bench-scale freezing trials with and without heating of the tank wall

INVESTIGATIONS

Simulated waste

To ensure a representative study of the freezing behaviour of Savannah River Site tank waste a simulant was required. The wastes in the Savannah River tanks were generated from nuclear reprocessing operations carried out at the Savannah River.

Selection of the simulant composition and preparation method was made in agreement with SRNL. It was agreed that simulant preparation should follow protocols developed previously by SRNL and used in other process development programmes. These methods essentially follow the original process that generated the waste sludge by precipitating oxides and hydroxides from an acidic solution.

Within the scope of the Phase 2 programme, only a single waste simulant could be produced and clearly no single simulant can be said to represent the full range of chemical and physical properties of all the residual waste heels in the tanks. The purpose of the trials was to understand the thermal properties of the waste simulant and potential changes in the physical properties that might impact on the downstream processing. The thermal properties of the sludge are likely to be dominated by the high water content rather that the precise solids composition. In addition, changes in the physical properties are expected to modest and it was judged sufficient to illustrate the typical changes that could be expected from the freeze-thaw cycle. Therefore it was not considered necessary to target extreme properties in the simulant, and sufficient to ensure that it was reasonably representative of the materials in the tanks.

Characterization included total suspended solids analysis; particle size distribution (using a Malvern Instruments Ltd. Mastersizer 2000); rheology (Bohlen CVO100 rheometer using a coaxial cylinder and bob setup); thermal conductivity (- 30ºC to 30 ºC) (K-Analyse AB, located in Sweden);

Evaluation of freezing rate and thermal profiles through waste

A bench scale rig was manufactured to test several parameters. the cryohead is positioned centrally in a tank at the selected height for the trial for all trials. Temperature measurements were made in the central plane bisecting the cryohead and parallel to the length of the tank. The rig components are shown in Figure 2.

Before each trial the waste simulant was homogenised in the tank and a ~50 mℓ sample of the simulant was taken for total and dissolved solids, particle size distribution and rheology analysis.

The duration of experiments were limited by the working day length and they lasted typically 5-8 hours. This was sufficient to typically build up a ~5 cm layer of ice on the surface of the cyrohead.

At the end of each run the cryohead was removed from the tank and the attached frozen sludge was photographed to allow the dimensions to be calculated before allowing it to thaw under ambient conditions in the laboratory. The thawed simulant was weighed and retained for analysis.

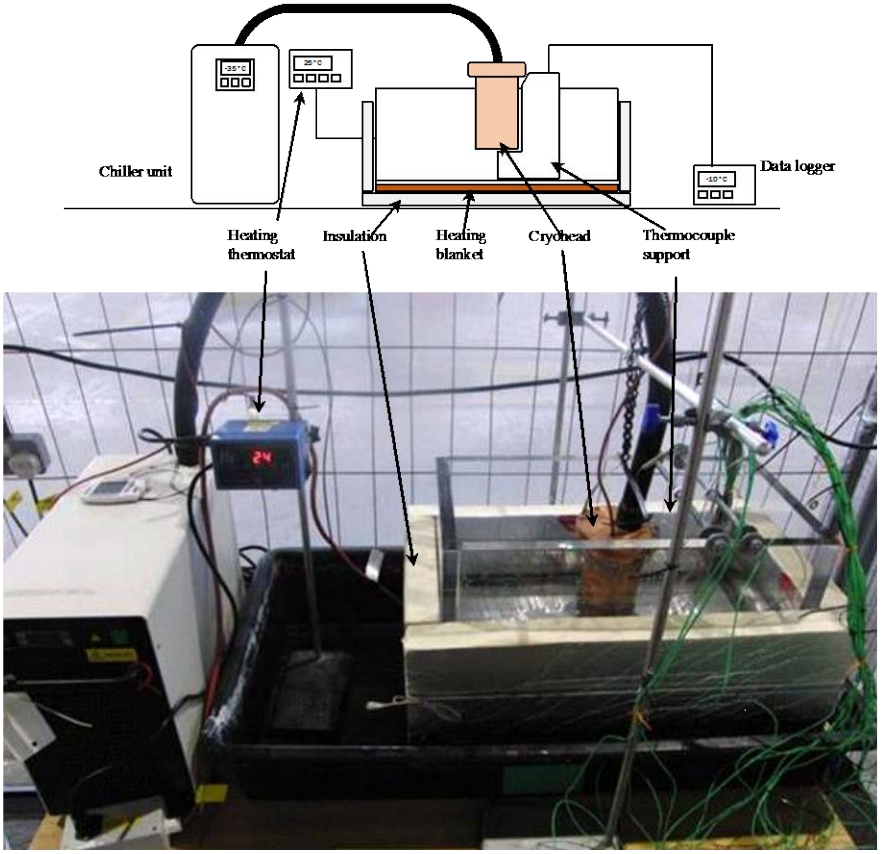

Figure 1 Bench scale rig

Seven freezing trials were performed using the waste tank sludge simulant. In addition, several experiments using water and saturated sand were performed during commissioning of the rig but are not reported in detail. . Three sets of cryohead positions and temperature were investigated, each repeated with and without heating of the tank base applied giving a total of 6 different trials. Trials 11 and 12 were nominal repeats due to a malfunction of the chiller unit.

Experimental results

Freezing of the waste produces a solid mass with no obvious heterogeneity at a macroscopic scale, apart from the formation of a frozen supernate layer of the upper surface of the waste caused by a small degree of settling, in the order on 1 cm in depthsee Figure 2a
As the sludge thawed it fell cleanly from cryohead into the collection vessel. Thawing the waste results in partial dewatering, with substantial separation of the solid and liquid phase, illustrated in Figure 2b. For example the mass fraction of supernate that could be decanted/poured from the vessel with minimal solids carryover for Trials 11 and 12 was approximately 58 wt% and 61 wt% respectively. This dewatering effect is a well-established effect that can be varied with the rate of freezing and is used on an industrial scale for dewatering waste sludge.

(a) (b)

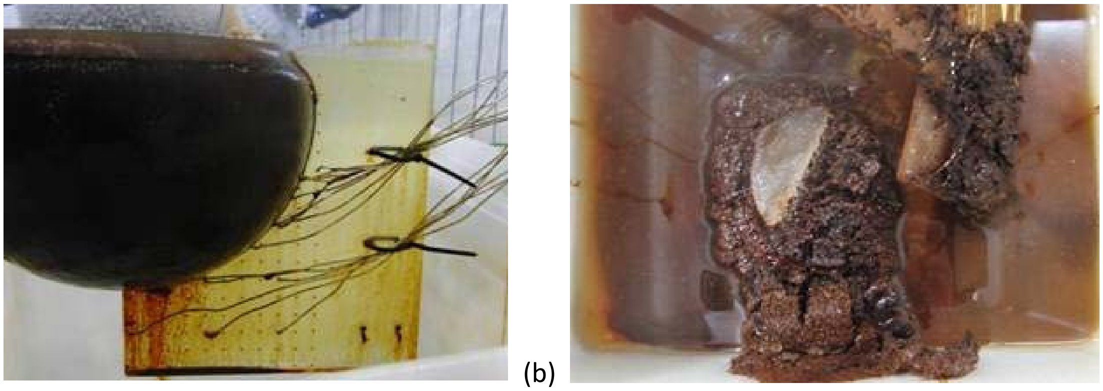

Figure 2a) Frozen sample retrieved at the end of Trial 11, 2b) thawed simulant illustrating dewatering of sludge

Particle size distribution

Particle size distributions were measured by the laser scattering technique. However, the available instrument was only able to suspend particles up to 120 µm in diameter and therefore particle size distribution are given as the volume fraction of sub 120 µm particles. To characterize larger particles optical microscopy was used.
Prior to freezing the waste, the particle size distribution is fairly narrow and falls largely in the 2-60 µm range, Figure 3. As expected there is little variation between the starting waste simulant of the various trials as the four batches of simulant prepared had similar particle size distributions.

The sub 120 µm particle size distribution only shows modest changes after freezing, but there is an increase in the distribution around 80-120 µm and microscopy shows the presence of agglomerations of particles. These agglomerations are typically 100-250 µm in size, but in a few cases exceed 500 µm. These correspond to the rapidly settling solids observed when handling the thawed simulant.

The agglomerates are weakly bound together and whilst low shear mixing did not appear to break them down to a significant extent they were easily broken up by mild grinding between two surfaces during handling, suggesting high shear mixing may readily disperse the agglomerations.

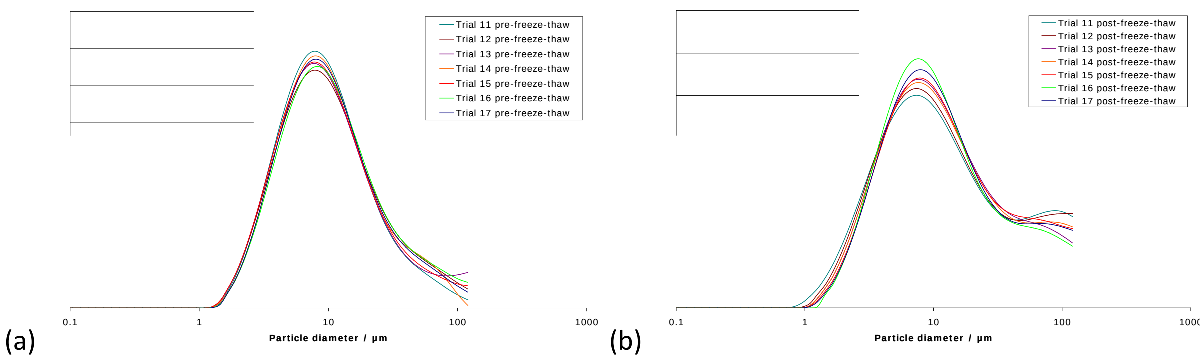

Figure 3 Particle size distribution measurements of simulant for the sub-120 µm fraction of solids 3a) pre-freeze-thaw cycle and 3b) post-freeze-thaw cycle.

Total and soluble solids analysis

The total solids content measurements are judged to be accurate to within ±0.25 wt% and indicate that there is may be a small reduction in the total solids content during freezing. A decrease in the total solids content would imply that a fraction of the insoluble solids or soluble salts were displaced in the remaining unfrozen sludge as the freezing front grows. However, caution is needed interpreting the results because of the difficulty in obtaining representative samples of the thawed simulant with relatively fast settling solids after the freeze-thaw cycle. This is illustrated by the total solids content measured for sample decanted after allowing the slurry to settle for 1 minute following mixing; these show a further systematic decrease in the solids content in the sample. Therefore it is considered more likely that the apparent reduction in the total solids content is caused by solids settling during preparing the sample for analysis. This is supported by the soluble salts content analysis of the sludge before and after the freeze-thaw cycles, that show no significant change. This demonstrates that as the sludge freezes the dissolved salts are not displaced into the surrounding slurry as pure ice crystals grow. Instead the dissolved salts are incorporated into the frozen sludge as the freezing front grows, presumably as pockets of salt solution. This implies that the salt solution is in equilibrium with ice as the sludge freezes, which may affect its thermal properties during freezing.

Rheology

The rheology of the slurry prior to the freeze-thaw cycle was non-Newtonian and broadly characterized by Bingham type behaviour. Similar flow curves were recorded for all. .
The yield stress prior to freezing was in the range 0.4-0.8 MPa, with a similar plastic viscosity. Measurements using a pre-shear phase before the flow curve measurement were found to give similar results as in the absence of pre-shear. In addition there is hysteresis in the flow curve, with a lower shear stress as the shear rate is reduced. A reproducible step in the flow curve at ~50 s-1 was seen for all the samples. This appeared both with and without a pre-shear and also using the serrated bob designed to minimize surface slippage and therefore seems to be a real effect but it has not been possible to determine its origin.

After the freeze-thaw cycle there is a significant reduction in the yield stress of the sludge but the plastic viscosity is slightly higher. This is likely to be caused by the agglomerations of particles reducing number concentration of particles, in addition some settling of the large particles may occur during measurements effectively leading to a lower suspended solids fraction in the slurry. In summary the Savannah River Site tank waste simulant shows only modest changes in properties during the freeze thaw cycle. The most significant effects are the agglomeration of particles from a proportion of solids in the slurry and the dewatering of the slurry as it thaws. This effect as also been seen in other studies undertaken by the NNL of ferric floc. The impact on downstream handling and processing operations after the freeze-thaw cycle is likely to be minimal, but would need to be considered.

Freezing performance

The freezing experiments measured the temperature profile across a radial plane bisecting the cryohead trials as a function of time. In addition, the dimensions for the frozen sludge were measured at the end of each run. It was not possible to directly measure the growth of the freezing front during the trial, owing to the opaque simulant, but this can be estimated from the contour plots of the temperature profile over time.

The relatively low thermal conductivity of the sludge and relatively high viscosity that prevents large scale convection means that bulk cooling to sludge in the tank does not occur. Instead there is a relatively narrow freezing front with a steep temperature gradient that progresses gradually from the surface of the cryohead, and sludge at a distance remains largely unaffected. This behaviour can be contrasted with trials using water that showed relatively uniform temperature distributions across the water tank as convection currents caused effective mixing of the water and transfer of heat. Initially all thermocouples show the same decreasing temperature as the liquid water in the tank is gradually cooled and well mixed by convection currents. Once the temperature reaches 4^{o}C water is at its densest [4] and convection is significantly reduced. At this point further cooling occurs as the freezing front progresses into the water, illustrated for example by the drop in temperature seen in the thermocouples nearest the cryohead at ~3 hours. This observation illustrates that a natural convection term may be needed in cases where for example there is a significant over-standing layer of water above sludge.

Heating the base of the tank causes an increase in temperature of the sludge adjacent to the steel base because the initial sludge temperature was initially lower than the base temperature. Despite this, the low thermal conductivity of the sludge means that the impact on the growth of the freezing front is relatively small and the freezing rate is quite similar with and without heating of the base, except when the front approaches close to the base surface.

As the freezing front approaches within 1-2 cm of the base, some cooling of the base surface occurs. Figure 7 shows the temperature distribution of the upper surface of the base at the end of Trial 17, the external temperature of the base was 27±4°C (the temperature controller caused the external base temperature to oscillate around 27°C) and the freezing front was just under 1 cm above the surface of the base.

These results do not transfer directly the Savannah River Site tank conditions because, for example, the initial temperature of the waste simulant was less that 21°C and the tanks base heating is not representative of the tanks. However, retrieval to within 1 cm of the wall surface is significantly better than is required for successful heel retrieval, the tank wall is very large and maintained at a temperature significantly above 21°C and is a large heat reservoir, and only a small fraction of the steel wall would be in the region of the cryohead. Consequently the observations provide a good indication that a cryohead design can be designed that will allow freezing within a close distance of the tank was without compromising the integrity of the steel by lowering its temperature below 21°C.

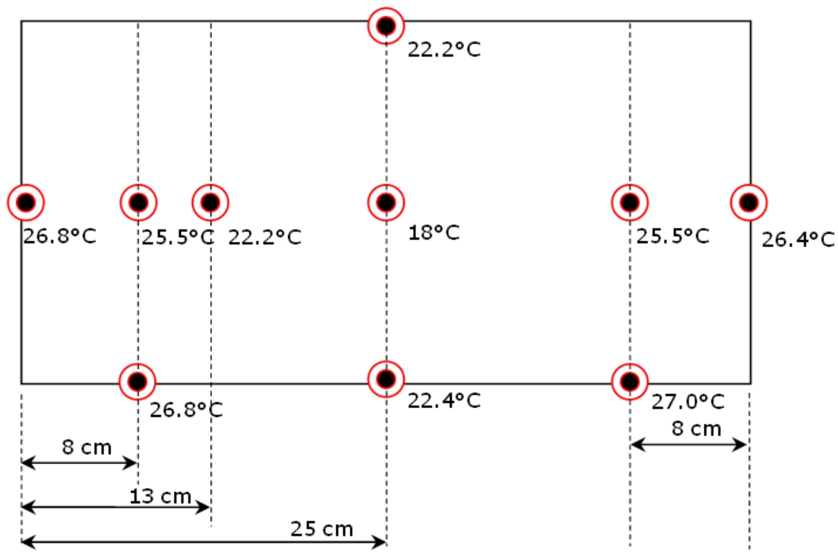

Figure 4 Base plate temperature distribution at the end of Trial 17

The rate of ice growth on the surface of the cryohead decreases as the thickness of ice increases, but it is illustrative to estimate and average rate of growth since the cryohead temperatures and dimensions as well as trial durations are of a similar in magnitude as might be used in practice for the waste tank application. The rates have been estimated from the maximum radial thickness of ice and thickness underneath the cryohead and are summarized in Table 5. The results emphasize the relatively small effect of base heating on the rate of ice growth and the modest impact of varying the cryohead temperature between -25°C and -35°C.

Table 1 Average ice growth rate in Trials 11-17

Trial	Cryohead height above base / cm	Heater setting / °C	Average internal cryohead temperature / °C	Trial duration / hours	Radial ice growth rate / cm.hr^{-1}	Ice growth rate under cryohead / cm.hr^{-1}
11	11	-	-34.9	5.8	0.9	1.0
12	11	-	-28.6	5.9	1.1	0.8
13	11	25	-34.6	6.5	1.0	0.9
14	6	-	-30.1	5.8	0.9	0.9
15	6	25	-35.7	6.7	0.8	0.9
16	6	-	-26.6	6.7	0.8	0.7
17	6	25	-26.9	8.1	0.6	0.6

FREEZE TRIAL ON CONTAMINATED MATERIAL

Studsvik Nuclear AB has done tests on real contaminated sludges. The sludges consisted of gravel, sand and some organic materials. The sample was firstly measured to determine the total activity. However this turned out to be difficult due to the selling time of the sample which was very short in comparison to the measuring time. The sample was thereafter poured into a container and froze for 16 hours after which it was thawed on geotextile.

The activity in the sample as it arrived was 2890 Bq, in total dominated by Co-60 and Cs-137. After the sample had been frozen activity was separated into the liquid and the solid phase, where the liquid phase only gave less than values, $<1\times10^{-2}$ Bq/g for each of Co-60 and Cs-137 which equals <5.6 Bq for Co-60 and <5.4Bq Cs-137 in total activity.
The solid phase contained the rest of the activity but due to the inhomogeneity of the sample as well as a large portion of the finer particles being stuck in the geotextile it was not possible to make a full activity balance. The liquid was however measured on a representative sample.

DISCUSSION

Freeze technology has been used in a variety of related nuclear and non-nuclear sludge recovery operations [1,4]. A principal advantage of the technology over other grab or hydraulic methods is the ‘complete’ nature of the grab achieved, coupled with minimal disturbance of the waste which prevents re-distribution of the waste during retrieval (so-called “chasing the waste”).

Prior successful deployments for the recovery of sludge and items in nuclear environments would suggest a high Technology Readiness Level (TRL) for both the freeze technology and deployment system. Deployment in certain tanks at the Savannah River complex requires particular attention to maintenance of the temperature of the tank wall to prevent damage to tank infrastructure and hence a conservative TRL is currently claimed. Modelling and bench scale experiment has indicated that it is possible to satisfy this criteria, however a more conservative approach to waste recovery (relative to previous deployments) is required and additional engineering features may be required (e.g. thermally insulated stand-offs).

CONCLUSIONS

- Freeze technology has been effectively employed for the recovery of nuclear and non-nuclear sludge. The principle advantage of the technology over other grab based technologies, and hydraulic methods is that waste re-distribution is minimized. This reduces the number of deployments required to recover waste.

- Freezing rates and temperature profiles have been measured for a simulant of the Savannah River Site tank waste. Modelling results match the experimental results very well in terms of the temperatures profiles observed and demonstrates the predictive capability of the model. Where differences have been identified these can be explained as resulting from simplifications in the model (the cryohead is modelled to have a constant temperature throughout the trial) or discretization in the model.

- While the modelling can be developed further. The current model is sufficient to support the engineering design of a cryohead.
- The conditions needed to meet the requirement to maintain the tank wall temperature above 21°C has been investigated experimentally. The relatively low thermal conductivity of the sludge allow large temperature gradients to occur in the sludge such that the freezing front can approach close to the steel surface with relatively small decrease in the steel temperature if there is background heating applied to the steel. The model shows accurate prediction of the temperature of the steel wall provided the thermal conductivity and heat flux in the steel is included. Definition of the wall structure in the tank and sources of heat is needed to model and asses the potential wall cooling and to optimise the design of the cryohead. Experimental and modelling results indicate the temperature constraint is likely to be achievable through use of insulated standoffs on the cryohead.

- Experimental freezing studies performed with a bench scale cryohead and simulant of the Savannah River Site tank waste demonstrate that minor changes in the physical properties of the sludge occur during the freeze thaw cycle:
    - Partial dewatering of the sludge occurs during thawing of the waste. This may require the thawed sludge to be mixed and homogenized prior to pumping from the in-tank corral.
    - The freeze thaw cycle causes agglomeration of some solids in the waste sludge that are not broken up during low shear handling and mixing. These settle relatively quickly compared with the parent sludge. It is unlikely that these will significantly impact of downstream pumping and handling operation, but this requires review by Savannah River Site. If there are perceived risks, mitigation by high shear mixing could be considered.

- The Phase 1 feasibility statement for application of the cryograb method to waste heel sludge retrieval in the Savannah River Site waste tank has been confirmed. A waste recovery rate of approximately 53 ℓ per week has been estimated. The current development work has raised the preliminary technical readiness level of the method for this application to 3-4.

- Cryograb provides a viable technology option to accelerate tank closure, specifically in cases where the presence of residual mounds of sludge are an issue and access is physically restricted.

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