Document Discussion

Return To Library > Records 2 > ERID-102500 through ERID-102999 > ERID-102711 1) DEMONSTRATION OF A SYSTEM FOR IN-SITU TANK WASTE HEEL IMMOBILIZATION AT LANL

Created By:	Aurelia A. Martinez/USERS/LANL
File name:	Target-ERID # for Domino.txt
Version:	1.0
Document Type:	RPF Record
Description:	SUBMITTED BY JOANNA KRAMER EP-TA21

Document Details:

Title:	ERID-102711 1) DEMONSTRATION OF A SYSTEM FOR IN-SITU TANK WASTE HEEL IMMOBILIZATION AT LANL
ERID Number.StartPage:	ERID-102711
Office of Record:	WES-DO
Date Received:	08/22/2008
Official Use Only:	N
Page Count:	100
Record Type:	Letter
Document Date:	01/02/2004
To:(Addressees - Organization) *(separate multiple values with semicolons)*	N/A
From:(Senders - Organization) *(separate multiple values with semicolons)*	AEA TECHNOLOGY
Other Document Number(s): *(separate multiple values with semicolons)*	N/A
TA: *separate multiple values with semicolons)*	N/A
PRS Number(s): *(separate multiple values with semicolons)*	
Record Box Number:	

*** Denotes Fields that are mandatory.**

To download this file, right mouse click on the file and select 'Save to Disk' or 'Save Target as'

Target-ERID # for Domino.txt <-- This link points to this version.

To check-out and/or edit this file, select Edit Document or Check Out Document from the Document menu above.

File Cabinet: Records 2

Binder Category: ERID-100000 through ERID-109999

10 2711

AEA Technology Engineering Services, Inc.

Demonstration of a System for In-Situ Tank Waste Heel Immobilization at LANL

Final Report

Prepared for

US Department of Energy under International Agreement Number DE-GI01-00EW56054

PTP # DOE/Heel Grouting/01/v1

January 2004

Prepared by	J Faldowski	Approved By	J Faldowski
Signature	[signature]	Signature	[signature]
Date	4/27/05	Date	4/27/05
Reviewed by	P Griffiths	~~Quality Assurance~~	~~R~~ Mullens
Signature	[signature]	Signature	[signature]
Date	4/27/05	Date	4/27/05

AEA TECHNOLOGY ENGINEERING SERVICES, INC
184-B Rolling Hills Road
Mooresville, NC, 28117
Tel: (704) 799-2707
Fax: (704) 799-6426

ESI Document No. **2173-6-003**

REVISION	0					
DATE	4/27/05					
APPROVED	JAF					

DOCUMENT CHANGE RECORD

Document Title	Document Number & Revision
Demonstration of a System for In-Situ Tank Waste Heel Immobilization at LANL Final Report File Name: 2173-6-003 Rev 0 (Final Report).doc	*ESI Document No.*: **2173-6-003** *Revision*: **Rev 0**

Pages Changed	Description of Change

Prepared	__________	Project Manager	__________
Signature	__________	Signature	__________
Date	__________	Date	__________
Verified/Reviewed	__________	Quality Assurance	__________
Signature	__________	Signature	__________
Date	__________	Date	__________

1. Contents

2. Introduction

Experience has demonstrated that when retrieving waste from tanks across the DOE complex, there is a point where the limits of a retrieval technology are reached and a small heel is left in the tank. Current tank closure practice is to pour grout into the tank, covering the heel but without attempting to mix the waste and the grout together. The result is that the waste and grout are unlikely to mix and form a homogeneous mass and the remaining waste heel may, therefore, still be in a mobile form which could leak into the environment. Increasingly strict regulatory requirements are making this an increasingly difficult strategy to defend. Consequently, an effective means of carrying out in-situ stabilization (i.e. intimate mixing of waste with grout) for varying quantities of residual waste material in tanks would be of considerable benefit to tank waste retrieval and closure operations throughout the DOE complex.

AEA Technology has previously developed and demonstrated an effective means of mobilizing and retrieving tank waste contents using its Power Fluidics™ equipment. To date, this equipment has been deployed successfully at several tank projects where the work has been completed within the proposed cost and schedule. Adapting this safe, proven and effective technology for carrying out in-situ stabilization of waste heels would represent a considerable improvement to current technology employed in tank closure operations. Additional benefits include the ability to mix, retrieve, and sample the bulk waste and stabilize the tank for closure using the same equipment. Applying such a unified approach to tank closure would save capital equipment costs, consolidate safety documentation, reduce field deployment schedule/costs, reduce secondary waste generation, and reduce worker radiation exposure levels.

This report documents the method of accomplishment and results of the scope of work carried out under International Agreement Number DE-GI01-00EW56054; Project Technical Plan DOE/Heel Grouting/01/v1 (Reference 3). The principles of Fluidic Pulse Jet Mixing (PJM) and the technical issues to be addressed in using Power Fluidics™ equipment to grout tank heels are presented. The requirements for the development of grout formulations suitable for use in such applications are discussed. The inactive waste heel stabilization demonstration program is described, covering the development of a suitable grout formulation and the application of this grout to waste heel stabilization using a prototype PJM system. The data, results, and conclusions of the work are presented along with considerations for future work and field deployment of the equipment into a radioactive waste tank.

3. Principles of Fluidic Pulse Jet Mixing

Power Fluidics™ Pulse Jet Mixers (PJM's) have been operating in UK nuclear plants since 1970. The technology is proven across a range of applications and is standard technology in UK nuclear facilities.

All Power Fluidics™ mixing systems use compressed air as the motive force for the movement of liquid or liquid/solids slurries. Each system features a charge vessel (CV) which is a fluid reservoir that is filled or discharged by the evacuation or pressurization of the void space above the liquid level. The control of the air into and out of the Charge Vessel is accomplished using a Jet Pump Pair (JPP), designated the fluidic system Primary Controller. The JPP comprises two back-to-back ejector elements as shown in **Figure 1** below. Its purpose is to:

- Supply a positive air flow and pressure to the charge vessel during the drive phase
- Provide a vent path for the air during the vent phase
- Produce a partial vacuum in the charge vessel during the suction phase

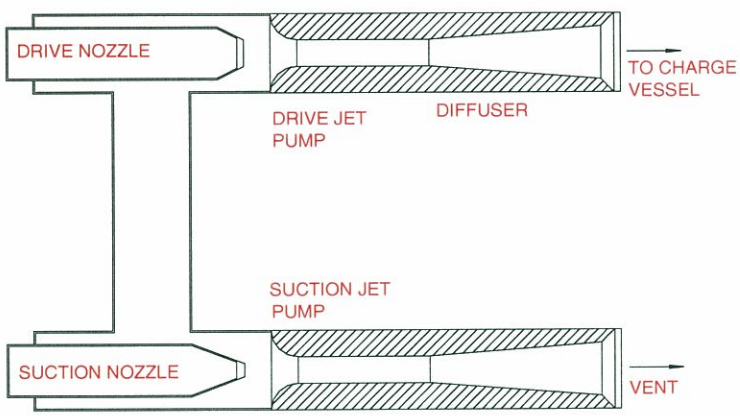


Figure 1: Jet Pump Pair

The equipment upstream of the Jet Pump Pair is designated the fluidic system Secondary Controller. Its purpose is to:

- Control the duration of the drive phase and to supply compressed air to the "drive" part of the JPP during this phase
- Control the duration of the vent phase and to switch off the air supply to the JPP during this phase
- Control the duration of the suction phase and supply compressed air to the "suction" part of the JPP during this phase

The phase durations are regulated electronically by AEAT's PRESCON™ controller. The PRESCON™ computer both analyzes the input from the process instrumentation and controls the sequencing and operation of the plant. The controller automatically compensates for variations in the system (e.g., changes in liquid level, specific gravity, and viscosity) and so maintains the fluidic system operation at optimum efficiency.

The PJM mobilizes the material contained within the waste tank by first drawing liquid out of the tank into the charge vessel. This liquid is then repeatedly forced backwards and forwards between the tank and the charge vessel through an engineered nozzle designed to give a desired flow pattern for the fluid exiting the Charge Vessel. The mixing process is repeated until the tank is well mixed. The system configuration may also include remotely operated directional "wash" nozzles incorporated into the system above the liquid level in the waste tank to aid the mixing process and dislodge encrusted solids adhering to the tank walls.

3.1. POWER FLUIDICS™ PULSE JET MIXING SYSTEM OPERATION

The Power Fluidic pulse jet mixer process is designed to mix sludge with existing supernatant or added liquid to homogenize and mobilize sludge and liquid waste. The mixer system typically has the ability to transfer waste via a discharge line to a waste receipt facility and provides a means of taking a sample of the waste at any point during operations. The major components of the system are:

- Charge vessel – pressure vessel which acts as a reservoir for the system.
- Suction tube – pipe in the tank used to draw the tank contents into the charge vessel and discharge them back into the tank for mobilization. The end of the pipe contains an engineered nozzle that produces a focused jet of liquid for effective mixing.
- Jet Pump Pair - provides the gas pressure and flow conditions in the charge vessel and acts as a barrier between the clean incoming compressed gas and the potentially hazardous liquid.
- Valve skid - handles only clean gas and provides the gas flow to the jet pump pair as required.
- Remote directional nozzle system for wall washing. This may be a hydraulically controlled nozzle or an advanced custom designed nozzle depending on system requirements.
- Off-gas Skid – provides HEPA filtration of the air vented from the system during all phases of operation prior to discharge to the atmosphere.

3.2. MOBILIZATION MODE

During the suction phase, the jet pumps are used to create a partial vacuum in the charge vessel, which in turn draws material up from the storage tank into the vessel. This is shown in Figure 2

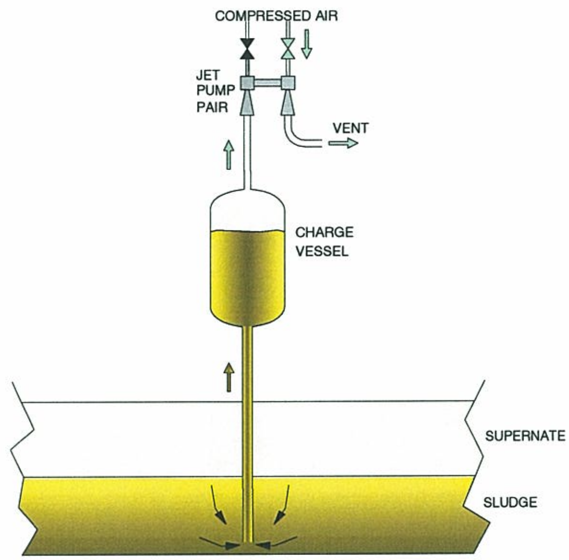


Figure 2: Suction Phase

Once the charge vessel has been filled with material, the jet pumps pressurize the charge vessel, which drives the liquor back into the storage tank, agitating and mixing the contents of the tank. This is the drive phase and is shown in Figure 3.

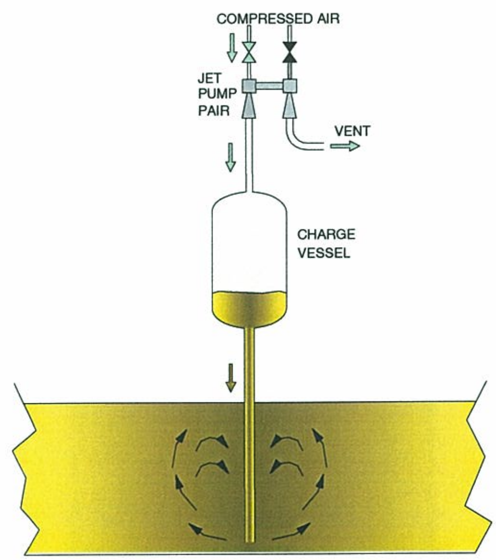


Figure 3: Drive Phase

When the level has reached the bottom of the charge vessel, the drive phase is terminated and the charge vessel is depressurized through the jet pumps in the vent phase. This is shown in Figure 4. The cycle is then repeated until the tank contents have been mixed.

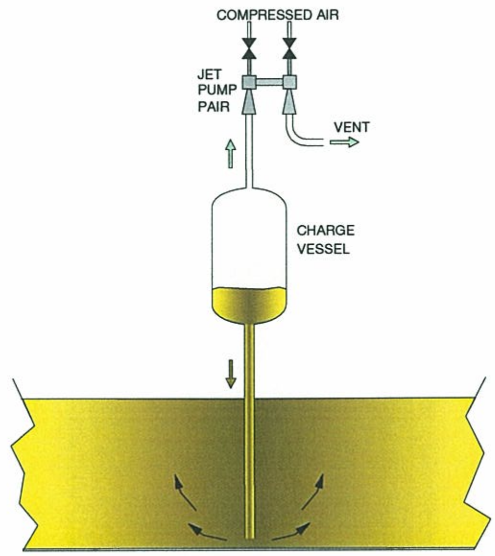


Figure 4: Vent Phase

3.3. TRANSFER MODE

The diagram below illustrates a system which is capable of transferring the contents out of the tank; a transfer line is added below the charge vessel.

During the suction phase, the jet pumps are used to create a partial vacuum in the charge vessel, which in turn draws the mixed slurry up from the storage tank into the vessel. This is shown in Figure 5

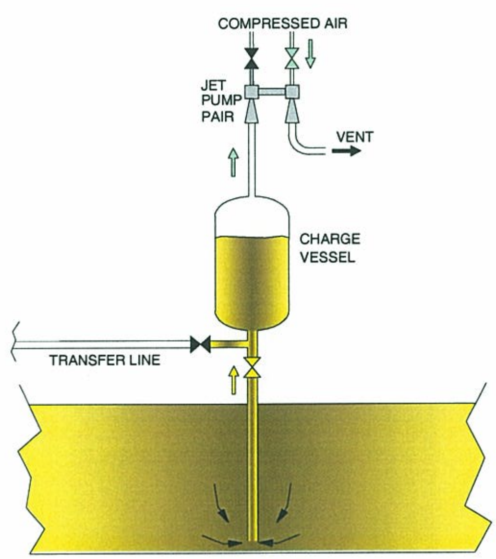


Figure 5: Suction Phase – Transfer Mode

Once the charge vessel has been filled with the slurry, the jet pumps pressurize the charge vessel, which drives the slurry along the transfer line as shown in Figure 6.

When the level has reached the bottom of the charge vessel, the drive phase is terminated and the charge vessel is vented in the same manner as in the mobilization mode (Figure 4)

This sequence can be repeated until the required amount of material has been transferred

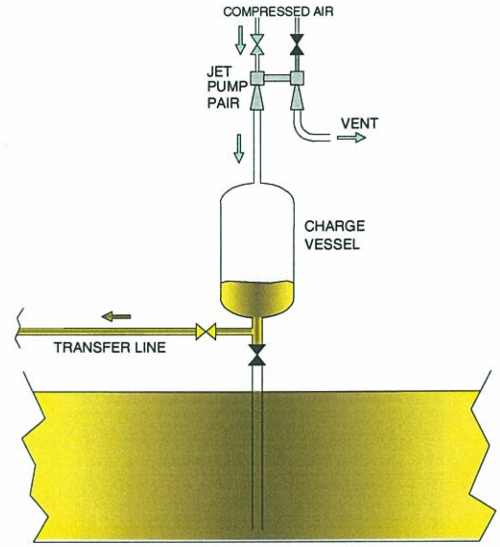


Figure 6: Drive Phase – Transfer Mode

3.4. SAMPLE MODE

The diagram below illustrates the system configuration for collecting a sample of the tank contents. Tank material is initially drawn from the tank to fill the charge vessel as in the transfer operation (Figure 5 above).

When the sample is being collected, the system is designed so that the liquid is drawn out of the charge vessel using a pump installed in the sample line discharging into a collection vessel.

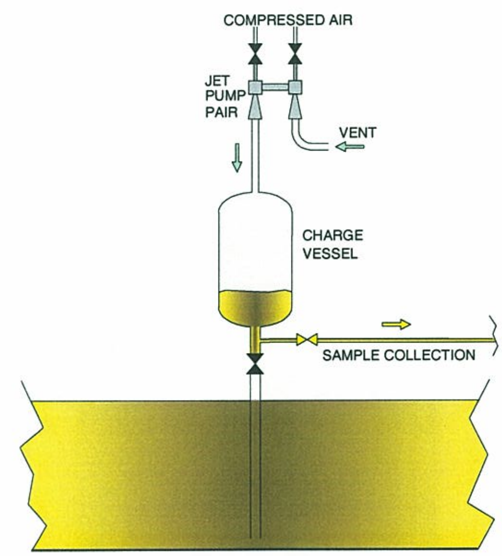


Figure 7: "Drive" Phase – Sample Mode

3.5. WALL WASH MODE

The diagram below illustrates the system configuration for wall washing. A remote directional nozzle is incorporated into the system below the charge vessel and above the waste tank liquid level. Tank material is initially drawn from the tank to fill the charge vessel as in the transfer operation (Figure 5 above).

During the drive phase, the liquid jet emerging from the nozzle dislodges sludge adhered to the tank walls. The sludge, which then falls to the bottom of the tank, can be maintained in suspension using the mobilization mode of operation described above.

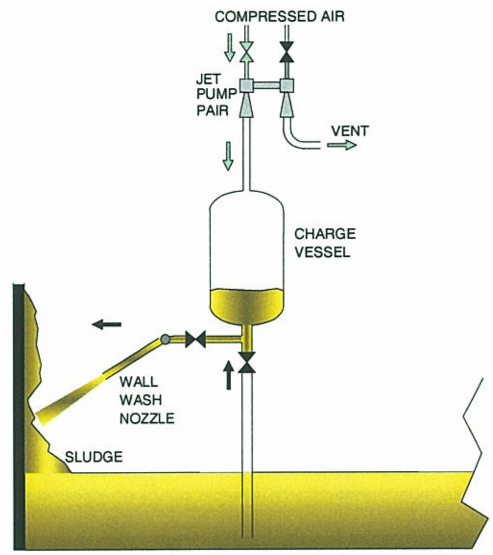


Figure 8: Drive Phase – Wall Wash Mode

4. Grout Formulation Development

AEA Technology plc and its forerunners have been at the forefront of UK cementation technology development and performance evaluation for the treatment of radioactive wastes for over twenty years. This study relied heavily on that experience in the development of a suitable grout for stabilization of a tank waste heel simulant.

Two primary considerations are important for the formulation of a grout for stabilizing a waste heel; the grout must have good flow properties for mixing and it must meet applicable standards for waste stabilization characteristics. This section reports how the grout formulation was designed and developed for the inactive demonstration program to:

- optimize the mixing process by maximizing grout flow and workability; and
- meet the minimum requirements of the NRC Technical Position for Grouted LLW: Appendix A.

4.1. THE FORMULATION DEVELOPMENT PROCESS

The design and demonstration of a cementation treatment process for a given waste consists of five interdependent factors. These factors are:

1. Waste characterization: To determine chemical and physical composition of the waste, and potential variability. The waste characterization data are used to make a preliminary selection of a cement formulation, waste loading and process method.

2. Product specification: To determine the applicable specification, which will provide product performance targets such as leachability, strength and durability. It is essential that all specification and process criteria are incorporated into the formulation development process at the earliest opportunity.

3. Formulation development: To identify an acceptable grout recipe and identify the specification of raw materials used in the recipe. Formulation development work is carried out using methods of increasing scale. Initial work is carried out at bench scale to identify a suitable formulation to treat a waste. Suitability of a formulation includes evaluation of mix viscosity, flow, temperature, setting time and presence of bleed water after setting. Once a suitable formulation is identified, intermediate scale mixes are carried out to produce product evaluation test specimens and to better understand the likely full-scale production process.

4. Product evaluation: To test the product performance both on a short time scale (days) and over longer periods (months). The type of tests carried out may include: leachability, strength, durability, dimensional stability and permeability. If the formulation does not meet a specific criterion then the formulation must be modified until the full specification is met.

5. Process optimization: In addition to meeting the product specification, the waste treatment process must be practical to operate. This factor is considered throughout the formulation development process and can be demonstrated by carrying out large-scale mixes (e.g. 200 liter) of the finalized formulation.

4.2. SPECIFIC FORMULATION DEVELOPMENT FOR WASTE HEEL JET GROUTING DEMONSTRATION

The specific goal of this demonstration work was to develop a grout formulation to immobilize a 40 $^{w}/_{o}$ solids kaolin clay / water simulant waste heel. This simulant was selected as it is a generally recognized and accepted waste simulant that has been used successfully in previous PJM tank mixing and retrieval development work. The formulation development work was carried out by AEA Technology, Waste Management Technology (WMT) based at Winfrith, Dorset, UK.

The outline waste heel treatment method enabled the basic rheological requirements of the grout and wasteform formulation to be defined:

- The grout was required to have a suitable flow and workability to enable it to be pumped to the tank, and to allow the waste heel and grout to be well mixed by the Power Fluidics™ System. This was achieved by using a high water to cementitious solids (w/s) ratio, thereby minimizing the viscosity of the grout suspension.

- A large volume of grout relative to the volume of waste retained in the tank was required to enable the waste heel to be mobilized and to allow the waste to be adequately mixed with the grout. This was taken to be the case because retrieval efforts using Power Fluidics equipment in the past have drawn the tank down to unmixable levels of less than 2". The addition of grout raises the tank level enough to facilitate withdrawal and reinjection of material by the Pulse Jet Mixer, thus, initiating mixing of the grout and waste heel together.

- The simulant waste slurry has a high water content (i.e. 60 $^{w}/_{o}$ water), as could be expected in a tank waste heel. Therefore a fluid grout with high waste loading would have increased the effective water/solids (w/s) ratio of the product compared to that of the grout alone. This would have led to an unacceptably large volume of bleed water. i.e. over standing water on the set product. One of the aims of the work was to give a final mixed product with zero bleed, as this removes the need for any secondary waste water treatment. These factors necessitated that the waste loading of the formulation be kept low, e.g. 10 $^{w}/_{o}$.

- The final wasteform must meet the minimum requirements of the NRC Technical Position for Grouted LLW: Appendix A (Reference 1).

- Availability of raw materials for grout production must be taken into consideration during the small- scale formulation development work.

4.2.1. Selection Of Materials

The properties of a grout/waste formulation, such as flow and workability, are strongly controlled by the raw materials used (Reference 2). Since the waste heel jet grouting demonstration was to be performed in the US, to enable the development of a reproducible grout (allowing the effects of raw materials to be understood and minimized), samples of blast furnace slag (BFS), pulverised fuel ash (PFA) and ordinary Portland cement (OPC) available in the US were sent to AEA Technology WMT, Winfrith, UK. Examination of the materials resulted in a PFA/OPC based formulation being selected to treat the simulant waste heel. A 3:1 ratio by weight of PFA/OPC grout was anticipated to have the correct proportions of PFA/OPC to ensure good strength development in the wasteform without excessive heat generation. The selection of a PFA/OPC grout was also preferred to that of a BFS/OPC grout due to the lower density of a PFA/OPC grout. A low density grout is preferable for maximizing the lift distance in the Power Fluidics™ Pulse Jet Mixer.

4.2.2. Formulation Development

The formulation development work was carried out using 150 ml scale scoping trials, 2 liter scale mixes of selected formulations and 200 liter scale pumping tests.

4.2.2.1. 150 ml scale scoping trials

Following the initial assessment of the grout property requirements, small-scale scoping trials were used to investigate the properties of the:

- Kaolin/water simulant waste at $40^{w}/_{o}$ solids
- 3:1 PFA/OPC control grout with increasing w/s ratio
- Grout/simulant mixes where the waste loading was increased incrementally at a fixed w/s ratio

Viscosity of the fluid grout and bleed on the set product at 24 hours curing were the two principle grout properties investigated by the 150ml scoping trials. The scoping trials identified the range of w/s ratios at which acceptable (high) grout fluidity and zero / minimal bleed were achieved (minimal bleed was defined as a volume of overstanding water on the 150 ml scale sample of set product, which experience has shown on increasing the size of the product will give zero bleed at large scale).

Using the viscosity and bleed data from these trials, a grout with acceptable viscosity, minimal bleed at 24 hours curing and predicted workability was selected for further testing. The selected formulation was a 3:1 PFA/OPC grout, with a w/s ratio = 0.688. This was mixed with the $40^{w}/_{o}$ kaolin slurry to achieve a $10^{w}/_{o}$ waste loading in the final product, resulting in a final w/s=0.80.

Small scale testing at w/s ratios > 0.80 were not carried out as no further significant decrease in viscosity would have been achieved.

4.2.2.2. 2 liter scale mixing

The chosen formulation was further evaluated using a 2 liter scale mix where the grout was continuously mixed for three hours, with samples taken at regular intervals for viscosity and bleed measurements. Previous work has shown that the recirculation of a high w/s grout over several hours reduces the volume of bleed water on the set product at 24 hours curing. The 2 liter mix demonstrated that the formulation had adequately low viscosity, low bleed at 24 hours and excellent workability over a three hour period.

4.2.2.3. 200 liter scale mixing

Following the successful 2 liter scale mix of the above formulation, three mixes were carried out at 200 liter scale. Two mixes were of the 3:1 PFA/OPC with 10 $^{w}/_{o}$ slurry, w/s=0.80 formulation, and one mix was of the control grout formulation only, 3:1 PFA/OPC w/s=0.688.

The kaolin/water simulant was prepared at 40 $^{w}/_{o}$ solids in a high shear mixer. The appropriate weight of simulant was then added to a 250 liter capacity holding tank fitted with a low pressure recirculation pump. The appropriate weight of 3:1 PFA/OPC grout w/s=0.688, was mixed in a conventional low shear concrete mixer and added to the simulant in the holding tank. On contact with the grout, the simulant slurry immediately coagulated and the mix could not be pumped. As grout continued to be added to the tank, the extent of coagulation of the simulant waste reduced; after grout addition had been completed the grout / simulant mixture could be recirculated by the holding tank pump. The mix was then recirculated for 3 hours with pipe infill samples taken at 1 hour intervals. Viscosity, flow, and bleed at 24 hours curing were measured on these samples.

The 200 liter scale mix demonstrated that after 2.5 hours of recirculation, the grout and simulant were adequately mixed, (based on visual observation of set samples). The viscosity and flow of the formulation was acceptable and the wasteform samples had no bleed at 24 hours curing.

100mm test cubes and prism samples were taken for non destructive testing up to 90 days of age and compressive strength testing of cubes at 28 days. These results indicate that the wasteform will meet the specified NRC requirements for cemented LLW. The full report including test data from the formulation development work is in Appendix A.

4.2.3. Conclusions from formulation development work

The formulation development work identified a formulation of 3:1 PFA/OPC with 10 $^{w}/_{o}$ waste loading, with a final w/s=0.80, as suitable for the treatment of the selected tank waste simulant.

After 2 to 3 hours of recirculation by pumping, the grout and simulant were adequately mixed, the viscosity and flow of the formulation were acceptable, and wasteform samples had no bleed at 24 hours curing. The destructive testing indicated that the wasteform would meet the specified NRC requirements for cemented LLW.

It must be emphasized that the reaction seen on addition of the grout to the simulant is specific to the use of a kaolin simulant. This result does however illustrate the importance of characterizing wastes to be treated by grouting and the need for careful formulation development when the technology is applied to active wastes.
The full grout formulation development report is included in Appendix A.

5. Jet Grouting of a Simulated Waste Heel

The final element of the scope of work performed was to test the feasibility of using a PJM system to mix tank waste heels with the previously formulated grout mixture to achieve a uniformly solidified heel. The PJM system was installed into a framework above a demonstration test tank in the AEA Technology ESI facility in Mooresville, NC.

The specific purpose of the testing was to:

- Demonstrate that a fluidic mixing system can successfully mix grout with a simulated tank waste heel
- Demonstrate that complete mixing of the grout/ waste heel simulant is achieved, leaving no regions of the tank heel 'ungrouted'

5.1. PJM SYSTEM CONFIGURATION

The PJM system was configured in a "typical" arrangement as depicted in Figure 9 and pictured in Figure 10 below. The top of the Charge Vessel was 15' above the base of the waste tank. This height was chosen to ensure the maximum depression in the vessel could draw grout with a maximum specific gravity of 2.0 high enough to fill the vessel and also to facilitate gravity draining of the lines back into the tank. A standard "PRESCON™" controller was connected to control the air flow to the Charge Vessel and the sequencing of the mixing phases.

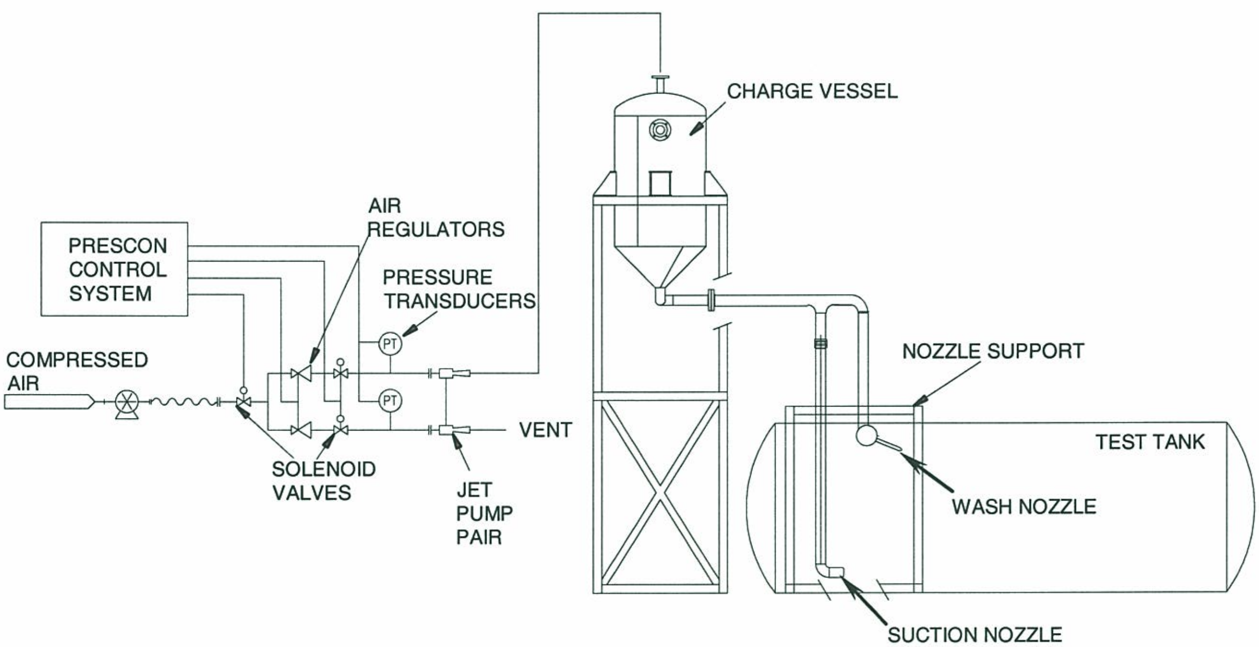


Figure 9: Test Rig Schematic

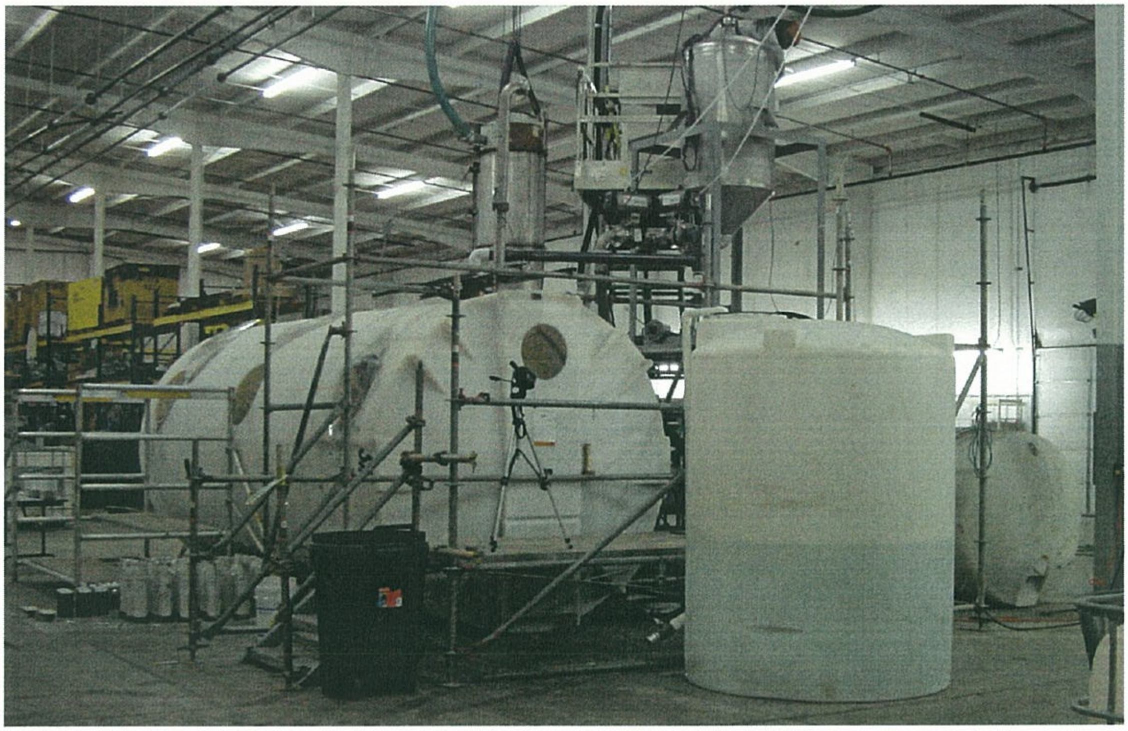


Figure 10: Photograph of the test rig for the jet grouting demonstration.

5.1.1. Test Tank

In order to simulate a full–size horizontal tank, a 7500 gallon XLDPE tank, 102" in diameter and 232" long, was used. A temporary scaffold was constructed over the tank to facilitate instrumentation and equipment deployment through the top of the tank. Access penetrations were cut in the top of the tank to allow nozzles and equipment to be deployed. Additional ports were cut in the side of the tank to allow access for sampling and viewing.

5.1.2. Nozzle Support Structure

Mixing of the simulant and grout was performed using a rotating suction nozzle and an articulated wash nozzle in a configuration representative of previous installations in active waste tanks. These nozzles were mounted at one end of the test tank. The suction nozzle was mounted so that the inlet/discharge was below the liquid level and utilized a swivel joint to allow rotation. The wash nozzle was a hydraulically controlled articulated nozzle mounted near the top of the tank. The nozzles were supported on a scaffold frame. Rotation of the suction nozzle was done manually for purposes of the demonstration but would be controlled remotely in a field installation.

5.1.3. Charge Vessel

The charge vessel was a 150 gallon ASME, "U" stamped pressure vessel. The base of the vessel was conical to allow complete draining of any entrained material. The grout/simulant is drawn up into this vessel before being discharged back to the tank. Both float style and conductivity probe level switches were used to detect a full charge vessel.

5.1.4. Grout Plant

Mixing of the grout materials and introduction of the grout into the test tank was achieved using a custom built grout mixing and delivery system. The grout mixer consisted of a 200 gallon vertical, cylindrical tank with a conical bottom. A pneumatic mixer with impellers near the top and bottom of the tank was used to initially mix the grout. The grout plant is pictured in Figure 11 below. The grout was further mixed by recirculation from the bottom of the tank back into the top of the tank using a 150gpm double diaphragm pump. Valving was installed on the pump to facilitate delivery of grout to the test tank once the grout was sufficiently mixed. The grout was introduced into the tank via the articulated wash nozzle in batches of 139 gallons. This was done to help facilitate mixing of the grout with the heel upon introduction into the tank.

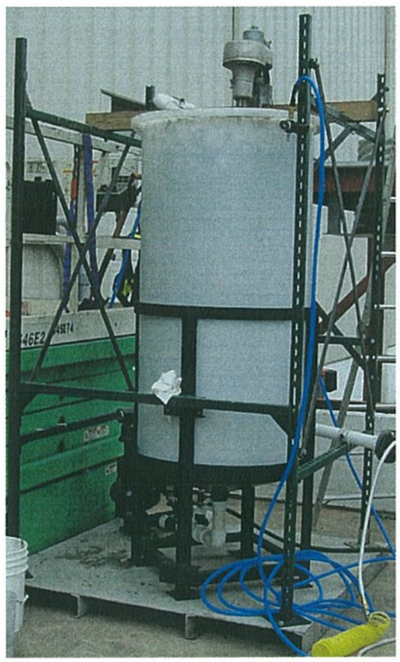


Figure 11: The grout plant consisted of a 200gal vertical tank with a pneumatic mixer and double diaphragm pump.

5.2. TEST PREPARATION

Kaolin clay and water was added to the test tank in the appropriate proportions to create a 40 $^{w}/_{o}$ mixture. 74 gallons (3" depth) of simulant was put in the tank prior to the test demonstration. Although previous tank retrieval efforts using Power Fluidics PJM systems has demonstrated the capability of leaving less than 2" of residual material in a waste tank, a slightly larger volume was chosen to represent a less than optimum pre-closure tank condition and greater final grouted waste volume for analysis.

5.3. TEST EXECUTION

Once the simulant was prepared in the test tank, the grout was pre-mixed and introduced into the tank in four batches of 139 gallons each (Figure 12a). Following introduction of the fourth batch of grout, the PJM was operated to mix the tank continuously for 3 hrs. A combination of suction and wash nozzle operation was used during the mixing period.

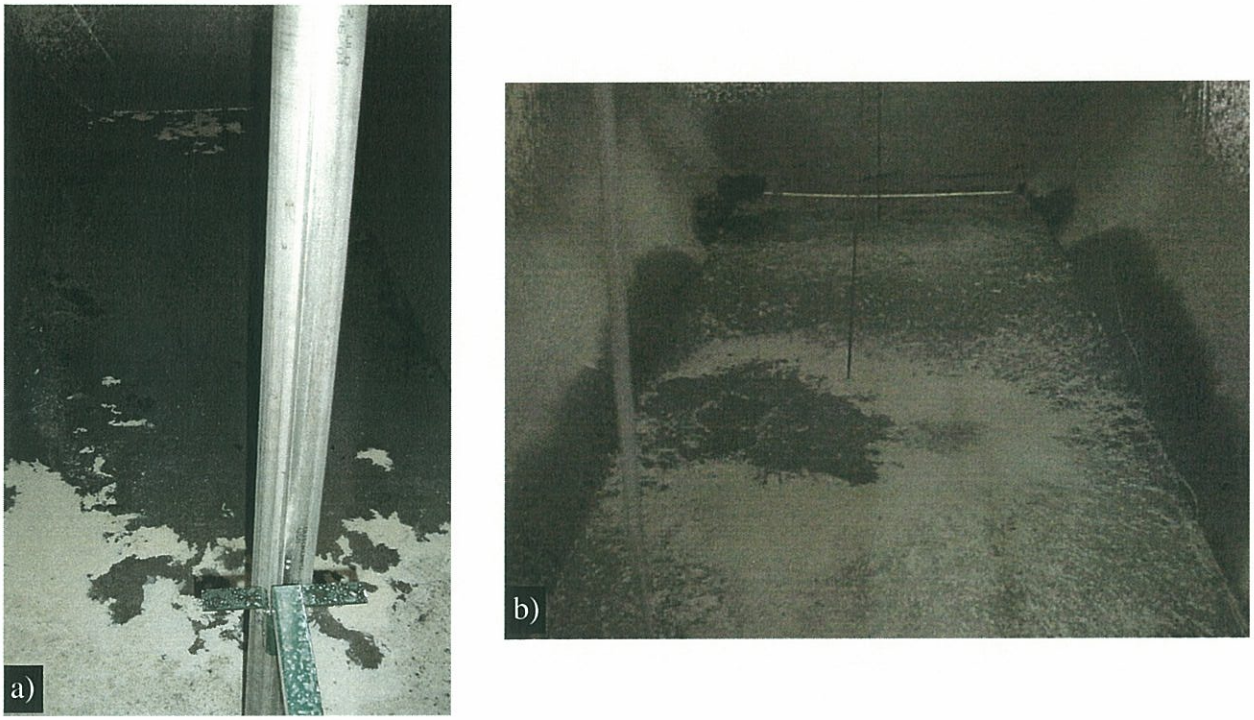


Figure 12: Inside the test tank a) just after grout addition but before mixing and b) one day after the demonstration.

Upon completion of mixing, the pulse tube was removed from the tank and the fluidic equipment was thoroughly flushed. The mixed grout/simulant was allowed to cure for 28 days prior to compressive strength testing. During the initial cure period, the grout was monitored for bleed water formation (Figure 12b).

5.4. DATA COLLECTION

The following data was collected during the test demonstration to evaluate the performance of the PJM and the grout:

- Key parameters from the PJM were recorded during mixing of the grout/simulant mixture including key system pressures and cycle times. System pressures remained stable throughout the trial. The cycle time increased slightly with time due to increased suction times as shown in Figure 13 below. This small increase correlates with the measured increase in grout viscosity over the mixing period. The change in suction time did not adversely affect the mixing process in any way and may provide an indicator of viscosity change in the grout during future application of the technology.

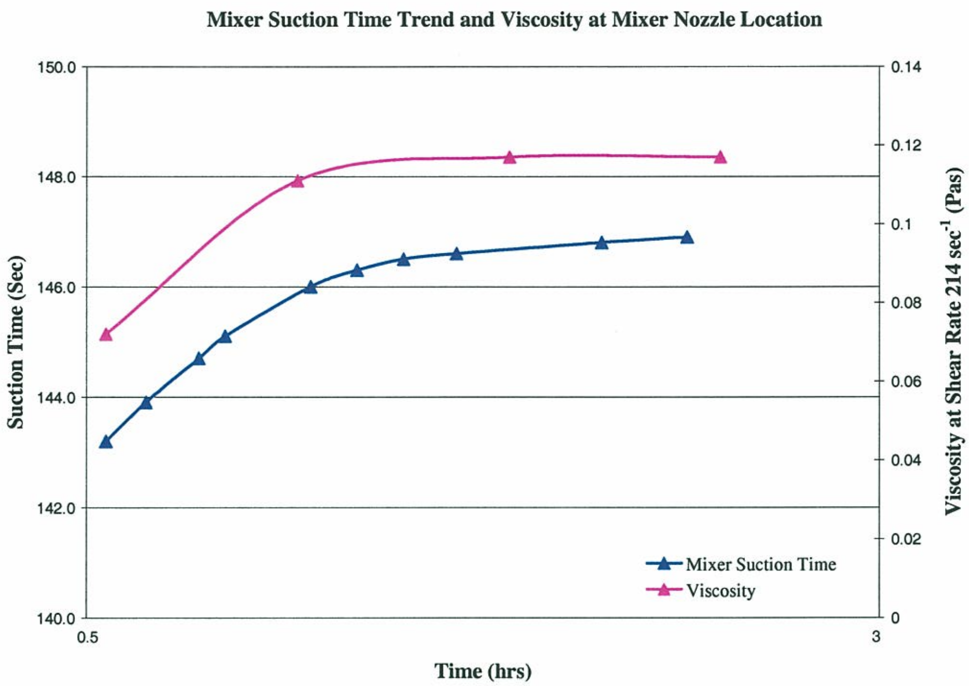


Figure 13: Mixer suction time and viscosity both increased with time during the mixing phase of the demonstration.

- Qualitative assessment was made of the jet produced by the nozzle, the level of agitation in the tank, the effective range of the nozzle, and the mixing effectiveness of the system. The jet from the suction nozzle located below the surface of the liquid produced effective mixing of the tank, even at the far end, some 15' from the nozzle outlet. The direction of the nozzle was changed periodically during the three hour demonstration to discharge down the middle of the tank and at a slight angle toward each side of the tank. In each case, the agitation in the tank reached the end. The mixing action could be described as a vigorous rolling action.

- The number of cycles required to achieve a uniform appearance of the grout/simulant mixture was recorded. After five to ten cycles (i.e. 15-30 minutes of mixing) the tank contents took on a uniform appearance.

- The grout/simulant mixture viscosity was measured and recorded at one hour intervals. This data is presented in Figure 13 above. The mixture remained very flowable for more than three hours mixing.

- Temperature in the grout / simulant was measured after the completion of mixing during the first 48 hours of curing. This data is presented in below in Figure 14. The temperature was measured using an RTD 6" from the bottom of the tank in the bulk material as it cured. Probes were installed in three locations axially along the tank with location 1 being closest and location 3 being furthest from the suction nozzle location and location 2 in the center of the tank. The temperature peaked at 88.9 ^{o}F sixteen hours after the conclusion of mixing. The low exotherm was expected due to the high water content of the grout leading to a slow curing process.

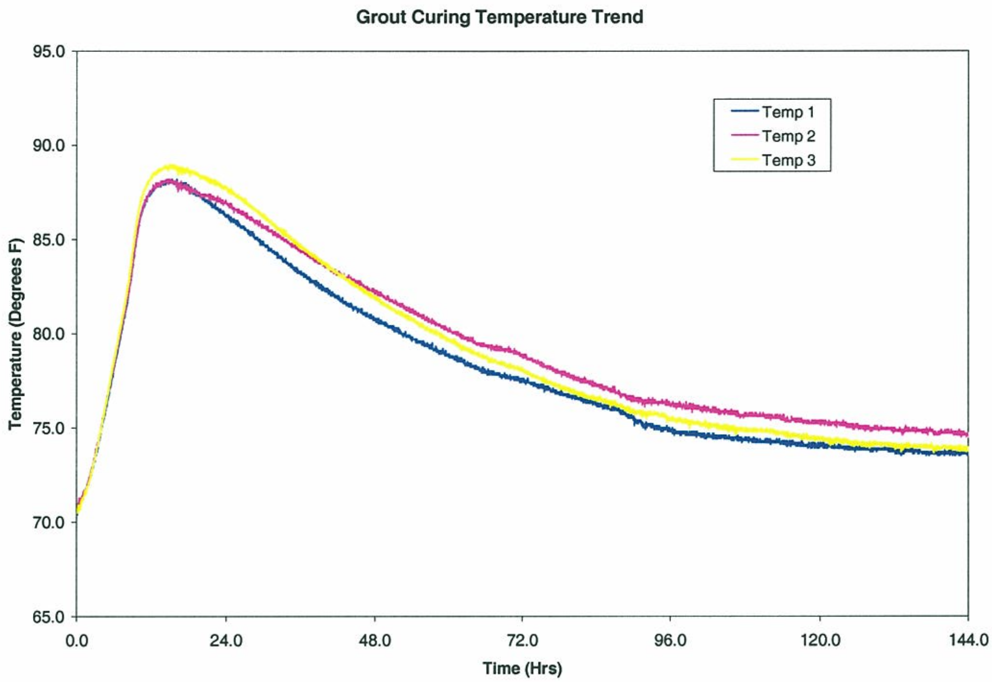


Figure 14: The temperature of the grout/simulant mixture peaked at 89.9°F sixteen hours after mixing was stopped.

- Grab samples of the grout / simulant mixture were taken from three axial points within the tank at one hour intervals and poured into 4" PVC pipe molds. Analysis of these samples gives an indication of the homogeneity of the grout / simulant mixture at that point in the mixing process. Bleed at 24 hours and density were measured on each of these samples. As seen in the data presented in Table 1, the density remained consistent across the length of the tank and throughout the mixing time. Bleed on the samples decreased slightly with mixing time but was less than 1% on each sample.

- After a 28 day cure period, the stabilized tank heel was visually examined and cored to assess the effectiveness of the mixing. A photograph of the cores taken from three axial positions in the tank is presented below in Figure 15 showing the set product at 26 days had a uniform appearance with no evidence of stratification or non-uniform mixing.

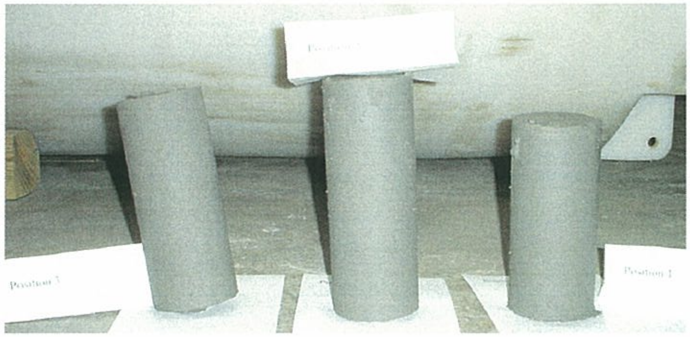


Figure 15: The core samples taken from the set product at 26 days had a uniform appearance with no evidence of stratification or non-uniform mixing.

Compressive strength, density and pulse velocity were measured on the cured grout/waste product. This data is presented in Table 1 below. The full set of data collected during the jet grouting demonstration and the demonstration logbook are included in Appendix B and Appendix C, respectively. Pulse velocity is directly proportional to product compressive strength and density. Therefore, it provides a qualitative indication of strength development over time and differences in density between samples. Other factors affecting pulse velocity are the development of cracks or water loss leading to void creation in the product as it cures. Either of these factors would lead to a slower pulse velocity. Therefore, increasing pulse velocity proportional to cure time is an indicator of a good final product.

- XRF analysis was conducted on the cured grout/simulant product at each of the three sample locations at three depths. This data is not reported here, as the quality of the data was determined to be questionable due to the test method used.

Table 1: Product evaluation data for full-size demonstration of 3:1 PFA/OPC grout formulation with 10 wt % waste simulant loading, w/s=0.80

In-Process Samples						
Recirculation time (hours)	Sample position	Age for Pulse Velocity and Density (days)	Pulse velocity (km/s)	Density (kg/l)	Compressive strength at 28 days (MPa)	Bleed at 24 hours (vol%)
1	1 (near nozzle)	28	N/D	1.5	N/D	< 1
	2 (tank center)	28	N/D	1.5	N/D	
	3 (end of tank)	28	N/D	1.5	N/D	
2	1	28	N/D	1.5	N/D	< 1
	2	28	N/D	1.5	N/D	
	3	28	N/D	1.5	N/D	
3	1	28	N/D	1.5	N/D	< 1
	2	28	N/D	1.5	N/D	
	3	28	N/D	1.5	N/D	
Cast Cylinder Samples						
3	1	21	1.08	N/D	1.2	N/D
	2	21	1.09	N/D	1.5	
	3	21	1.07	N/D	1.6	
Core Samples (Average of two measurements)						
3	1	41	1.13	N/D	1.5	N/D
	2	41	1.25	N/D	1.1	
	3	41	1.17	N/D	0.9	

6. Conclusions

The Pulse Jet Mixing system was proven effective at mixing the grout/ waste simulant mixture to achieve a uniformly solidified heel. Visual observation indicated that the combination of the nozzle near the bottom of the tank and the "wash" nozzle near the tank top introduced sufficient mixing energy to produce good mixing in all areas of the tank. There was minimal bleed water in the hours immediately following mixing and none at 24 hours curing on the set product. A comparison was made of the heel condition after adding the grout but before mixing to the mixed end state of the heel. This is documented in Figure 16 below.

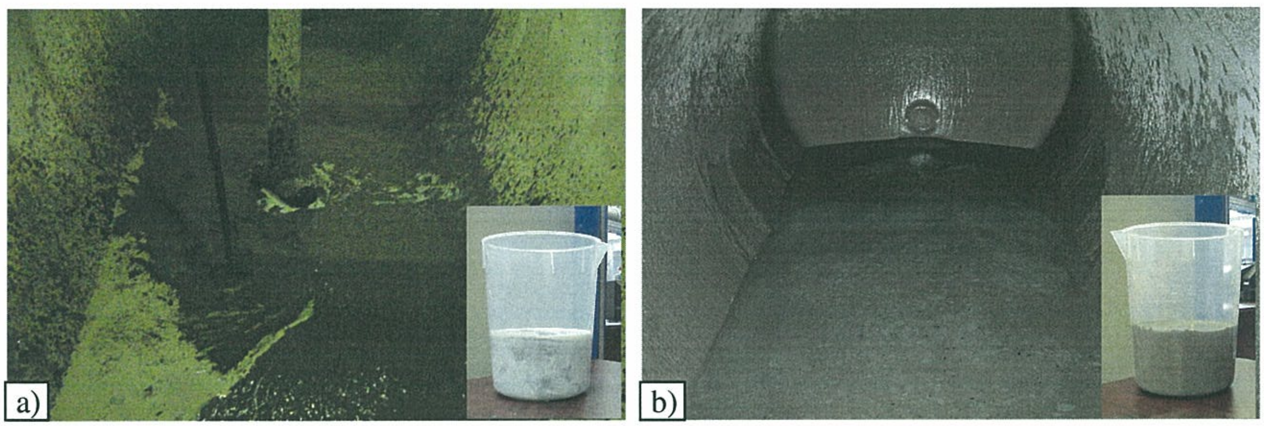


Figure 16: Bench scale (inset) and demonstration trials of: a) grout poured on top of simulant waste without mixing and b) grout mixed with simulant waste

The mixing system performed as expected. The first two cycles were necessary to break up the coagulated grout/simulant material and obtain a fluid mixture. Following that, the system performed similarly to previous mixing campaigns to mobilize existing tank heels. The key parameters monitored changed only slightly over the three hour mixing time indicating a trend toward higher viscosity as mixing progressed but the change did not affect performance. Following the mixing trial, the system proved moderately difficult to clean. The waste lines were cleaned by flushing with water. However, the charge vessel and level switches required pressure washing to remove grout solids. Modifications to the system design are possible to eliminate/greatly reduce buildup of grout on crucial system control components.

The data produced in the demonstration trial were consistent with those measured during the formulation development studies. Further, the data indicates a uniformly mixed waste form. The bleed at 24 hours, density, visual examination of the core samples, pulse velocity, and compressive strength data are all consistent with this conclusion.

The demonstration proved the efficacy of using a Power Fluidics™ Pulse Jet Mixer for mixing specially formulated grout with a simulated waste heel. Adapting this safe, proven and effective technology for carrying out in-situ stabilization of residual tank waste material has the potential to be of considerable benefit to tank waste retrieval and closure operations throughout the complex. The benefits of this approach include:

- A greatly improved waste end state, wherein contaminants are mixed and stabilized in a grout matrix rather than unmixed with pockets of mobile contaminants remaining.
- A final waste form that meets current US regulations for grouted LLW.
- Utilization of a single system for bulk waste retrieval and heel stabilization resulting in:-
  - decreased capital equipment costs
  - reduced secondary waste generation
  - shorter schedule / lower labor costs for field activities
  - lower radiation dose to workers
  - a consolidated approach to safety documentation preparation.

It is anticipated these successful trials will provide a basis for development of field deployable equipment.

6.1. IMPLICATIONS FOR FUTURE WORK

It should be emphasized that application of this technology to an active tank waste heel must include development work initiated as early in the process as practical.

The grout development work should include:

- Characterization of the waste heel
- Development of a representative simulant
- Formulation of a grout for the simulant with the broadest effective design envelope possible
- Complete testing of the grout/simulant mixture against applicable governing regulations
- Testing of the grout with a sample of the active heel material (when possible to do so)

Mixing system development work should include:

- Waste tank geometry (e.g. tank size, configuration, in-tank obstructions, etc.)
- Access options to the tank (e.g. number and size of current risers, etc.)
- Retrieval / Operational strategies to be employed (e.g. in-tank nozzle disposal, off-gas treatment, method of grout addition, etc.)
- Consideration of the site elevation with regard to Charge Vessel elevation above the waste tank – may lead to development of a lower density grout and thus feed into the grout development work above or alternative designs with in-tank charge vessels.
- Sampling requirements and methods
- System cleaning and decommissioning requirements

7. References

1. United States Nuclear Regulatory Commission (NRC), Technical Position on Wasteform (Revision 1), January 1991, Office of Nuclear Material Safety and Safeguards, Division of Low-Level Waste Management and Decommissioning.
2. Lee DJ and Fenton A (1992). The development of cement formulations for radioactive waste encapsulation. p 348-358. Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes. Ed Gilliam and Wiles. ASTM STP 1123.
3. Project Technical Plan No. DOE/Heel Grouting/01/v1 – "Demonstration of a System for In-Situ Waste Heel Mobilization at LANL", February 2004.
4. AEA plc Document No. AEAT/R/NS/0755 – "Test Plan for development of a grout for demonstration of a system for in-situ tank waste heel immobilization at LANL"

Appendices

Appendix A – Grout Formulation Development Report

AEAT/NS/R/0770 Issue 2 Final Report

Development of a grout formulation for in situ tank waste heel immobilisation at LANL

A report produced for USDOE

M Board
R Simmons

February 2005

AEAT/NS/R/0770 Issue 2 Final Report

Development of a grout formulation for in situ tank waste heel immobilisation at LANL

A report produced for USDOE

M Board
R Simmons

February 2005

Title	Test plan-demonstration of a system for in-situ tank waste heel immobilisation at LANL
Customer	USDOE
Customer reference	PO 10586
Confidentiality, copyright and reproduction	Unclassified This document has been prepared by AEA Technology plc in connection with a contract to supply goods and/or services and is submitted only on the basis of strict confidentiality. The contents must not be disclosed to third parties other than in accordance with the terms of the contract.
File reference	VD10711/LANL Tank Heel Immobilisation Issue 2
Report number	AEAT/NS/R/0770
Report status	Issue 2 Final Report

AEA Technology plc
Waste Management Technology
Winfrith
Dorchester
Dorset DT2 8WQ
Telephone +44 (0)1305 202191
Facsimile +44 (0)1305 202784

	Name	Signature	Date
Author	M Board R F Simmons		
Reviewed by	R F Simmons		
Approved by	M A Twissell		

Executive Summary

Work carried out in the USA by AEA Technology Engineering Services Inc (AEAT ES Inc) has demonstrated that when pumping waste suspensions from storage tanks situated above or below ground, there is a point at which no further waste recovery is possible and a small volume of waste, termed a heel, is left at the bottom of a tank. The current US method of treating a residual waste heel is to pour a cementitious grout into a tank to solidify the remaining liquid waste. This grouting method is not designed to intimately mix the waste and grout and may, therefore, result in a heterogeneous wasteform, which may still have the potential to release mobile contaminants into the surrounding environment. Increasingly strict US environmental regulations require a more reliable treatment method for tank heels. An effective means of carrying out in-situ stabilisation for varying quantities of residual waste material in tanks would be of considerable benefit to US tank waste retrieval operations.

A test programme has been carried out by AEA Technology to investigate the in-situ cement grout stabilisation of a waste tank heel using a Fluidic Pulsed Jet Mixing System (PJMS). The aim of the test programme was to investigate technical issues associated with such a process and to demonstrate the potential application of the process using simulated waste material.

This report describes how the cementitious grout formulation was designed and developed to immobilise a 40 weight per cent (wt%) clay slurry simulant waste. The simulant represents a residual heel of waste left in a tank following waste extraction using a PJMS. This grout formulation was used in two full-scale simulant tank heel immobilisation demonstrations at AEAT ES Inc Mooresville Test Facility in November 2004.

The conclusions of this work are:

1 The PFA and OPC used for the formulation development were UK sourced powders with physical properties shown to be similar to samples of US sourced PFA and OPC powders supplied to AEAT Winfrith.

2 All formulation development work was based on a 40 wt% kaolin / water waste simulant slurry, i.e. 40 parts by weight dry kaolin to 60 parts by weight water.

3 The formulation development work identified a 3:1 PFA/OPC, w/s = 0.688 grout with a 10 wt % slurry loading, giving a total effective w/s=0.80, as a formulation with suitable rheological and set product properties for the investigation of in situ treatment of a simulated tank heel waste using the PJMS.

4 The use of X-ray fluorescence analysis has been shown to offer the potential to demonstrate quantitatively the homogeneity of mixed grout / waste simulant products by making use of specific chemical constituents within the kaolin and cement powders, notably strontium and iron.

5 The full-scale tank heel immobilisation demonstration trials showed that the pumpability of the grout formulation, when pumped by the PJMS, was largely controlled by the specific gravity of the grout formulation, rather than the grout viscosity and flow. Minimising the density of a grout is likely to improve the pumpability (particularly in terms of head) of a grout when using the PJMS in grouting applications. Grout viscosity and flow will however, remain key rheological properties to be considered during grout design.

Maximising grout pumpability for the in situ grouting of tanks by the PJMS is likely to be especially important if the tank is located at a high altitude site or is deeply buried. The potential to develop a grout with lower specific gravity than that developed in this work has been identified, for example, by the use of cenospheres, (gas filled PFA particles) as a component of a grout formulation.

6 The potential need to introduce a large volume of the grout into a tank as rapidly as possible was seen during the full-scale tank heel immobilisation demonstration trials. In this work, the simulant reacted with the first batch of grout added to the tank, creating a viscous sludge. The sludge could have been pumped by the PJMS, however it is considered that the initial addition of a larger volume batch of grout into the tank would have led to a more readily pumpable mix.

In practice a tank waste would be drawn down to the lowest level practicable by the PJMS, an increase in the volume of liquid in the tank by grout addition is then required to allow the mixing of the grout and waste heel. Therefore the start of grout/waste mixing and recirculation by the PJMS is likely to be controlled by the rate of grout addition into the tank. It is advisable to commence grout recirculation with the PJMS as soon as possible to avoid loss of formulation workability. Thus, the capability of producing and holding large volumes of grout for rapid transfer to a tank requiring in situ grouting is a desirable component of this technology when treating a radioactive waste.

7 For application to a full-scale radioactive process, the following programme design is suggested to minimise the risks:

Waste characterisation
Identification of product specification
Formulation development (using inactive simulant material)
Product evaluation
Small-scale radioactive tests

Contents

Tables

Figures

Appendices

1 Introduction

Work carried out in the USA by AEA Technology Engineering Services Inc (AEAT ES Inc) has demonstrated that when pumping waste suspensions from storage tanks situated above or below ground, there is a point at which no further waste recovery is possible and a small volume of waste, termed a heel, is left at the bottom of a tank. The current US method of treating a residual waste heel is to pour a cementitious grout into a tank to solidify the remaining liquid waste. This grouting method is not designed to intimately mix the waste and grout and may, therefore, result in a heterogeneous wasteform, which may still have the potential to release mobile contaminants into the surrounding environment. Increasingly strict US environmental regulations require a more reliable treatment method for tank heels. An effective means of carrying out in-situ stabilisation for varying quantities of residual waste material in tanks would be of considerable benefit to US tank waste retrieval operations.

A test programme has been carried out to investigate the in-situ cement grout stabilisation of tank waste heels using AEA Technology's Fluidic Pulsed Jet Mixing System (PJMS) equipment. The aim of the test programme was to investigate technical issues associated with such a process and to demonstrate the potential application of the process using simulated waste material. A prototype PJMS was built to demonstrate the large-scale grouting of a tank with a simulated residual heel. A series of pump tests were carried out to demonstrate the grout and heel mixing process.

This report describes how the cementitious grout formulation was designed and developed to immobilise a 40 weight per cent (wt%) clay slurry simulant waste (40 parts by weight clay to 100 parts by weight total slurry). The simulant represents a residual heel of waste left in a tank following waste retrieval using a PJMS. In practice, tanks emptied by AEAT ES Inc, using Fluidic PJMS's have resulted much smaller waste heels than was demonstrated in this work e.g. Tank T-2 at ORNL was emptied to less than 40 gallons residual heel in the spring of 2004.

This grout formulation has been used in two full-scale simulant tank heel immobilisation demonstrations at AEAT ES Inc Mooresville Test Facility in November 2004. Details of the findings of these demonstrations pertinent to the grout formulation are also provided.

The results of the work are presented as follows:

- basic requirements of the grout formulation - Section 2
- selection of the raw materials- Section 4
- grout formulation development - Section 5
- assessment of use of X-ray fluorescence as a means of determining product homogeneity - Section 6
- discussion and conclusion of results - Sections 7 and 8.

2 Basic requirements of the grout formulation

In order to permit the development of the grout formulation, a number of assumptions were made regarding the specification of the test rig and the details of the demonstration itself. These may be summarised as [1]:

- It was assumed that the grout will be pre-mixed external to the test tank, introduced into the tank by pumping, and then mixing with the simulated tank heel accomplished by repeated cycles of removal / return of aliquots of the tank contents with the power fluidic device.

- In the absence of detailed information on the characteristics of the waste contained within the Los Alamos National Laboratory (LANL) tank(s) for which it is planned to ultimately apply this tank heel closure technique, the potential interaction between the grout and the waste will not be considered in detail in this particular project. A simulant 'sludge waste, based on a kaolin clay, will be used to demonstrate the principle of the grout / waste mixing and closure technique. (The actual simulant used was a 40 wt% solids kaolin slurry; this simulant was selected as it has been successfully used by AEA ES Inc in previous PJMS demonstrations).

- The grout will meet the requirements of Appendix A of the Nuclear Regulatory Commission (NRC) Technical Position for grouted low level waste [2], with a minimum compressive strength of 500 psi. The ability of the grout to meet these requirements will be demonstrated by a combination of experimental measurements (for strength) and by reasoned arguments, making use of previous work carried out for DOE, e.g. [3, 4].

- Whilst, AEA Technology is able to perform all of the experimental tests detailed in the NRC Technical Position, the timescales of these measurements (e.g. underwater immersion is a minimum of 90 days duration) are such that they would unnecessarily extend the reporting timescales for the overall project. Therefore the grout performance against these criteria will be inferred from previous work and experience.

- In the absence of waste characterisation data, the ability of the grouted wasteform to meet the RCRA standards for leaching of toxic chemicals [5] by the Toxicity Characteristic Leaching Procedure (TCLP) [6] will not be demonstrated. However, previous development programmes, e.g. [3, 4], have demonstrated the ability of grouts of the type to be developed in this programme to meet RCRA leach standards for toxic materials such as cadmium, lead, mercury and barium.

- A multi-stage grout injection process is acceptable for filling the voidage within the tank, reducing the size of the batch of grout required for the demonstration of mixing with the tank heel. In practice, this would result in partial filling of the tank with the first grout addition and tank heel mixing process, with the remaining voidage in the tank filled with further grout batch(s) after the first grout batch had been allowed to set.

- In order to give a grout with sufficient fluidity over the timescale of the tank grout / heel mixing process, the use of an organic superplasticiser to extend the 'working time'[1] of the grout will be acceptable to LANL, if it is required. For the purposes of the demonstration, a minimum acceptable 'working time' for the grout of 2 hours will be demonstrated.

The usual approach adopted for radioactive waste immobilisation is to maximise waste loading and, thus, minimise the final product volume for disposal. However, given that the simulant waste slurry had a relatively high water content, the use of a fluid grout incorporating a high waste loading would have resulted in a final product with a high water to cementitious solids (w/s) ratio. The high water content would have led to an unacceptably large volume of bleed water i.e. the volume of over standing water on the set product. Thus, for the purposes of this demonstration, the waste loading of the grout formulation was kept low, at approximately 10wt%. In addition, prior to the full-scale demonstration trials performed at the Mooresville test facility, the ability of the PJMS to pump a cementitious grout was unknown. Therefore the 'pumpability' of the grout had to be optimised and this was achieved by using a high w/s ratio, thereby minimising the viscosity of the grout suspension.

3 Small-scale test methods

3.1 VISCOSITY

A 75 ml sample of the cement/waste mix was placed in a pot and stirred with an AEAT gate paddle [7] connected to a Contraves viscometer. The shear rate was ramped up from 0 to 260 s^{-1} then down to 0 s^{-1} at a controlled rate. This enabled a viscosity / shear rate profile to be produced. Single point viscosity measurements were taken at a shear rate of 106.5 s^{-1} and quoted in units of Pa s. The accuracy of the rheology system is ± 0.05 Pa s within the approximate operating limits 0.4 to 3.5 Pa s.

3.2 TIME TO SET

This test measured the time to achieve 'initial' and 'final' set using the Vicat testing apparatus [8]. Both manual and automatic Vicat apparatus are used. Set is defined by zero penetration of the cement sample by a weighted needle.

3.3 BLEED

Bleed was determined by measuring the volume of overstanding water (bleed) removed from the surface of a sample after 24 hours curing. Results are expressed as a percentage of the total volume of the sample (solid and bleed).

[1] 'Working time' is defined as the period of time after grout preparation is completed for which the grout must demonstrate a minimum set of process characteristics (e.g. fluidity) such that it is capable of being 'handled', e.g. pumped, during this time, whilst remaining capable of producing a product with the required product performance.

3.4 GROUT FLOW

The fluidity of the mixed grout was measured by placing a known volume of grout into a Colcrete flow channel and measuring the distance the grout 'flows' down the channel. A flow of less than 200 mm is typically considered to be unacceptable.

3.5 MOULD SAMPLE PREPARATION

Some of the mixed cement product from small-scale mixes was poured into standard moulds (100 mm cubes, 286 x 26 x 26 mm prisms) and vibrated according to British Standard procedures [9]. After setting, the samples are demoulded (typically after 1 to 2 days curing) and left to cure in sealed polythene bags to prevent desiccation during storage. These wrapped samples were stored at a temperature of 20 ± 2 °C and a relative humidity of greater than 90 per cent prior to testing.

3.6 COMPRESSIVE STRENGTH

Compressive strength was measured using standard 100 mm cubes, which were loaded continuously at a rate of 0.3 N $m^{-2}s^{-1}$ until no greater load can be sustained [10]. The equipment used for this test was an EC32-401 automatic compressive testing machine supplied by ELE International Ltd. The manufacturer's operating limits for this device are 50 to 2000 kN (5 to 200 MPa).

3.7 ULTRASONIC PULSE VELOCITY

The velocity of pulsed ultrasound through 100 mm cubes can, with comparison to destructive testing techniques, be used to determine strength development [11]. The equipment used for this test was a 54 kHz Pundit Ultrasonic Concrete tester supplied by ELE International Ltd.

3.8 DENSITY

Density of 100 mm cubes was calculated from weight difference when weighed in air and water [12].

4 Selection of materials

4.1 CEMENT POWDERS

The full-scale tank heel immobilisation demonstration was performed at AEAT ES Inc Test Facility at Mooresville, using raw materials, such as the cement powders, sourced locally in order to minimise shipping costs. However, the properties of a grout formulation, such as flow and workability, are strongly controlled by the raw materials used. Consequently to enable the development (in the UK) of a reproducible grout with defined performance characteristics, it was necessary to identify what types of cement powders were available local to AEAT ES Inc's

Mooresville Test Facility, and replicate these in the grout development work to be performed by AEA Technology in the United Kingdom. Due to the quantity of materials required for the development work and demonstration - typically expected to be several tonnes - it was considered that it was not practicable to ship materials from the USA to the UK or vice versa, unless it proved impossible to identify an appropriate match in material specification.

Grouts developed in the United Kingdom for performing mixing work such as that planned for the tank heel immobilisation demonstration project are typically based on a combination of the following raw materials:

- Portland cement (OPC)
- Ground granulated blast furnace slag (BFS)
- Pulverised fuel ash (PFA)

So that the effects of raw materials on formulation properties were understood and minimised, samples of BFS, PFA and OPC materials available to the AEAT ES Inc Mooresville site were sent to AEA Technology, Winfrith, UK.

On visual examination, it was apparent that the US sourced BFS was unsuitable for use in a grout due to its large particle size distribution (PSD).

This finding resulted in a PFA/OPC based formulation being selected as the grout to treat the simulant waste heel. A 3:1 ratio, by weight, of PFA/OPC was considered to have the correct proportions of PFA/OPC to ensure good strength development of the wasteform, without excessive heat generation during mixing and curing.

Following PSD, density and fineness tests on the US sourced powders, UK powders with similar properties were sourced to carry out the formulation development work. Advice from the UK Quality Ash Association, Castle Cement Ltd and Kirton Concrete services was taken to find the best match of PFA and OPC available.

The UK powders selected for the formulation development work were:

- PFA to EN:450 standard from Drax power station, supplied by RWE Innology [13].
- OPC to EN: 197-1-CEM1 42.5R standard from Padeswood kiln, supplied by Castle Cement Ltd [14].

The PSDs and chemical contents of the UK and US OPC and PFA powders are provided in Appendix 1. These data demonstrate the high degree of similarity between the UK and US cement and PFA powders used for the grout formulation development work and demonstration trials respectively.

4.2 SIMULANT SLURRY

Thiele EG-44 kaolin clay was the simulant initially specified by AEAT ES Inc. Whilst, Thiele EG-44 kaolin clay could have been purchased in the UK, this would have introduced a delay of six weeks for delivery. An alternative US sourced kaolin, Burgess No 28 supplied by Burgess Pigment Co, was however available in the UK and was, thus, selected for use in the work instead of the Thiele EG-44 kaolin clay. Testing on both clays showed them to have very similar viscosity and dispersive properties.

All formulation development work was based on a 40 wt% kaolin/water slurry, i.e. 40 parts by weight dry kaolin to 60 parts by weight water.

5 Formulation development

The formulation development work was carried out using several scales of mixing:

- 150 ml scale scoping trial;
- 2 litre scale mixes of selected formulations; and
- 200 litre scale pumping tests.

5.1 SCOPING TRIALS

Following the initial assessment of the formulation requirements, small scale scoping trials were used to investigate the properties of the:

- Kaolin slurry simulant at 40wt% solids
- 3:1 PFA/OPC control grout with increasing water to solids ratio (w/s)
- Grout/simulant mixes where the waste loading was increased incrementally at a fixed w/s ratio

The small scale scoping trials were performed by preparing hand mixed 150 ml samples. Viscosity immediately after mixing and bleed at 24 hours product curing were the two principle grout properties investigated.

The scoping trials identified through viscosity measurements, at what w/s ratios grout fluidity increased substantially, and when bleed at 24 hours curing began to appear in grout mixes, if used immediately after mixing, i.e. with no grout recirculation.

Using the viscosity and bleed data shown in Table 1, a grout with acceptable viscosity, bleed at 24 hours and predicted workability was selected for further testing. The selected formulation was 3:1 PFA/OPC with 10 wt% slurry, with a total effective w/s=0.80. This formulation is equivalent to 90 wt% 3:1 PFA/OPC grout, w/s=0.688, plus 10 wt% kaolin slurry at 40 wt% solids, giving an effective w/s ratio =0.80 for the mixed product.

Small scale testing of the formulation at w/s ratios > 0.80 was not carried out as no further significant decrease in viscosity would have been achieved.

5.2 2 LITRE SCALE MIX

The chosen formulation was further evaluated using a 2 litre scale mix where the grout was continuously mixed for three hours with viscosity and bleed measurements taken at intervals. The results are shown in Table 2.

The 2 litre mix demonstrated that the formulation had adequate viscosity, acceptable bleed at 24 hours product curing and workability over a three hour period. It is known from previous work that the recirculation of a wet grout over several hours reduces bleed at 24 hours product curing.

5.3 200 LITRE SCALE MIXES

Following the successful 2 litre scale mix of the formulation 3:1 PFA/OPC with 10 wt % slurry w/s=0.80, three mixes were carried out at 200 litre scale:

- Mix 04/016 - 3:1 PFA/OPC, w/s = 0.688 with 10 wt % slurry; total effective w/s = 0.80
- Mix 04/017 - 3:1 PFA/OPC, w/s = 0.688 with 10 wt % slurry; total effective w/s = 0.80
- Mix 04/020 - control grout formulation only, 3:1 PFA/OPC w/s=0.688

5.3.1 200 litre scale mixing method

60 kg of simulant slurry was mixed for 3 minutes in a Colcrete SD10 high shear mixer. The appropriate weight of slurry was added to a 250 litre capacity Colcrete grout holding tank with a low pressure recirculation pump, and continually pumped.

300 litres of 3:1 PFA/OPC grout w/s=0.688, was mixed in a RP850 low shear mixer and the appropriate weight of the grout added to the grout holding tank.

5.3.2 Recirculation of the formulation

On contact with the 3:1 PFA/OPC grout, the simulant slurry immediately coagulated and the mix could not be pumped. As the grout was added to the tank, the mix became less lumpy and could be mixed / recirculated by the holding tank pump. Once the required weight of grout was added to the recirculation tank, the mix was recirculated by pump for 3 hours.

For mix 04/016 the recirculation pump outlet was fixed to one side of the holding tank. This resulted in poor mixing of the simulant and grout.

For mix 04/017 the grout was poured in evenly around the tank, to aid the distribution of grout within the tank. The outlet of the recirculation pump was also moved around the tank during the recirculation period. This resulted in improved mixing of the grout and waste simulant after 3 hours of recirculation, compared to mix 04/016.

Both 04/016 and 04/017 mixes showed the importance of having adequate grout flow rates to ensure that the simulant was mixed with the grout, and the potential need to vary the location of the pump inlet / outlet whilst recirculating the grout to achieve thorough mixing.

5.4 PRODUCT EVALUATION OF FORMULATION

5.4.1 Sample preparation

Product evaluation samples (100 mm cubes, prism samples and pipe sections) were produced from the two 200 litre mixes (04/017 and 04/020). A 10 litre sample of grout was pumped from the grout holding tank at hourly intervals during the 3 hour recirculation period, to infill a pipe of 0.102 m diameter to a height of 1 m. A single short (450mm high) pipe infill was also made. No vibration was used during pipe infilling. The pipe infill samples were stored under the same environmental conditions as the cubes and prisms (see section 3.5) and demoulded after 28 days curing.

A short-term product evaluation programme up to 90 days curing was carried out for selected mixes. The tests were performed on cores sectioned from pipe infills, cube samples and duplicate prism samples.

5.5 PRODUCT EVALUATION TEST RESULTS

The viscosity, flow and bleed data for mixes 04/017 and 04/020 are presented in Table 2. Product evaluation data for the cube, prism and core samples sectioned from the pipe infills are presented in Appendix 1.

After 2.5 hours recirculation of mix 04/017, the formulation was seen to be well mixed. The homogeneity of mix was later confirmed by the consistent density data of the cube and core samples. The viscosity and flow of the formulation were acceptable and the wasteform samples had no bleed at 24 hours.

The effect of the simulant on reducing bleed at 24 hours is demonstrated by comparing the high volume of bleed (8 vol%) measured on the control grout (mix 04/020) pipe infill after 3 hours of recirculation to the minimal bleed values recorded for the grout / waste simulant mix (mix 04/017).

Two 100mm test cubes from mix 04/017 had relatively low compressive strengths at 28 days of 1.6 and 1.7 MPa, significantly lower than the compressive strength at 28 days of the control grout 04/020 samples. At 28 days curing, both mixes failed to develop the 3.4 MPa (500psi) compressive strength specified by Appendix A of the Nuclear Regulatory Commission (NRC) Technical Position for grouted low level waste [2]. However, the compressive strength development is likely to continue with time. Continued strength development could be confirmed by further compressive strength tests.

Prism samples were tested over a 90 day period. Dimensional stability testing showed that both 04/017 and 04/020 formulations had expanded slightly. The weight loss of the samples over this period was minimal. The elastic modulus of the prism samples increased with age indicating continued strength development. These results are in accordance with previous PFA/OPC grouts tested by AEAT Winfrith.

6 X-Ray Fluorescence Analysis

6.1 X-RAY FLUORESCENCE METHOD

X-Ray Fluorescence (XRF) analysis was used to investigate the potential to use chemical constituents present within the grout and/or simulant as a means to quantitatively indicate the homogeneity of the mixed product. XRF analysis of anhydrous powdered (cement, PFA and kaolin) materials and samples of the formulation with increasing waste wt % addition were carried out by the Geosciences Advisory Unit, University of Southampton. UK.

Major elements

The samples were mixed with lithium tetraborate flux in a platinum-gold dish and fused at 1200 °C for 15 minutes before casting as a glass disk in a Pt-Au dish. The sample was measured by a Philips Magix-Pro wavelength dispersive XRF spectrometer (4kw Rh end-window X-ray tube).

Trace elements

The samples were pelletised using a manual press and measured by a Philips Magix-Pro wavelength dispersive XRF spectrometer (4kw Rh end-window X-ray tube).

6.2 XRF ANALYSIS RESULTS

The chemical data (see Appendix 2) from the powdered cement, PFA and kaolin materials were initially used to identify suitable tracers. The data indicated a potentially significant dilution in the concentrations of Sr and Fe_2O_3 as the waste loading of clay increased, compared to a 3:1 PFA/OPC grout with no clay. See Figures 1 and 2.

Samples of 3:1 PFA/OPC grout with no clay and increasing clay waste loading were prepared at the AEAT ES Inc Mooresville Test Facility using the demonstration trial cement powders and kaolin. The XRF data for these samples are provided in Appendix 3. Figures A3.1 and A3.2 show the proportional decrease in the concentrations of Sr and Fe_2O_3 with increasing waste loading of clay slurry. Therefore the concentrations of Sr and Fe_2O_3 in the demonstration trial product could be used to indicate the degree of mixing of the waste simulant and grout achieved by the PJMS.

7 Discussion

7.1 PRODUCT EVALUATION DATA

The product evaluation data produced by the 200 litre scale mix 04/017 indicated that the 3:1 PFA/OPC with 10 wt % slurry w/s=0.80 formulation had the rheological and set product properties that would enable the potential of the PJMS for in-situ grouting to be evaluated.

Although the mix failed to develop the 3.4 MPa (500psi) compressive strength specified by NRC specification for grouted low level waste [2] by 28 days curing, it should be recognised that the formulation was developed to provide maximum workability and viscosity without the use of grout additives. In addition, with continued curing of the samples, it is expected that the NRC guideline will be comfortably achieved by 90 days curing.

Once the capability of a PJMS for in situ grouting has been evaluated, and the required properties of a grout formulation better understood, specific formulation development can be undertaken to treat characterised wastes. Ensuring adequate compressive strength development would be an intrinsic part of any formulation development for the treatment of a real waste.

7.2 FULL-SCALE DEMONSTRATION TRIALS

Two full-scale PJMS in situ grouting demonstrations were carried by AEAT ES Inc at their site located near Mooresville, North Carolina, USA in November 2004. A member of staff from AEAT Winfrith attended each demonstration. The trials demonstrated that the PJMS was capable of the mixing of grout and the simulated waste heel using the 3:1 PFA/OPC with 10 wt % slurry w/s=0.80 formulation.

The 3:1 PFA/OPC, w/s = 0.688 grout with 10 wt % slurry, giving a total effective w/s = 0.80, was demonstrated to have suitable workability and viscosity over a three hour recirculation period, and the resulting product had minimal bleed and settlement after 24 hours curing.

There were three notable findings for grout formulation development that arose from the full-scale demonstration trials:

1 The height that a grout can be pumped to by the PJMS is largely controlled by the specific gravity of the grout formulation, rather than the grout viscosity and flow.

Increased specific gravity of a formulation results in a proportional decrease in the head that a formulation can be pumped to by a vacuum based pumping system.

The use of a PFA based grout resulted in a grout product with a lower specific gravity than if a BFS based grout had been used. The development of a low specific gravity grout formulation would maximise the head that a PJMS can pump a grout to. Maximising the pumpable head for the in situ grouting of tanks by the PJMS is likely to be important if the tank is located at a high altitude site or is deeply buried.

The use of cenospheres (gas filled PFA particles) as a component of a grout formulation is likely to be the best means of developing a low specific gravity grout.

2 The two PJMS in situ grout demonstrations highlighted the potential need to introduce a large volume of the grout into a tank as rapidly as possible.

The grout plant used for the two demonstrations allowed grout batches of 600 litres to be prepared. As the total volume of grout used was relatively large up $1.8m^3$, up to four batches of grout were required. Each batch took approximately 30 minutes to prepare resulting in a period of two hours, over which grout was added to the tank.

The simulant reacted with the first batch of grout creating a viscous sludge. It was not until a large proportion of the total grout volume was pumped into the tank that there was sufficient volume of grout and waste for recirculation by the PJMS. It was therefore apparent that the rate of grout addition controlled when the recirculation of the grout by the PJMS could start.

It is advisable to commence grout recirculation with the PJMS as rapidly as possible to avoid loss of formulation workability. The capability of producing and holding large volumes of grout for rapid transfer to a tank requiring in situ grouting is likely to be necessary if PJMS in situ grouting technology is to be applied to a real waste.

3 For application to a full-scale radioactive process, the following programme design is required to minimise the risks:

- Waste characterisation: To determine chemical and physical composition of the waste, and potential variability. The waste characterisation data are used to make a preliminary selection of a cement formulation, waste loading and process method.

- Product specification: To determine the applicable specification, which will provide product performance targets such as leachability, strength and durability. It is essential that all specification and process criteria are incorporated into the formulation development process at the earliest opportunity.

- Formulation development: To identify an acceptable grout recipe and identify the specification of raw materials used in the recipe using an inactive simulant waste material. Formulation development work is carried out using methods of increasing scale. Initial work is carried out at bench scale to identify a suitable formulation to treat a waste. Suitability of a formulation includes evaluation of mix viscosity, flow, temperature, setting time and presence of bleed water after setting. Once a suitable formulation is identified, intermediate scale mixes are carried out to produce product evaluation test specimens and to better understand the likely full-scale production process.

- Product evaluation: To test the product performance both on a short time scale (days) and over longer periods (months). The type of tests carried out may include: leachability, strength, durability, dimensional stability and permeability. If the formulation does not meet a specific criterion then the formulation must be modified until the full specification is met.

- Small-scale radioactive tests: To confirm the results of the inactive work and conform the applicability of the grout formulation. Testing may mirror all or some of the tests performed using inactive material, with particular emphasis on the product performance specification.

8 Conclusions

The conclusions of this work are:

1 The PFA and OPC used for the formulation development were UK sourced powders with physical properties shown to be similar to samples of US sourced PFA and OPC powders supplied to AEAT Winfrith.

2 All formulation development work was based on a 40 wt% kaolin / water waste simulant slurry, i.e. 40 parts by weight dry kaolin to 60 parts by weight water.

3 The formulation development work identified a 3:1 PFA/OPC, w/s = 0.688 grout with a 10 wt % slurry loading, giving a total effective w/s=0.80, as a formulation with suitable rheological and set product properties for the investigation of in-situ treatment of a simulated tank heel waste using the PJMS.

4 The use of X-ray fluorescence analysis has been shown to offer the potential to demonstrate quantitatively the homogeneity of mixed grout / waste simulant products by making use of specific chemical constituents within the kaolin and cement powders, notably strontium and iron.

5 The full-scale tank heel immobilisation demonstration trials showed that the pumpability of the grout formulation, when pumped by the PJMS, was largely controlled by the specific gravity of the grout formulation, rather than the grout viscosity and flow. Minimising the density of a grout is likely to improve the pumpability (particularly in terms of head) of a grout when using the PJMS in grouting applications. Grout viscosity and flow will however, remain key rheological properties to be considered during grout design.

Maximising grout pumpability for the in situ grouting of tanks by the PJMS is likely to be especially important if the tank is located at a high altitude site or is deeply buried. The potential to develop a grout with lower specific gravity than that developed in this work has been identified, for example, by the use of cenospheres, (gas filled PFA particles) as a component of a grout formulation.

6 The potential need to introduce a large volume of the grout into a tank as rapidly as possible was seen during the full-scale tank heel immobilisation demonstration trials. In this work, the simulant reacted with the first batch of grout added to the tank, creating a viscous sludge. The sludge could have been pumped by the PJMS, however it is considered that the initial addition of a larger volume batch of grout into the tank would have led to a more readily pumpable mix.

In practice a tank waste would be drawn down to the lowest level practicable by the PJMS, an increase in the volume of liquid in the tank by grout addition is then required to allow the mixing of the grout and waste heel. Therefore the start of grout/waste mixing and recirculation by the PJMS is likely to be controlled by the rate of grout addition into the tank. It is advisable to commence grout recirculation with the PJMS as soon as possible to avoid loss of formulation workability. Thus, the capability of producing and holding large volumes of grout for rapid transfer to a tank requiring in situ grouting is a desirable component of this technology when treating a radioactive waste.

7 For application to a full-scale radioactive process, the following programme design is suggested to minimise the risks:

Waste characterisation:
Identification of product specification
Formulation development (using inactive simulant material)
Product evaluation
Small-scale radioactive tests

9 References

1 M Board, R F Simmons, *Test Plan for Development of a Grout for Demonstration of a System for In-situ Tank Waste Heel Immobilisation at LANL*, AEAT/R/NS/0755, Issue 1 Draft, July 2004.

2 United States Nuclear Regulatory Commission (NRC), *Technical Position on Wasteform (Revision 1),* January 1991, Office of Nuclear Material Safety and Safeguards, Division of Low-Level Waste Management and Decommissioning.

3 R.F. Simmons, H.J. French, M.J. Dalton and J.R.A. Williams, *Cementation Studies on INEEL Sodium Bearing Waste*, AEAT-2178, Issue 1, September 1997.

4 M. Johnson, R.F. Simmons and J.R.A. Williams, *Cementation of INEEL Type 2 Waste*, AEAT-6095, Issue 1, September 1999.

5 United States Code of Federal Regulations, *Universal Treatment Standards,* CFR Title 40, Part 268.48.

6 U.S. Environmental Protection Agency, Toxicity Characteristic Leaching Procedure, Test Method 1311 (40 CFR 261.24) in *Test Methods for Evaluating Solid Waste, Physical / Chemical Methods*, EPA Publication SW-846.

7 M.J. Dalton, *Rheological Measurements on Cement Grouts*, AEEW-R2094, June 1989.

8 American Society For Testing And Materials, *Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle*, ASTM C191-79, 1979.

9 British Standard, *Testing Concrete, Method for Making Test Cubes from Fresh Concrete*, BS 1881, Part 108, 1983.

10 British Standard, *Testing Concrete, Specification for Compressive Testing Machines for Concrete*, BS 1881, Part 115, 1983.

11 British Standard, *Recommendations for Measurement of Velocity of Ultrasonic Pulses in Concrete*. BS 1881, Part 203, 1986.

12 British Standard, *Testing Concrete, Method for Determination of Density of Hardened Concrete*, BS 1881, Part 114, 1983.

13 British Standard Specification, *Fly ash for concrete. Definitions, requirements and quality control*, BS EN 450, 1995.

14 British Standard Specification, *Cement, Composition, specifications and conformity criteria for common cements*, BS EN 197-1, 2000.

Tables

Sample	Scale of mix	Water / solids ratio	Waste loading (wt%)	Viscosity (Pa s $^{-1}$)	Significant† bleed at 24 hours curing
Burgess No 28 kaolin (40 wt% solids slurry)	1 litre	N/A	N/A	0.017	N/A
Thiele EG-44 (40 wt% solids slurry)	1 litre	N/A	N/A	0.008	N/A
3:1 PFA/OPC	150 ml	0.40	N/A	0.409	No
		0.45	N/A	0.207	No
		0.50	N/A	0.121	Yes
		0.55	N/A	0.093	Yes
3:1 PFA/OPC with 40 wt% solids kaolin slurry, w/s = 0.60	150 ml	N/A	5	0.140	Yes
		N/A	10	0.293	No
		N/A	15	0.565	No
		N/A	20	1.106	No
		N/A	25	1.641	No
3:1 PFA/OPC with 10 wt% slurry* waste loading *(40 wt% solids kaolin slurry)	150 ml	0.60	N/A	0.264	No
		0.65	N/A	0.226	Yes
		0.70	N/A	0.168	Yes
		0.75	N/A	0.130	Yes
		0.80	N/A	0.121	Yes

† Significant bleed at 24 hours curing is defined as a volume of overstanding water on small scale sample of set product, such that bleed would occur at 24 hours in a large scale mix with no recirculation.

Table 1 Small scale scoping trial mix data

Sample	Scale of mix	Recirculation time (hours)	Viscosity (Pa s $^{-1}$)	Significant† bleed at 24 hours	Colcrete Flow (mm) (on a 1200ml sample)
04/015 **3:1 PFA/OPC** **with 10 wt % slurry,** **w/s=0.80** (40 wt% solids kaolin slurry)	2 litre	0.5	0.140	Yes	
		1.5	0.169	Yes	
		2	0.197	Yes	
		3	0.216	Yes	1000
04/020 **3:1 PFA/OPC, w/s=0.688**	200 litre	1	0.026	Yes	> 1400
		2	0.036	Yes	> 1400
		3	0.026	Yes	> 1400
04/017 **3:1 PFA/OPC** **with 10 wt % slurry** **w/s=0.80** (40 wt% solids kaolin slurry)	200 litre	0.5	0.149	Yes	> 1400
		1	0.168	Yes	> 1400
		2	0.159	No	> 1400
		3	0.168	No	> 1400

† Significant bleed at 24 hours curing is defined as a volume of overstanding water on small scale sample of set product, such that bleed would occur at 24 hours in a large scale mix with no recirculation.

Table 2 2 litre and 200 litre scale mix data

Figures

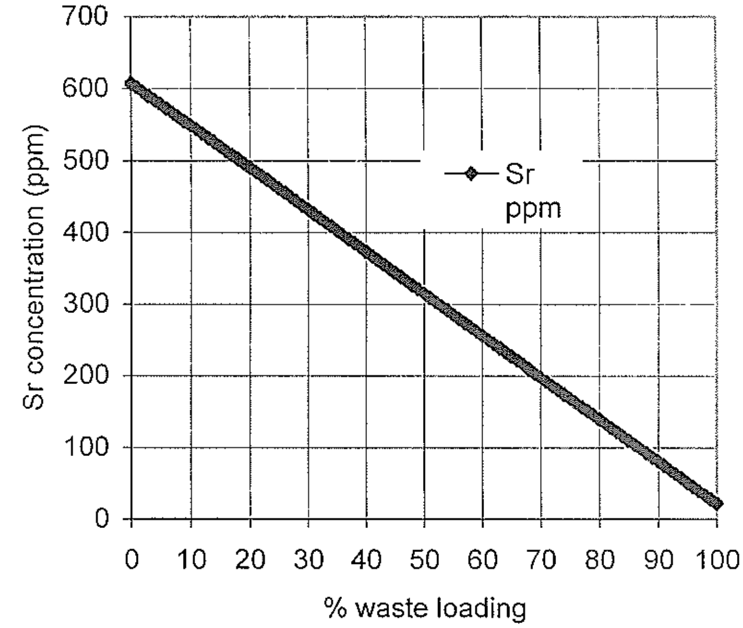


Figure 1 Variation in Sr concentration with increasing waste loading based on XRF analysis of US sourced cement powders and kaolin

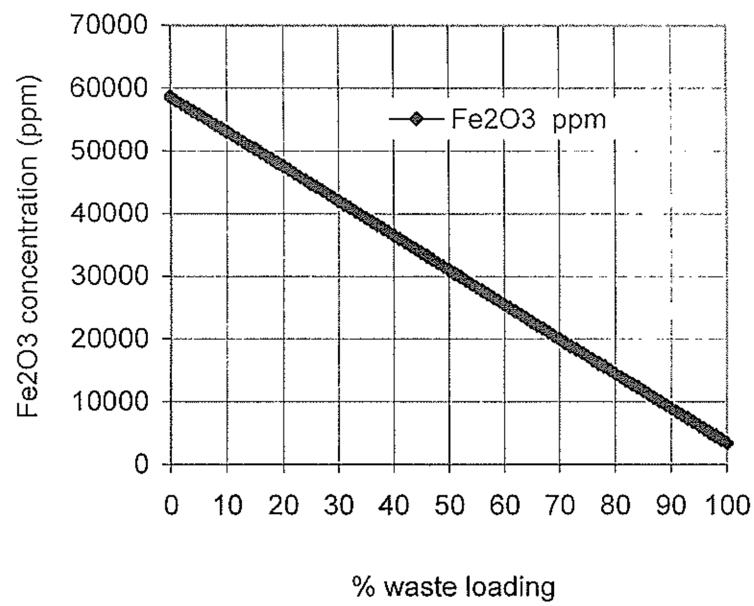


Figure 2 Variation in Fe concentration with increasing waste loading based on XRF analysis of US sourced cement powders and kaolin

Appendices

CONTENTS

Appendix 1
Product Evaluation Data

CONTENTS

100 mm cubes						
Sample No		Age (days)	Weight (g)	Pulse velocity (km/s)	Density (kg/l)	Compressive strength at 28 days (MPa)
1		2	1485.1	1.72	1.492	N/D
2		2	1494.0	1.71	1.497	N/D
3		2	1491.2	1.70	1.499	N/D
4		2	1496.8	1.71	1.493	N/D
5		2	1487.8	1.71	1.492	N/D
6		2	1484.8	1.70	1.49	N/D
7		2	1497.7	1.70	1.495	N/D
8		2	1494.1	1.70	1.494	N/D
9		2	1500.9	1.71	1.5	N/D
10		2	1495.6	1.70	1.5	N/D
1		28	1478.5	1.86	N/D	1.6
2		28	1490.7	1.85	N/D	1.7
3		90	1489.9	2.26	N/D	N/D
4		90	1485.8	2.28	N/D	N/D
200 mm Cores						
Recirculation time (hours)	Core position	Age (days)	Weight (g)	Pulse velocity (km/s)	Density (kg/l)	Bleed at 24 hours (vol%)
1	Top	30	2429.5	1.57	1.45	< 1
	Bottom	30	2355.0	2.04	1.49	
3*	Top	30	2435.5	1.77	1.46	< 1
	Middle	30	2399.5	1.93	1.47	
	Bottom	30	2447.0	1.89	1.48	
3	Short	30	2416.5	1.98	1.49	< 1

* 2 hour pipe infill broke on demoulding

Table A1.1 Product evaluation data for mix 04/017: 3:1 PFA/OPC with 10 wt % slurry (40 wt% solids kaolin), w/s=0.80

Prism samples			
Curing time	Dimensional movement	Elastic modulus	Weight change
days	microstrain	GPa	wt%
2	0	Not determined	0.0
7	45	Not determined	0.0
14	-32	Not determined	-0.1
21	44	Not determined	-0.1
28	107	1.72	-0.1
42	110	2.12	-0.2
62	191	2.83	-0.3
102	347	3.86	-0.4

Table A1.1 cont. Product evaluation data for mix 04/017: 3:1 PFA/OPC with 10 wt % slurry (40 wt% solids kaolin), w/s=0.80

100 mm cubes					
Sample No	Age (days)	Weight (g)	Pulse velocity (km/s)	Density (kg/l)	Compressive strength at 28 days (MPa)
1	4	1481.7	2.19	n/d	n/d
2	4	1495.1	1.98	n/d	n/d
3	4	1529.4	1.99	n/d	n/d
4	4	1489.0	2.01	n/d	n/d
1	28	1478.2	2.26	n/d	3.0
2	28	1495.1	2.23	n/d	2.6

Pipe infill samples						
Recirculation time (hours)	Sample position	Age (days)	Weight (g)	Pulse velocity (km/s)	Density (kg/l)	Bleed at 24 hours (Vol%)
1	Top	35	2525.5	2.02	1.51	6.9
	Middle	35	2587.0	2.18	1.55	
	Bottom	35	2672.5	2.31	1.58	
2	Top	35	2629.5	2.01	1.39	6.4
	Middle	35	2537.5	2.17	1.54	
	Bottom	35	2643.0	2.27	1.58	
3	Top	35	2542.5	2.14	1.52	6.0
	Middle	35	2541.5	2.14	1.53	
	Bottom	35	2553.5	2.13	1.52	8.8

Prism samples			
Curing time	Dimensional movement	Elastic modulus	Weight change
days	microstrain	GPa	wt %
4	0	Not determined	0.0
7	-171	Not determined	-0.1
14	-95	Not determined	-0.2
21	-10	2.33	-0.2
28	-9	2.53	-0.4
35	24	2.85	-0.4
55	84	3.65	-0.5
90	193	4.95	-0.7

Table A1.2 Product evaluation data for mix 04/020: 3:1 PFA/OPC w/s=0.688

Appendix 2
Characterisation data for UK and US sourced cement

CONTENTS

Major Elements (Wt %)	US OPC	AEAT Winfrith UK OPC Batch 55	Thiele EG-44 Kaolin	Burgess No 28 Kaolin	US PFA	AEAT Winfrith UK PFA Batch 36
SiO_2	20.39	20.77	44.13	44.79	50.24	52.13
TiO_2	0.360	0.204	2.362	1.040	1.155	0.933
Al_2O_3	4.68	4.83	37.84	39.02	24.44	25.46
Fe_2O_3	3.39	1.83	0.88	0.69	7.14	8.49
MnO	0.028	0.038	0.001	0.002	0.026	0.065
MgO	0.969	0.921	0.034	0.008	1.051	1.561
CaO	62.38	62.48	0.014	0.009	1.48	2.01
K_2O	0.12	0.79	0.152	0.032	2.93	3.72
Na_2O	0.005	0.012	0.024	0.09	0.29	1.05
P_2O_5	0.172	0.072	0.148	0.197	0.125	0.226
LOI	7.56	8.05	14.40	14.11	11.10	4.34
Sum	100.00	100.00	100.00	100.00	100.00	100.00

Table A2.1 XRF results for kaolin, OPC and PFA - major elements (by beads)

Trace Elements (ppm)	US OPC	AEAT Winfrith UK OPC Batch 55	Thiele EG-44 Kaolin	Burgess No 28 Kaolin	US PFA	AEAT Winfrith UK PFA Batch 36
As	17	9	< 5	< 5	66	88
Ba	311	235	150	79	880	1117
Br	< 2	< 2	< 2	< 2	< 2	< 2
Ce	44	18	112	74	145	139
Co	10	5	17	11	70	65
Cr	131	86	100	78	131	146
Cu	147	41	12	5	133	191
Ga	10	9	57	64	39	40
I	< 2	< 2	< 2	< 2	< 2	< 2
La	22	6	73	46	96	82
Mo	10	3	0	0	5	14
Nb	7	4	39	19	24	21
Ni	86	57	30	25	83	125
Pb	2	58	55	34	50	102
Rb	< 2	18	< 2	< 2	144	159
Sn	35	-1	6	6	5	4
Sr	703	743	72	56	576	417
Th	6	2	14	12	22	15
U	8	8	5	3	4	2
V	154	97	102	73	228	280
Y	31	17	17	11	90	62
Zn	162	58	55	46	98	183
Zr	78	34	193	136	230	231

Table A2.2 XRF results trace elements (powder pellet)

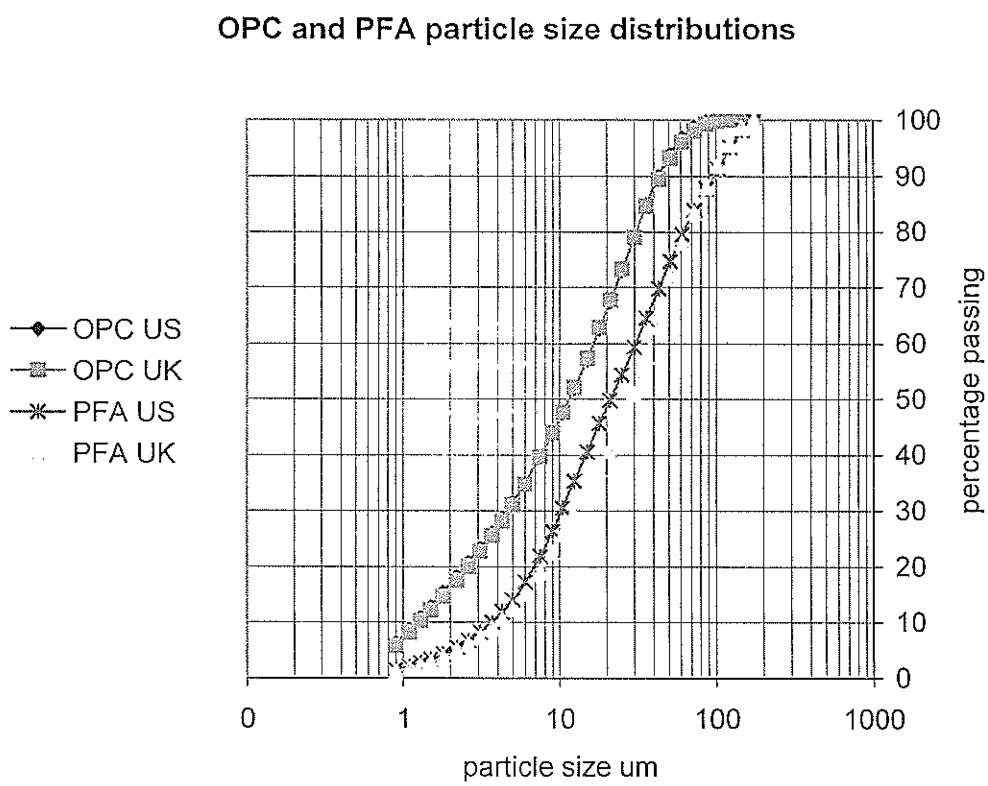


Figure A2.1 Particle size distribution of US and UK OPC and PFA powders

Appendix 3
XRF analysis data of grout samples with increasing waste loading

CONTENTS

Note: Samples were prepared at the AEAT ES Inc Mooresville Test Facility using the demonstration trial cement powders and kaolin

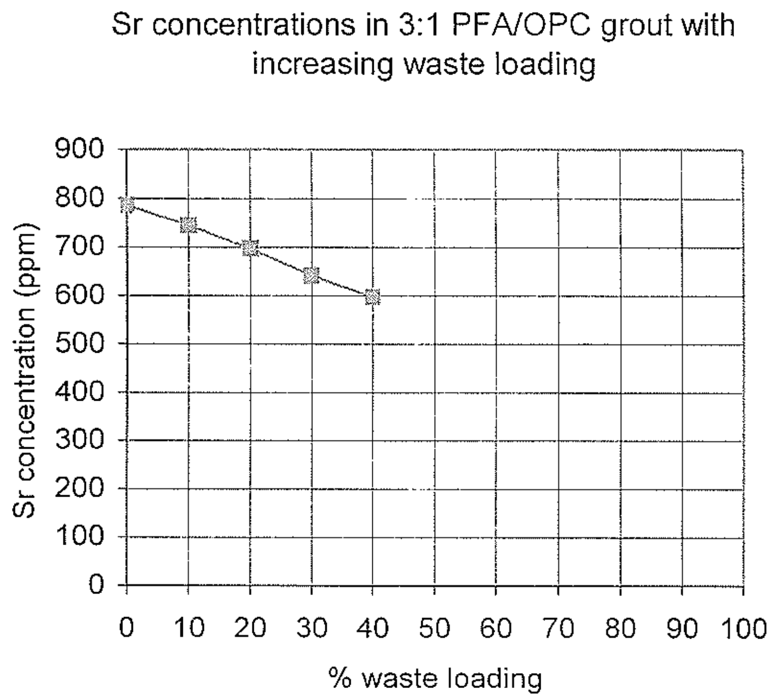


Figure A3.1 Sr concentration in 3:1 PFA/OPC grouts with increasing waste loading

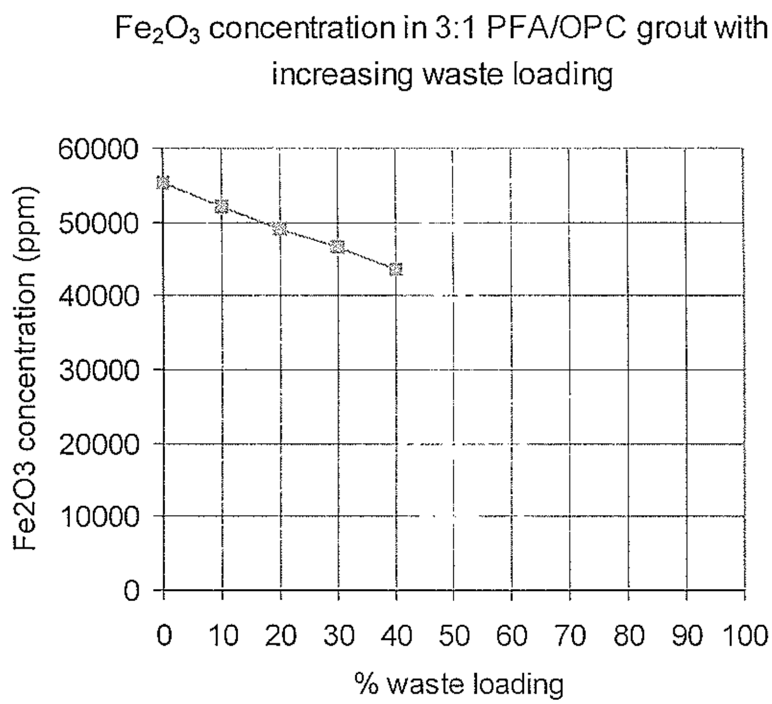


Figure A3.1 Fe_2O_3 concentration in 3:1 PFA/OPC grouts with increasing waste loading

Major Elements (Wt %)	**3:1 PFA/OPC** (no simulant)	**10wt% simulant**	**20wt% simulant**	**30wt% simulant**	**40wt% simulant**
SiO2	38.28	38.42	38.05	38.49	38.79
TiO2	0.98	0.97	0.95	0.94	0.93
Al2O3	18.24	19.45	20.28	21.54	22.6
Fe2O3	5.54	5.21	4.91	4.67	4.36
MnO	0.04	0.04	0.04	0.03	0.03
MgO	1	0.93	0.88	0.82	0.76
CaO	18.57	17.59	16.72	15.05	15.08
K2O	1.76	1.63	1.52	1.44	1.32
Na2O	0.12	0.12	0.12	0.12	0.11
P2O5	0.21	0.21	0.2	0.2	0.2
S	0.76	0.71	0.5	0.47	0.46
LOI	14.5	14.72	15.84	16.22	15.36
Sum	100	100	100	100	100

Table A3.1 XRF results major elements (by beads)

Trace Elements (ppm)	3:1 PFA/OPC (no simulant)	10wt% simulant	20wt% simulant	30wt% simulant	40wt% simulant
As	51	48	44	41	38
Ba	897	828	743	718	652
Ce	133	182	167	131	116
Co	50	46	43	40	33
Cr	162	156	155	148	154
Cu	133	122	117	107	99
Ga	33	39	40	46	46
La	91	92	75	81	64
Mo	13	11	9	9	7
Nb	22	20	21	20	20
Ni	119	79	75	71	68
Pb	44	43	41	42	43
Rb	89	80	75	71	65
Sn	282	287	284	287	285
Sr	786	745	697	642	598
Th	24	23	22	22	20
U	10	8	9	9	9
V	275	265	252	217	209
Y	62	59	57	52	50
Zn	126	118	114	107	101
Zr	192	187	182	183	176

Table A3.2 XRF results trace elements (powder pellet)

Appendix B – Jet Grouting Demonstration Data

Table B1: Density and Bleed Data

Sample Reference No.	Sample Description	Sample Location	Time	SG	Density (pcf)	Density (kg/l)	Measured Bleed @ 24hrs (g)	Bleed @ 24hrs (Vol %)
2173-001	Grout Batch 1	N/A	N/A	1.54	96.0	1.5	266	8.6
2173-002	Grout Batch 2	N/A	N/A	1.58	98.4	1.6	244	7.9
2173-003	Grout Batch 3	N/A	N/A	1.57	97.8	1.6	256	8.3
2173-004	Grout Batch 4	N/A	N/A	1.57	97.7	1.6	258	8.4
2173-005	Mixed Grout & Simulant	1	0:15	1.49	92.9	1.5	98	3.2
2173-006		2	0:15	1.51	94.4	1.5	88	2.9
2173-007		3	0:15	1.46	91.1	1.5	96	3.1
2173-008		1	1:15	1.51	94.1	1.5	34	1.1
2173-009		2	1:15	1.51	94.0	1.5	36	1.2
2173-010		3	1:15	1.49	93.3	1.5	34	1.1
2173-011		1	2:00	1.53	95.4	1.5	24	0.8
2173-012		2	2:00	1.50	93.9	1.5	26	0.8
2173-013		3	2:00	1.50	93.8	1.5	26	0.8
2173-014		1	3:00	1.51	94.0	1.5	9	0.3
2173-016		2	3:00	1.47	91.7	1.5	11	0.4
2173-018		3	3:00	1.50	93.8	1.5	13	0.4

Table B2: Cast Cylinder Compressive Strength Data

Sample No./Location	Cast Date	Test Date	Test Age	Area (sq. in.)	Breaking Load (lbs)	Compressive Strength	
						psi	MPa
1	11/18/2004	12/16/2004	28	12.38	2060	170	1.20
2	11/18/2004	12/16/2004	28	12.38	2740	220	1.50
3	11/18/2004	12/16/2004	28	12.30	2780	230	1.60

Note: 1. Samples taken after 3 hours recirculation
2. Tested in accordance with ASTM C39

Table B3: Core Sample Compressive Strength Data

Sample No./Location	Mix Date	Test Date	Test Age	Area (sq. in.)	Breaking Load (lbs)	Compressive Strength	
						psi	Mpa
1	11/18/2004	12/16/2004	28	16.93	3770	220	1.50
1	11/18/2004	12/16/2004	28	16.91	3360	200	1.40
2	11/18/2004	12/16/2004	28	17.05	1540	90	0.60
2	11/18/2004	12/16/2004	28	16.93	3870	230	1.60
3	11/18/2004	12/16/2004	28	16.93	2550	150	1.00
3	11/18/2004	12/16/2004	28	17.05	1800	110	0.80

Note: 1. Samples taken after 3 hours recirculation
2. Tested in accordance with ASTM C39

Table B4: Ultrasonic Pulse Velocity Data

Sample No./Location	Mix Date	Test Date	Test Age	Path Length (in)	Transmit Time (μsec)	Ultrasonic Pulse Velocity (ft/sec)	Ultrasonic Pulse Velocity (km/sec)
C1	11/18/2004	12/9/2004	21	7.25	170.9	3530	1.08
P1	11/18/2004	12/29/2004	41	10.79	241.8	3720	1.13
C2	11/18/2004	12/9/2004	21	7.24	168.8	3580	1.09
P2	11/18/2004	12/29/2004	41	4.11	83.8	4090	1.25
C3	11/18/2004	12/9/2004	21	7.08	168.4	3500	1.07
P3	11/18/2004	12/29/2004	41	10.52	228.7	3830	1.17

Note:
1. Samples taken after 3 hours recirculation
2. Tested in accordance with ASTM C597
3. Core P2 split in half during transit prior to testing
4. P= Drilled Cores; C= Cast Cylinders

Appendix C – Demonstration Logbook

Appendix 2 – Log Book

DATE: 11/18/04

TEST DESCRIPTION:
See Test Demo. Doc 2173-6-001

SYSTEM CONFIGURATION:
See Test Demo. Doc. 2173-6-001

SENSING AND MEASUREMENT EQUIPMENT LIST

ITEM DESCRIPTION	SERIAL NUMBER	ID NO.	OPERATING RANGE, ACCURACY, PRECISION	CALIBRATION DATE

OPERATIONS CONDUCTED AND DURATIONS:
Grout plant pump was replaced during batch 1 mixing due to pump failure.

NAMES OF OPERATIONAL PERSONNEL

NAME	DEMONSTRATION ROLE
Peter Griffiths	Test Facility Manager
Ellay Henderson	Technician
Ryan Dylla	Technician
Richard Simmons	Grout Formulation Consultant

NOTES:

DATE: ____________

SIMULANT PREPARATION			
QUANTITY OF WATER ADDED:	491 lb	QUANTITY OF KAOLIN ADDED:	327 lb
DESCRIPTION: water added over dry clay powder and hand mixed to remove most of the lumps.			

GROUT ADDITION			
BATCH CONSTITUENTS:			
QUANTITY OF PFA:	818 lb	QUANTITY OF OPC:	272 lbs
QUANTITY OF WATER:	750 lb (90 gal)		
BATCH 1			
TEMPERATURE OF PFA/OPC:	72.3°F	TEMPERATURE OF WATER:	68.9°F
Powder addition ~150 secs	START 10.28	TEMPERATURE OF GROUT:	65.5°F
MIX TIME:	1 hr 20 min STOP 11.48 (PUMPED OVER 11.48–11.55)	VISCOSITY: 2173-001.dat	
SET/BLEED CHARACTERISTICS:	266g Bleed		
@ 24 HOURS	@ 9.20 19/11 Product soft Settlement ~ 13/8"		
BATCH 2			
TEMPERATURE OF PFA/OPC:	71.5°F	TEMPERATURE OF WATER:	69.0°F
Powder Addition ~240s	START 12.14 STOP	TEMPERATURE OF GROUT:	72.5°F
MIX TIME:	12.26 [12 mins] PUMPED OVER 12.26–12.29	VISCOSITY: 2173-002.dat	
SET/BLEED CHARACTERISTICS:	244g Bleed		
@ 24 HOURS	@ 9.20 19/11 Product soft ; Settlement ~ 7/8"		
BATCH 3			
TEMPERATURE OF PFA/OPC:	70.1°F	TEMPERATURE OF WATER:	62.1°F
START 12.47 POWDER ADDITION TIME ~8 mins	STOP 13.04 [17 MINUTES]	PUMPED OVER TEMPERATURE OF GROUT:	69.2°F
MIX TIME:	13.04–13.07	VISCOSITY: 2173-003.dat	
SET/BLEED CHARACTERISTICS:	256g Bleed		
@ 24 HOURS	@ 9.20 19/11 Product soft settlement ~ 1 1/8"		
BATCH 4			
TEMPERATURE OF PFA/OPC:	70.9°F	TEMPERATURE OF WATER:	61.8°F
START POWDER ADDITION TIME	STOP → 13.41	PUMPED OVER TEMPERATURE OF GROUT:	68.3°F
MIX TIME:	~20 MINUTES	13.44–13.47 VISCOSITY:	2173-004.dat
SET/BLEED CHARACTERISTICS:	Bleed 258g		
@ 24 HOURS	@ 9.25 19/11 Product soft ; settlement ~ 1 1/4"		

NOTES:
Batch 1 – bottom take-off part of mixing vessel blocked with dry powder
– pump then failed requiring change of pipe connection; some water injected to reconstitute lumps to unblock dry powder.
Batch 2 + subsequent batches, powder addition rate slowed down

JET MIXING COMMENCED 13.

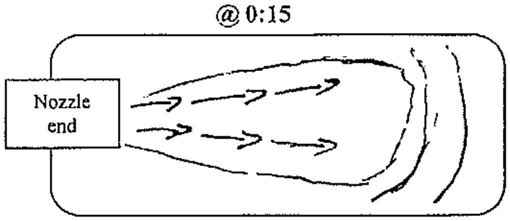
DATE: ____________

JET MIXING PARAMETERS:		
PARAMETERS LOGGED BY SOFTWARE DURING MIXING:		
PARAMETER	UNITS	LOGGING FREQUENCY
Suction Pressure	Bar g	every 0.2 s
Drive Pressure	Bar g	every 0.2 s
Phase Time	s	every 0.2 s
Suction Time	s	every 0.2 s
Phase. ~~Cycle~~ Time	s	every 0.2 s

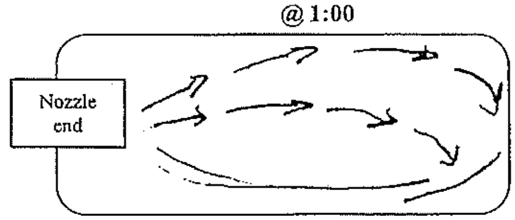
MANUAL DATA LOGGING:						
PARAMETER:	SUCTION PRESSURE	DRIVE PRESSURE	SUCTION TIME	DRIVE TIME	CYCLE TIME	NOTES
TIME INTO MIXING						Data recorded electronically
0:15	4.3	3.7	147.5	12.2	167	
1:00	4.3					
2:00	4.3					
3:00	4.3					
NOTES:						

OBSERVATIONS	@ 0:15	@ 1:00	@ 2:00	@ 3:00
APPEARANCE OF JET CAUSED BY NOZZLE:	good	good	same	same
AGITATION IN TANK CAUSED BY JET:	v. good	good	same	same
IS JET REACHING FAR EXTREMITIES OF TANK:	no	yes	same	same
ARE THERE ANY VISIBLE DEAD SPOTS:	yes - behind nozzle.	Behind Nozzle	same	Appears mixed
ESTIMATED NUMBER OF CYCLES TO MIX TANK CONTENTS:	~5-10			

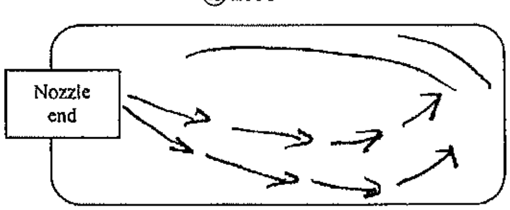
@ 0:15



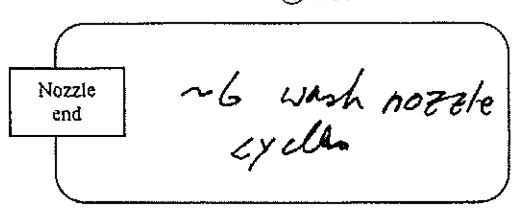
@ 1:00



@ 2:00



@ 3:00



@0.15 Sample 1 noted as "lumpy" ; presumably lumps of unmixed kaolin ~ by ~ 3" diameter
No other lumps observed @ 0:15 on samples 2 + 3

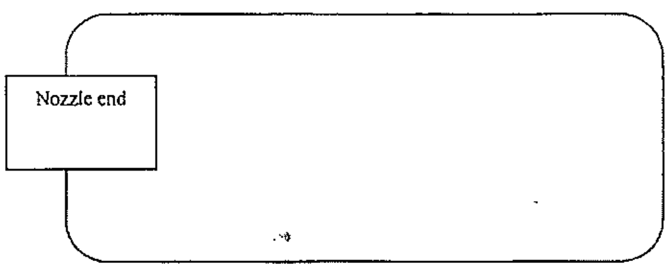
From 1:15 onwards no lumps observed.

DATE: ______________

IN-SITU DATA COLLECTION		SAMPLE POINT 1	SAMPLE POINT 2	SAMPLE POINT 3
TIME 0:15	VISCOSITY:	2173-005.dat	2173-006.dat	2173-007.dat
	TEMPERATURE:	69.7 °F	69.7 °F	70.2 °F
	SET / BLEED CHARACTERISTICS @ 24 HOURS: 11/19 @9:30	98g Bleed; Surface soft; 3/4" settled	88g Bleed; Surface soft; Settlement 1/2"	96g Bleed; Surface soft; Settlement 5/8"
	PIPE INFILL :	YES/~~NO~~	YES/~~NO~~	YES/~~NO~~
TIME ~~1:00~~ 1:15	VISCOSITY:	2173-008.dat	2173-009.dat	2173-010.dat
	TEMPERATURE:	70.3°F	70.7°F	70.4°F
	SET / BLEED CHARACTERISTICS @ 24 HOURS: @9:40 11/19	34g Bleed; Surface soft; Settlement – 3/8"	36g Bleed; Surface soft; Settlement – 3/8"	34g Bleed; Surface soft; Settlement – 3/8"
	PIPE INFILL :	YES/~~NO~~	YES/~~NO~~	YES/~~NO~~
TIME 2:00	VISCOSITY:	2173-011.dat	2173-012.dat	2173-013.dat
	TEMPERATURE:	70.7°F	70.9°F	70.7°F
	SET / BLEED CHARACTERISTICS @ 24 HOURS: @9:45 11/19	24g Bleed; Surface soft; Settlement 3/8"	26g Bleed; Surface soft; Settlement – 3/8"	26g Bleed; Surface soft; Settlement – 3/8"
	PIPE INFILL:	YES/~~NO~~	YES/~~NO~~	YES/~~NO~~
TIME 3:00	VISCOSITY:	2173.014.dat	2173-018.dat	2173-018.dat
	TEMPERATURE:	71.3°F	71.1°F	71.5°F
	SET / BLEED CHARACTERISTICS @ 24 HOURS: @9:50 11/19	Bleed 8g / 10g; Surface soft; Settlement – [illegible]	Bleed 10g / 12g; → Negligible	Bleed 12g / 14g; →
	PIPE INFILL × 2	YES/~~NO~~	YES/~~NO~~	YES/~~NO~~
	CUBE × 2	YES/~~NO~~	YES/~~NO~~	YES/~~NO~~
	CYLINDER × 2	YES/~~NO~~	YES/~~NO~~	YES/~~NO~~
	THERMOCOUPLE INSERTED	YES/NO	YES/NO	YES/NO

POST TEST TANK OBSERVATIONS / MEASUREMENTS	
SET/BLEED CHARACTERISTICS @ 24 HOURS CURING: PIC	@ [illegible] 11/19 – [illegible] ~~[illegible]~~
ANY AREAS OF UNMIXED PRODUCT:	None observable
EXTENT OF SPLATTERING ON TANK WALLS:	

[illegible handwritten margin note]



DESTRUCTIVE ANALYSIS:	SAMPLE POINT 1	SAMPLE POINT 2	SAMPLE POINT 3
CORES TAKEN × ~~2~~ 4	(YES)/NO	(YES)/NO	(YES)/NO