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In Situ Grouting Technology Demonstration and Field Specifications Overview for Hot Deployment of the Multi-Point-Injection™ System in Gunite and Associated Tank TH-4

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CONTENTS

LIST OF FIGURES v

LIST OF TABLES vii

ACRONYMS ix

ACKNOWLEDGMENTS xi

EXECUTIVE SUMMARY xiii

1. INTRODUCTION 1

2. GENERAL FEATURES OF THE MPI™ TECHNOLOGY 5
   2.1 IMPLEMENTATION OF MPI™ PROCESS 6
      2.1.1 Core Drilling Through GAAT Roof 6
      2.1.2 Plastic Casing To Penetrate Tank Sludge 6
      2.1.3 MPI™ Jetting Tools 8
      2.1.4 Lifting Frame Assembly and Local Site Containment 9
      2.1.5 High-Speed Injection 10
      2.1.6 MPI™ General Equipment Requirements 11
      2.1.7 Capability of MPI™ Process To Cut Gunite and Steel Plate 11
   2.2 PRELIMINARY TESTS TO FORM HOMOGENOUS LOW-CONDUCTIVITY MONOLITHS 12
      2.2.1 Solidification of B-25 Box Waste 13
      2.2.2 Shallow Buried Waste in Pits 14

3. 1996 BENCH-SCALE DEVELOPMENT OF GROUTS FOR GAAT TANK SLUDGE 17
   3.1 GAAT SURROGATE 18
   3.2 ORNL GAAT GROUT DEVELOPMENT 18
   3.3 GAAT GROUT SENSITIVITY TESTING 22
      3.3.1 Compression Strength 22
      3.3.2 Leachability and Diffusion Characteristics 24
   3.4 CONCLUSIONS FROM BENCH-SCALE STUDY 25
      3.4.1 Grout Formulation Used During Full-Scale Cold Demonstration 25

4. FULL-SCALE COLD FIELD DEMONSTRATION OF MPI™: TRIAL FIELD DETAILS 27
   4.1 SITE LOGISTICS: EQUIPMENT AND TEST TANK 27
   4.2 PHYSICAL SURROGATE: FINE SAND AND COHESIVE CLAY PODS 29
   4.3 TRAINING 32
   4.4 SINGLE-POINT INJECTION 33
   4.5 MPI™ INJECTION SEQUENCE 36
      4.5.1 Injection Sequence 36
      4.5.2 Material Volumes and Rates 39
      4.5.3 Clogged Nozzle Issues 40

5. FULL-SCALE COLD FIELD DEMONSTRATION OF MPI™: ANALYTICAL RESULTS 43
5.1 LOCATION OF TEST SAMPLES AND TRENCH EXCAVATION 44
5.2 UNCONFINED COMPRESSION STRENGTH 44
5.3 EQUIVALENT SAND DENSITY VS MONOLITH THICKNESS 48
5.3.1 PSI Sand Density Data 48
5.3.2 Most Probable Monolith Uniformity Distribution 50
5.4 TEMPERATURE OF MONOLITH OVER TIME 51
5.5 CONCLUSIONS AND RECOMMENDATIONS 52
5.5.1 Lessons Learned from Cold Test for Application to Tank TH-4 Remediation 52

6. 1998 BENCH-SCALE DEVELOPMENT OF GROUTS FOR GAAT TH-4 SLUDGE 55
6.1 GAAT TH-4 SLUDGE SURROGATE USED IN THE 1998 TEST PROGRAM 55
6.2 PROPERTIES OF BULK DRY BLEND USED DURING THE COLD FIELD DEMONSTRATION 56
6.2.1 Unit Weight and Free Water 60
6.2.2 Unconfined Compression Strength 60
6.2.3 TCLP Extract for Chromium, Lead, and Mercury 61
6.2.4 Conclusions on Bulk-Blended Grout Used During Cold Field Demonstration 61
6.3 SENSITIVITY TESTING 61
6.3.1 Grout Mixes 62
6.3.2 GAAT TH-4 Surrogate Variation 62
6.4 SENSITIVITY TESTING: DATA ANALYSIS 64
6.4.1 Dry Sludge and Levels of Treatment in TH-4 Monolith 65
6.4.2 Percentage of Pozzolan in Monolith 68
6.5 MECHANICAL STRENGTH AND LEACH RESISTANCE OF TREATED TH-4 SURROGATE SLUDGE 69
6.5.1 Unconfined Strength vs Levels of Treatment 70
6.6 TCLP LEACH TESTS AND ANS 16.1 DIFFUSION MEASUREMENTS 72
6.6.1 Diffusion Resistance from ANS 16.1 Tests 73
6.7 HOT TESTING OF ACTUAL TH-4 SLUDGE SAMPLES 75
6.8 CONCLUSIONS 77

7. REMEDIATION OF GAAT TH-4 SLUDGE 79
7.1 PENETRATIONS THROUGH GAAT TANK ROOF 79
7.2 INSTALLATION OF PLASTIC CASING INTO SLUDGE 80
7.3 MPI™ TREATMENT OF TANK HEEL MATERIAL 82

8. SUMMARY AND CONCLUSIONS 83

9. REFERENCES 85

APPENDIX A: ALARA WORKPLAN—SOUTH TANK FARM SITE DEVELOPMENT A-1

APPENDIX B: SELECTION OF THE DRY BLEND ADDITIVES B-1

LIST OF FIGURES

2.1	Schematic representation of Multi-Point Injection (MPI™) tools being used to treat tank waste	5
2.2	Multiple small-diameter holes through HDPE plastic pipe from high-speed jets on MPI™ jetting tool	7
2.3	Schematic of MPI™ jetting tool	8
2.4	Lifting frame used for MPI™ treatment of shallow buried waste	10
2.5	Hose-suspended jetting tool cutting through steel drum	11
2.6	Photograph of shallow buried waste	13
2.7	Dissected block of cemented shallow buried waste	15
2.8	Excavated monolith of cemented buried waste	15
4.1	Layout of in situ grouting equipment used in cold field demonstration	28
4.2	Test setup used in the cold field demonstrations at the Halliburton test facilities	29
4.3	Close-up of vertical steel stanchions used to secure the PVC pipes and jetting tools	30
4.4	Elevation view of 15-ft-diameter steel ring, used in the cold field demonstration at the Halliburton test facilities	30
4.5	Particle-size distribution for Ottawa sand used in the cold field demonstrations at the Halliburton test facilities	31
4.6	Photograph of placement of clay pod	32
4.7	Location of five clay/red dye tracer pods	33
4.8	Turbulent jet streams produced by MPI™ jetting tool during operator training	34
4.9	High-pressure jets from single-injection tool cutting through PVC pipe	34
4.10	High-pressure jet pattern in sand from single-injection tool	35
4.11	High-pressure jet pattern near tank wall from single-injection tool	35
4.12	Schematic plan view of MPI™ injection tool layout and jetting configuration used in the cold field demonstration at the Halliburton test facilities	37
5.1	Surface of monolith after 12 h of consolidation	43

5.2 Location of test trench, 3-in. cylinders, and steel tube samples 45

5.3 Backhoe digging test trench 46

5.4 Sample tube imprint after extraction of steel sample tubes 46

5.5 Removal of loose material from side walls of test trench 47

5.6 Compilation of sand distribution within grouted monolith; Halliburton data and WXYZ samples measured by PSI within 24 h 49

5.7 Compilation of PSI sand distribution data within grouted monolith 49

5.8 Most probable sand distribution within 15-ft-diameter grouted monolith formed using the MPI™ process 51

6.1 Volumetric water content vs percent waste loading of wet sludge used in 1998 bench-scale tests with GAAT tank TH-4 surrogates 64

6.2 Comparison between percentage of TH-4 surrogate dry sludge and water: pozzolan ratio in final monolith 67

6.3 Comparison between percentage of pozzolan and water:pozzolan ratio for various solidified TH-4 surrogate samples 69

6.4 Comparison between unconfined compression strength and water:pozzolan ratio in TH-4 solidified surrogate 70

6.5 Comparison between RCRA metal TCLP extract concentration and unconfined compression strength for the TH-4 surrogate sludge used in the 1998 ORNL studies 72

6.6 Comparison between chromium TCLP extract and percentage of pozzolan in final mixture for the TH-4 surrogate sludge used in the 1998 ORNL studies 73

6.7 Comparison between lead TCLP extract and percentage of pozzolan in final mixture for the TH-4 surrogate sludge used in the 1998 ORNL studies 74

6.8 Comparison between mercury TCLP extract and percentage of pozzolan in final mixture for the TH-4 surrogate sludge used in the 1998 ORNL studies 74

6.9 Leachability index for strontium-85 in ANS 16.1 test and percentage of pozzolan in final mixture for the TH-4 surrogate sludge used in the 1998 ORNL studies 75

6.10 Leachability index for cesium-137 in ANS 16.1 test vs percentage of pozzolan in the TH-4 surrogate used in the 1998 ORNL studies 76

7.1 Schematic of MPI™ jetting tool installation in a gunite tank 80

LIST OF TABLES

2.1 Hydraulic conductivity values measured on municipal waste solidified using the multi-point injection (MPI™) process in Tank 3, Duncan, Oklahoma (1994) 14

3.1 Summary of surrogate GAAT sludge design 19

3.2 Summary of target surrogate elemental and ionic concentrations compared with the weighted average and the maximum tank average concentrations 20

3.3 Compilation of constituents required in ORNL solidification formulation 21

3.4 Grout compositions for testing sensitivity of the in situ grout formulation for the GAAT sludges to variations in composition 22

3.5 Results of performance testing of sensitivity of in situ GAAT grouts 23

3.6 Results of leach testing of sensitivity of in situ GAAT grouts 24

3.7 Dry blend solidification agents used in ORNL formulation 25

4.1 Compilation of jetting data measured during MPI™ Duncan, Oklahoma, cold field demonstration (1997) 38

4.2 Compilation of monolith constituents injected during the MPI™ cold field demonstration vs material requirements for ORNL monolith formation 39

5.1 Compilation of unconfined compression test on samples taken from MPI™ grouted monolith; Duncan, Oklahoma, cold field demonstration (1997) 47

5.2 Compilation of unconfined compression test on fresh grout samples taken from Halliburton grout plant MPI™ cold field demonstration (1997) 48

6.1 Composition of TH-4 sludge sample and GAAT surrogates 57

6.2 Composition of the surrogate TH-4 sludge used in the 1998 bench-scale studies 58

6.3 Chemical analysis of sludge sample from GAAT TH-4 59

6.4 Grout composition for screening tests with surrogate TH-4 sludge 60

6.5 TCLP extract concentrations for screening tests with surrogate TH-4 sludge 61

6.6 Grout mix water, dry blend, and TH-4 surrogate used during 1998 bench-scale study 63

6.7 Composition of final mixtures, measured strength and leach resistance, TH-4 surrogate sensitivity tests 1998 66

6.8 Density, penetration resistance, and compressive strength of grout with TH-4 sludge (35 wt% hot test) 76

6.9 TCLP results for grouted and ungrouted GAAT TH-4 sludge sample 77

ACRONYMS

ALARA	As Low As Reasonably Achievable
ANS	American Nuclear Society
DOE	Department of Energy
GAAT	Gunite and Associated Tanks
GES	Ground Environment Services, Inc.
HDPE	high-density polyethylene
HEPA	high-efficiency particulate air
INEEL	Idaho National Engineering and Environmental Laboratory
IRPC	Indian Red Pottery Clay
LDR	land disposal restriction
MPI™	Multi-Point Injection
MVST	Melton Valley Storage Tanks
OHF	Old Hydrofracture Facility
ORNL	Oak Ride National Laboratory
OUs	operating units
PNNL	Pacific Northwest National Laboratory
PVC	polyvinylchloride
QA/QC	quality assurance/quality control
RCM	recirculating cement mixer
RCRA	Resource Conservation and Recovery Act
TCLP	Toxicity Characteristics Leaching Procedure
TFA	Tanks Focus Area
UTS	universal treatment standards

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EXECUTIVE SUMMARY

The best management practices for in-tank treatment of wastes requires an integrated approach to develop appropriate treatment agents that can be safely delivered and mixed uniformly with sludge in the tank. It is unacceptable to formulate grouts that can immobilize the sludge contaminants of concern and then merely pour them atop the tank sludge with little quality control to ensure intimate mixing. In-tank solidification of radioactive wastes offers several advantages over exhumation and may represent the best management practices for handling wastes in underground storage tanks. In-tank treatment can be designed to be simple, single-step processes that have the potential of immobilizing sludge and forming uniform, low-conductivity monoliths that are diffusion resistant. The final stabilized waste form can be designed to be exhumable at a future date, and therefore, would not significantly impact remediation decisions on the operating units (OUs) beneath the tanks. Solidified sludges can be exhumed, if necessary, by mechanical means and thus avoid generating the large-volume increases associated with using water jetting techniques to wash the sludge from the tanks.

The bench-scale testing and cold field demonstration discussed in this report have paved the way for the closure of Gunite and Associated Tanks (GAAT) TH-4. These efforts have helped to build confidence that the sludge in TH-4 can be successfully immobilized using in situ grouting techniques. The bench-scale work discussed in this report showed that a wide variety of GAAT surrogate sludges and also actual sludge taken from GAAT TH-4 could be effectively treated at sludge loadings from 35 to 65%. Both Resource Conservation and Recovery Act (RCRA) metals and radioactive contaminants were effectively treated. The RCRA metals (mercury, lead, and chromium) were immobilized to below their respective universal treatment standards. The radioactive contaminants (Sr-85 and Cs-137) typically had leachability indices of about 10 as measured in ANS 16.1 diffusion tests. The small amount of dispersant mixed into the grout to improve the pumping characteristics of the viscous grout had no impact on the strength, leaching, and diffusion resistance of the samples tested. The bulk blending (38 tons) of the Oak Ridge National Laboratory (ORNL) dry blend grout had chemical qualities equivalent to those measured on small-scale laboratory samples prepared from the individual constituents.

The cold-field demonstration of the Multi-Point-Injection™ (MPI™) process proved that it is a robust jet delivery system capable of forming a 32-ton uniform monolith in about 8 min. Analytical data showed that a zeolite-type physical surrogate (quartz sand 0.5 to 0.8 mm) was uniformly mixed over the 40-in.-thick monolith without lifting the jetting tools off the tank floor. The other physical surrogates used in the cold-field demonstration had cohesive characteristics with consistency similar to both GAAT TH-4 and Hanford sludges. Both cohesive surrogates were easily intermixed into the monolith. Review of the data from the cold field demonstration indicate the following:

- The MPI™ process successfully delivered the correct gross amount of treatment agents required in the ORNL formulation.
- A near homogeneous monolith was formed with physical surrogates that possessed both rapidly settling characteristics (zeolite-type particles) and pockets of cohesive material similar to Hanford type sludge.

The quantitative data cited in this report concerning the monolith’s homogeneity is further supported by visual evidence gathered in a test trench dug across the entire thickness of the monolith. Photographs of the test trench presented in this report show the creation of a uniform monolith, which was 15 ft in diameter and about 40 in. thick. There were no signs of untreated white quartz sand or red clay surrogate

at the contact of the monolith with the tank floor. Furthermore, the maximum internal core temperature of the monolith only reached ~100°F during curing.

The simplicity of the MPI™ process allowed the treatment of the physical surrogates to be accomplished remotely with all capital equipment and workers in the safety of a work zone about 200 ft away from the test tank. Only low-cost, disposable equipment (plastic pipe and steel tubes) came in contact with the sludge surrogate. The field quality controls implemented during the MPI™ cold-field demonstration showed that the required level of treatment could be reproduced accurately in the field. The bulk-blended grout used during the cold-field demonstration had chemical properties that were shown to be effective in treating GAAT surrogate sludge as well as actual sludge taken from GAAT TH-4. The data show that there was excellent quality assurance/quality control in the field and that the correct amount of grout was injected to form a mixture with the required gross amount of constituents.

The only remaining element of the MPI™ system requiring additional demonstration prior to hot deployment is the modification of the MPI™ drive shoes required for installation of the plastic casing used in the MPI™ process. The drive shoe redesign is anticipated to proceed smoothly because it is based upon a current design that has been used successfully in shallow buried waste applications.

1. INTRODUCTION

The Gunite and Associated Tanks (GAAT) were constructed at Oak Ridge National Laboratory (ORNL) between 1943 and 1951 and were used for many years to collect radioactive and chemical wastes generated by ORNL operations. These tanks are currently inactive and have not been used to collect waste solutions and sludges for many years. Much of the sludge accumulated in these tanks was removed and disposed of in the 1980s. Thus, some tanks are virtually empty, while others still contain significant amounts of sludge and supernatant. The sludges contain high levels of radioactivity (mainly strontium-90 and cesium-137). Some Resource Conservation and Recovery Act (RCRA) metal concentrations are high enough in the available total constituent analysis for the GAAT sludges to be potentially RCRA hazardous [the GAAT sludges have been found characteristically hazardous for mercury based on the Toxicity Characteristics Leaching Procedure (TCLP) tests]; therefore, these sludges are presumed to be mixed waste.

The tank sludge remediation approach currently preferred by the Department of Energy (DOE) is to exhume the tank sludge via sluicing and pump the diluted sludge to another holding tank for future treatment. Current exhumation techniques rely primarily upon water jetting technology coupled with various slurry-pumping methods. Sludge volume increases can be on the order of 500% of the original sludge volume to mobilize and remove the waste from the bottom of a tank. After exhumation, residual contaminated material remains in the walls and at the bottom of the tank (heel material). Exhumation does not address issues related to infiltration of surface water back into “empty” tanks, nor is the long-term structural stability of the tanks addressed. The temporary storage of the exhumed sludge only postpones future considerations of longer term treatment at an associated increased cost as a result of the issues related to exhumation and temporary storage.

In-tank solidification of radioactive wastes offers several advantages over exhumation and may represent the best management practices for handling wastes in underground storage tanks. In-tank treatment can be designed to be simple, single-step processes that have the potential of immobilizing sludge and forming uniform, low-conductivity monoliths that are diffusion resistant. The final stabilized waste form can be designed to be exhumable at a future date, and therefore, would not impact remediation decisions on the operating units (OUs) beneath the tanks. Solidified sludges can be exhumed by mechanical means and do not generate the large-volume increases associated with using water jetting techniques to wash the sludge from the tanks.

The full potential of in-tank treatment processes can only be realized if the appropriate solidification agents are chosen and delivered using a very robust injection system, capable of intimately mixing the sludge and solidification agents. This report will summarize the results from bench-scale testing performed at ORNL to develop treatment agents for the immobilization of GAAT sludge, especially the sludge in Tank TH-4.

Bench-scale testing at ORNL in 1996 proved that a grout formulation based on slag, fly ash, and clay prevented the physical segregation (35% waste loading) of zeolite-sized particles and produced little or no free water upon curing. The compressive strength of the stabilized RCRA/radioactive surrogate was relatively low at 100 to 500 psi but can adequately assure the stability of the tank shell. These low compressive strengths allow for conventional exhumation (clamshell or backhoe) of the stabilized waste in the future (if required). The RCRA metals [mercuric chloride salts, lead, chromium(VI)] were stabilized within TCLP limits, and the grout provided excellent diffusion resistance for the radionuclides (strontium-85 and cesium-137). Leachability indexes were measured in excess of 10 using American Nuclear Society (ANS) 16.1 test procedures. Additional bench-scale testing conducted in 1998 proved that the 38 tons of dry blend mixed by Halliburton Energy Services, during the cold in-tank field demonstration, also immobilized all RCRA metals and radioactive contaminants. The properties of the kilogram-size samples used during bench-scale testing were successfully replicated on a much larger scale (38 tons) that is similar to that required for hot deployment. The Halliburton bulk dry blend material was used in bench-scale tests to immobilize RCRA metals below the universal treatment standards even at a waste loading as high as 65%. The 1998 ORNL studies also revealed that the unconfined compression strength of the treated GAAT sludge was not well correlated to the grout's ability to immobilize RCRA metals and radionuclides. A strong correlation was established between leach resistance and the percentage of slag, fly ash, and cement in the final mixture. The composition of the monolith formed during the cold field demonstration had the highest concentration of these three constituents when compared with nine other grout formulations tested at ORNL. The main issues not resolved in the laboratory were related to field deployment, such as the pumpability of the viscous grout and the uniformity with which the grout could be inter-mixed with large volumes of tank sludge.

The successful development of a grout capable of immobilizing all the contaminants of concern for GAAT TH-4 resulted in a cold in-tank field demonstration of the high-speed jet delivery system termed multi-point injection (MPI™). This is a patented process developed by Ground Environmental Services (GES). A near full-scale mock-up of Tank TH-4 was set up at the Duncan, Oklahoma, test facility of Halliburton Energy Services in December 1997. The success of the MPI™ system to deliver the ORNL grout was confirmed by the exhumation of the treated sand/clay surrogate. Visual observations confirmed that the internal structure of the monolith was uniform across the 15-ft diameter and 40-in. thickness of the treatment. Eleven (11) tons of surrogate was transformed into a relatively homogeneous 32-ton monolith in less than 8 min of field operations. Furthermore, the procurement for the test setup, execution, and report documentation of the cold test were all accomplished in about a month.

The details of the Oklahoma trial field and analytical results used to document the formation of a uniform, monolithic structure are discussed at length in this report. On the basis of experience in using the MPI™ jetting system to treat miscellaneous shallow buried waste (steel drums, construction debris), it is evident that the MPI™ system would be useful in the treatment of various types of radioactive and hazardous wastes (i.e., hardpan and saltcake) inside underground storage tanks.

Because of the robustness of the jetting technique, the field quality controls associated with the MPI™ system are relatively simple. Issues related to relying upon anecdotal information and limited sampling data on the mechanical properties of the tank sludge are less of a concern when compared with low-pressure grouting or tremie concrete methods. Recent enhancements to field quality assurance/quality control (QA/QC) procedures are discussed in relationship to performing in-tank reconnaissance as a integral part of the MPI™ process. Visualization techniques based upon borehole cameras placed at strategic points within the sludge may be useful in examining the layering of the sludge prior to injection. The cameras may also be used to monitor the grout injection process in real time during active treatment of the sludge.

The flexibility of the MPI™ process allows a much simpler method for the treatment of heel material than that allowed for the implementation for general treatment of a tank filled with sludge. When an entire tank is treated, there must be broader placement of the MPI™ injectors because there is little information about the consistency and type of sludge (weak, cohesive, zeolite, hardpan, saltcake). Exhumation typically removes the weaker components of the sludge and leaves behind a potentially more robust material.

The following alternatives exist for treating residual tank wastes:

1. Pour flowable fill into the tank directly from concrete trucks and try to mix or encapsulate the waste as much as possible and then fill.

2. Use a robust mixing/cutting process, such as the MPI™ system, to strategically treat bulk heel material (zeolite, hardpan, saltcake) and thereafter uniformly mix the waste with solidification agents.

A white paper was written to examine the potential of using the MPI™ process and tremie concrete methods for filling tanks with concrete or flowable fill. The white paper was partially based upon tremie concrete research conducted at the University of California for the Federal Highway Administration. The general findings of the tremie concrete research applicable to treating tank sludge residual heel material were

- For low-slump concrete mixtures (5-in. slump or less), the concrete tends to flow for a certain distance (20 ft in test setup) and sweep the residual on the tank floor outward toward the walls of the tank. There is little to no mixing of the concrete and residual. The effect of the concrete placement is to concentrate the bottom sludge along the outer perimeter of the tank. This is the least attractive position for the tank sludge, and it is also more concentrated and confined to one area of the tank.

- For very flowable mixes (8- to 10-in. sumps), the concrete tends to push the residual contamination outward. Then as the residual contamination hits the wall of the tank, the residual material tends to flow over the top of the placed concrete. There is no treatment of the residual in contact with the tank floor. The residual at the edges of the tank resides atop the concrete and portions remain exposed.

These situations do not represent best management practices, especially if proven treatment agents, such as the ORNL grout formulation, can be injected using the MPI™ system to form a homogeneous monolith of the residual heel material for only a slight increase in cost over tremie concrete placement.

The cost reduction for the MPI™ process to treat heel material vs performing general tank remediation is related to the more definitive information about the type of waste in the tank and its distribution. This information allows better control over the placement of the MPI™ injection lances and most importantly the amount of pumping horsepower needed at the site. The specific strategy to be used for MPI™ treatment of residual tank heel material is addressed in this report.

A brief discussion of the MPI™ process is included along with preliminary results to illustrate the types of waste forms (shallow buried waste, tank sludge) that can be converted into low-conductivity, homogeneous monoliths. This discussion is followed by a presentation of the bench-scale development of the ORNL grout to immobilize the contaminants of concern. Lastly the results from the Duncan, Oklahoma, cold field demonstration are presented, along with the details of the construction required for full-scale implementation for the remediation of GAAT TH-4.

2. GENERAL FEATURES OF THE MPI™ TECHNOLOGY

The MPI™ technology is a general-purpose jet delivery system for the in situ treatment of radiological and/or chemical wastes deposited in underground storage tanks, shallow trenches, or pits. The MPI™ system relies upon the interaction of multiple, high-speed mono-directional jets to cut and mix wastes with various chemical agents. The interaction of two MPI™ injection lances is schematically represented in Fig. 2.1. The mono-directional jetting focuses the energy of the jet stream for more efficient cutting close to the injection point. The equipment used during the injection is greatly simplified because rotation/oscillation of the jetting tools is not needed. Instead of rod rotation, the mixing of the waste occurs as multiple jet streams expand as they travel through the waste. This leads to very large turbulent jet action which helps to uniformly intermix the waste with the treatment agents. Perturbations in the path of the jet stream, such as other jet streams or obstructions (piping in a tank), helps to disperse all the jet streams for more efficient mixing within the tank. The MPI™ jets are located in the best possible position with respect to the geometry of the tank sludge, which is usually thin and spread out along the entire bottom of the tank. The injection operations are performed over a limited thickness to incrementally form thin plates of treatment. The jet nozzles during the cold field demonstration were placed within 1.5 in. of the tank bottom with the jet streams projected horizontally. For shallow tank sludge (2 to 3 ft), the injection tools need not be lifted. For relatively thick sludge (> 3 ft), jetting tools can be lifted remotely because they can be suspended from hoses that can be attached to electrical winches. These winches can be operated from the safety of a support zone that is far removed from the contamination area.

The MPI™ techniques were devised to protect construction workers and capital equipment from becoming contaminated in an As Low As Reasonably Achievable (ALARA) manner. Once this safety requirement was satisfied, emphasis was redirected at making the delivery system as robust and broadly applicable as possible. The constraints of safety and robustness naturally drove the delivery system to be based upon jetting technology. The major capital investment for jetting is related to the cost of the high-

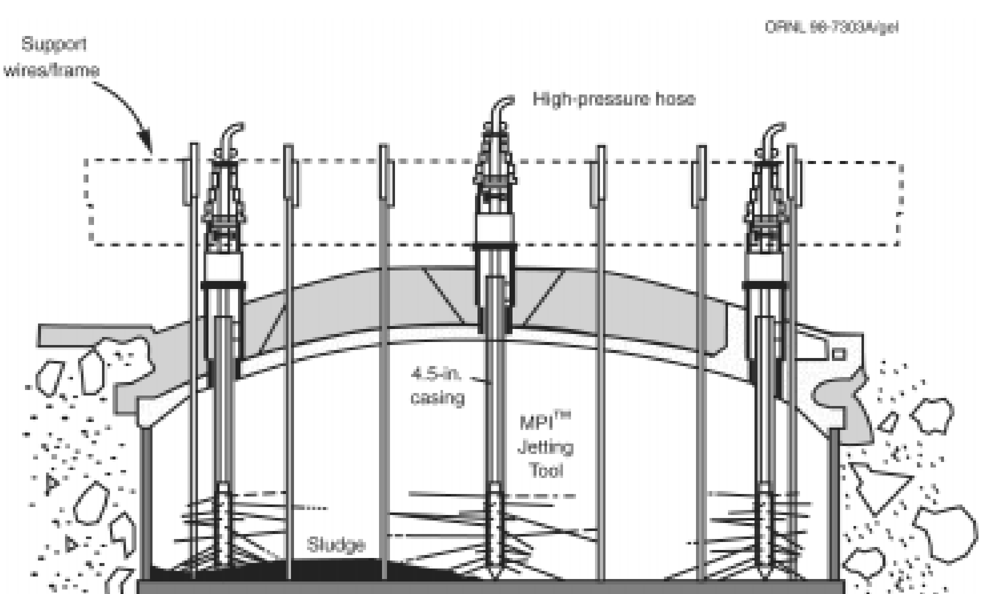

Fig. 2.1. Schematic representation of Multi-Point Injection (MPI™) tools being used to treat tank waste.

pressure pumps and surface piping, which is conventional oil field rental equipment. During the MPI™ process this expensive equipment is located in a support zone. The power generated by the pumps is brought to bear upon treating contamination via very inexpensive and disposal equipment (plastic pipe, hoses, carbide jet nozzles). Therefore, the cost of the remediation can be better predicted since loss of expensive capital equipment as a result of contamination is highly unlikely because the major equipment is always located in an uncontaminated zone.

The following sub-sections discuss the details of the construction steps and the type of equipment utilized for each activity. This information provided a more detailed knowledge of the process for better planning the safe execution of the MPI™ process.

2.1 IMPLEMENTATION OF MPI™ PROCESS

The uniqueness of the MPI™ process is better understood when the technology is discussed in relationship to the sequence of construction activities used to deploy the technology inside of an underground storage tank. The following major construction activities must be accomplished:

1. Core drill small-diameter holes through the roof of the tank (if required). Install plastic casing through the waste and perform visual reconnaissance of tank sludge using borehole cameras (physical appearance, layering, bottom of tank, etc.).

2. Build and install a lifting frame over the roof of the tank and load the jetting tools into each plastic casing. The frame allows remote lifting of the jetting tools for treating thick tank sludge (> 3 ft) and can provide local containment over the injection area.

3. Perform high-speed MPI™ jet treatment of the waste; abandon all jetting tools in place.

2.1.1 Core Drilling Through GAAT Roof

The core drilling of the GAAT roofs and installation of tank riser pipes has been performed repeatedly as part of the GAAT waste retrieval operations. A recent ALARA Workplan (dated August 1997) for the GAAT project has been attached as Appendix A of this report. Many of the other activities listed in this workplan would be required for installation of the estimated eight MPI™ injection lances required for remediation of GAAT TH-4. The MPI™ process only requires 6-in. diameter core holes instead-of the 31-in. diameter hole required for the access by the robotic arm. These smaller diameter holes also permit the use of conventional coring techniques to emplace steel riser pipes through the dome of the tank. These riser pipes permit placement of plastic casing and the MPI™ jetting tools. A T-preventer can also be attached to the riser pipe for connecting the top of each injection hole to a positive air containment system.

2.1.2 Plastic Casing To Penetrate Tank Sludge

A plastic casing was chosen for creating access through the waste for the MPI™ jetting tools, because plastic is relatively strong yet inexpensive (disposable), and readily available. Most importantly the plastic casing can be quickly penetrated by the high speed MPI™ jets. The penetration through the plastic casing wall takes the form of multiple small-diameter holes through the sidewall of the plastic casing, which is shown in the photograph in Fig. 2.2. The holes in the black high-density polyethylene (HDPE) plastic pipe were formed using a highly eccentric five-nozzle jetting tool. The self-penetrating high-speed jets allow treatment of the tank sludge at any elevation within the tank without

Fig. 2.2. Multiple small-diameter holes through HDPE plastic pipe from high-speed jets on MPI™ jetting tool.

predetermining the level of the injection. This can have important implications when treating tank sludge layers of varying consistency. A further advantage of the plastic casing is that it is not destroyed by the MPI™ mono-directional jets. The intact casing helps keep the jetting tools stable when highly eccentric jet arrangements are used, even for hose-suspended jetting tools (which was the case for the jetting tool used in Fig. 2.2). The small-diameter (1/8-in.) holes prevent any backflow of contamination or grout during injection. Therefore, there is no cross-communication between injection holes nor any geyser effect out of any plastic casing.

Installation of the plastic casing can be done using locally available drilling crews who have the appropriate site-access training. This allows for a very cost-efficient jet delivery system, because the expensive high-pressure pumping plant is only brought on site at the last minute, when it is actually needed to treat the tank waste.

A wide variety of plastic materials are applicable for use as disposable casing. The exact type of plastic used depends upon the application. For treating shallow buried waste, HDPE casing has been used (see Fig. 2.2). The installation of the plastic pipe is accomplished via percussion drilling, which is similar to the method currently used at ORNL for installing observation wells. This drilling technique does not generate spoil material, and the percussion equipment can be easily adapted for remote control. HDPE plastic pipe has been installed through 16 ft of miscellaneous, shallow buried waste (including steel drums, construction debris). The HDPE pipe withstood more than 1000 impacts per foot from a 140-lb hammer dropped 30 in. Even after a total of 5000 hammer impacts, the plastic casing was still intact and easily accommodated insertion of the MPI™ jetting tools through the shallow buried waste.

For buried tank sludge it is envisioned that a clear plastic pipe, such as lexan or butyrate, will be used. The clear plastic provides significant improvements to the field QA/QC over the black HDPE pipe. Furthermore, flush butt joints of this clear plastic pipe can be easily formed in the field to produce any required length. Once the clear plastic pipe is installed through the waste, a borehole camera can be placed inside the plastic pipe and used to view the layering of the tank sludge prior to injection. This type of information is useful when positioning the injection tools during treatment of thick sludge. The borehole camera can also be used to view through the bottom of the plastic pipe to assure contact with the tank floor. Integrating site reconnaissance into the remediation technique provides useful information when using MPI™ as an in situ treatment method. Furthermore, the borehole camera and clear plastic pipe can be placed in an appropriate location and be used to view the actual injection as it occurs below the level of the waste. The camera can be used as a visual aid to detect if sedimentation/separation of the sludge from the solidification agents occurs. If sedimentation/separation occurs, appropriate steps can be taken to mitigate this situation prior to the treated waste hardening. In subsequent sections, it will be shown that the ORNL grout formulation can immobilize the RCRA waste and form a diffusion-resistant solid for the radionuclides of interest in Tank TH-4. The grout/sludge mixture consolidates within about 24 h. This weak semisolid mass can be easily remixed by the MPI™ process (if necessary). Therefore, any sedimented solids that fall to the tank floor can be redistributed within the semisolid, which has a much higher solids content than the original untreated sludge. Furthermore, the ORNL grout formulation can easily suspend zeolite-sized particles (0.5 to 0.8 mm) uniformly throughout a relatively thick monolith (40 in.).

2.1.3 MPI™ Jetting Tools

When multiple, mono-directional jets form the basis for the jet delivery system, very simple jetting tools can be used for injection. The jetting tool shown in the sketch in Fig. 2.3 is illustrative of the simplicity of the MPI™ tool used. The multiple jet nozzles are usually directed around a short piece of steel rod to provide 360° of coverage. This jet arrangement allows multiple mono-directional jets to mimic rod rotation (without the need for a drill and workers to be located over the point of injection). The symmetric placement of the nozzles is only appropriate for use within the central portion of the tank sludge (away from the walls of the tank). The jets are usually arranged to develop a net zero jetting force, which creates a very stable jetting tool.

There are many instances in which highly eccentric jetting tools are needed to cover areas only 45 to 180° wide. This is the case when an MPI™ jetting tool is placed next to a tank

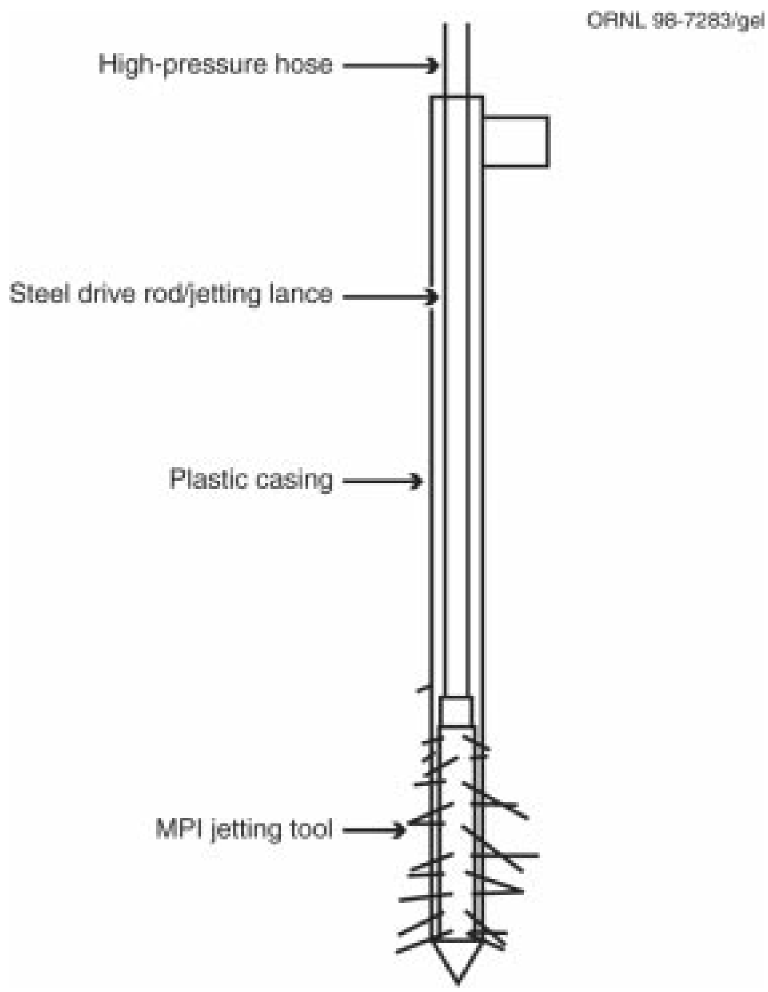

Fig. 2.3. Schematic of MPI™ jetting tool.

wall. It is preferable to only jet inward toward the sludge and not directly toward the tank wall. This placement has two major advantages for treatment of sludge in circular tanks:

- The vector sum of the jetting velocities creates a large vorticity component, which helps to stir the sludge off the tank floor by creating a whirlpool effect. The combination of linear jet turbulence and circular motion helps assure intimate mixing of sludge and solidification agents.

- The placement of jets pointing inward toward the tank sludge totally eliminates the possibility of the jets penetrating into the tank walls. In the case of single-shell steel tanks, the MPI™ jets can never cut through the thick steel plate, even if the jets are directly pointed at the wall (see Section 2.1.7 for discussion of the jet cutting ability of MPI™ process).

The jet force imbalance for the eccentric jetting tools used near the tank sidewall is countered by the reactive force generated by the plastic casing (which is grouted into a steel riser pipe that is embedded in the 6 ft of soil above a typical GAAT Tank). The stability of a highly eccentric jetting tool can be inferred by the hole pattern inscribed into the walls of the plastic pipe. A stable jetting tool only cuts small-diameter holes that reflect the size of the jet nozzle (2 to 3 mm). Conversely, an unstable tool would leave gashes in the plastic pipe as it moves around inside the pipe. The photograph of the HDPE plastic pipe, previously shown in Fig. 2.2, was taken after operating a five-nozzle jetting tool at 11,000 psi at a grout flow rate of 90 gal/min for a period of 60 seconds. It should be noted that the five small holes in the sidewalls of the plastic pipe are perfectly round indicating a stable jetting tool. This photographic documentation confirms the stability of a high-eccentricity MPI™ jetting tool that was hung from a flexible high-pressure hose that was suspended inside HDPE pipe.

2.1.4 Lifting Frame Assembly and Local Site Containment

After all the plastic casings are placed within the tank sludge, a lifting frame is assembled above grade over the roof of the buried tank. This lifting frame is used to facilitate remote lifting of the jetting tools (if required) and also to provide for local containment over the injection area. Fig. 2.4 shows one type of lifting frame that has been used for MPI™ treatment of shallow buried waste. The treated pit was about 16 ft × 16 ft × 16 ft deep, which is similar to the size of GAAT TH-4. The lifting frame not only provides for airborne release control but also prevents release of any liquids into the environment by the sand bag moat that totally surrounds the injection area.

Once the lifting frame is erected, all the jetting tools and any borehole cameras (if required) are attached to the lifting frame via steel wire cables (see cables suspended from frame in Fig. 2.4). The cables are hung from pulleys placed on the frame over each injection point. The steel cables are then run into winches outside the lifting frame. If remotely controlled lifting is needed, the winches can be electrically operated; manually cranked winches can be used if appropriate.

Each of the plastic casings are interconnected via polyvinylchloride (PVC) piping to create a manifold for controlling any gases that are released during active injection (see white PVC piping in Fig. 2.4). The skeletal lifting frame is then covered with heavy clear plastic, and video cameras are mounted to the roof of the frame. This allows remote viewing of the MPI™ injection from the safety of the support zone. The plastic sheet is illustrative of the type of secondary airborne containment that is provided by the MPI™ lifting frame.

Fig. 2.4. Lifting frame used for MPI™ treatment of shallow buried waste.

2.1.5 High-Speed Injection

The previous discussion showed that only low-cost, disposable items are placed into or near the tank contamination zone. The simplicity of the MPI™ process is carried through to the final stage wherein the actual injection of the chemical agents is performed. The MPI™ injection sequence is similar to an upstage grouting process in that treatment of the tank sludge is conducted first at the contact of the tank floor and then at higher stages. Typically, the high-speed injection requires simultaneous activation of from 8 to 32 jets that can be from 2.0 to 3.0 mm in diameter. The mono-directional injection is done in short bursts lasting from 30 to 120 seconds each. After each short burst, other jetting tools can be activated by opening and closing valves in the piping connecting the jetting tools with the high-pressure pumping plant. Also the time in-between activating the jetting tools can be used to slightly re-orient the jetting tool direction prior to commencing the next short burst of mono-directional injection. This too is done remotely. The process of injecting grout into a discrete layer of waste at a time allows precise control over the type of treatment that a particular zone of waste receives.

Once the entire thickness of tank sludge has been treated, the MPI™ jets can be rotated and used to cut apart the plastic casing to eliminate a conduit for surface water to flow into the tank. Thereafter, the tank can be filled using low pressure or gravity-flow delivery systems to pour the remaining solidification agents over the top of the treated sludge. This additional grout can act as a cover over the solidified monolith. At the end of the MPI™ injection the tank shell is fully supported inside, which provides full lateral restraint against any future tank wall movement.

2.1.6 MPI™ General Equipment Requirements

The amount of hydraulic horsepower required for conducting the MPI™ process can vary from about 800 hp up to 2000 hydraulic hp, which was the pump hydraulic hp used during the cold field demonstration (see Section 4). Although this hp is relatively large, it was only used for 8 min and coupled with the MPI™ injection strategy uniformly mixed 32 tons of material in approximately 8-min.

The bulk batching plant used for various MPI™ demonstrations mixes up to 4 tons of solidification agents per min. Halliburton Energy Services, headquartered in Duncan, Oklahoma, has been the pumping services supplier for implementing the MPI™ technology. The major equipment provided by Halliburton included HT-400 high-pressure pumps, a recirculating cement mixer (RCM), bulk storage containers, surface piping and valves, and a data-acquisition system for real-time monitoring of the injection process. The other major advantage of using Halliburton for the pumping services is that they can directly inject a bentonite gel slurry that contains sand. This may have advantages for cutting apart hardened saltcake deposited inside of a tank.

The Halliburton equipment is standard oil-field rental equipment and is available locally throughout the world. This has obvious implications with respect to the pricing structure of MPI™, because the mobilization costs of the equipment are based upon local transport. Furthermore, Halliburton possesses excellent blending facilities that can accurately mix the five-component dry-blend formulation required for the ORNL solidification agent.

2.1.7 Capability of MPI™ Process To Cut Gunite and Steel Plate

There has been some concern expressed about the MPI™ process possibly causing damage to gunite tank walls or even steel walls. The initial deployment of the MPI™ system was for the in situ treatment of shallow buried waste, in which 55-gal steel drums and heavy walled cardboard drums represented a significant part of the waste inventory. Much research was conducted to develop a detailed understanding of how the MPI™ jets cut steel drums. Treatment of shallow buried waste is done with a hose-suspended jetting tool that can efficiently cut through a steel drum in under 60 seconds (see Fig. 2.5). Corroded 55-gal drums no longer provide containment for liquid waste. The drum also tends to deflect rotating jets, which cause the so-called “shadow effect.” This phenomenon leads to untreated, pervious waste in the trench. Conventional jet grouting work conducted at the Idaho National Engineering and Environmental Laboratory (INEEL) required injection holes spacing of 24 in. for treating shallow buried waste. Similar shallow buried waste was converted into a homogeneous monolith (see Section 2.2.2 of this report) using a 60- to 72-in. spacing between the MPI™ injection points. This larger spacing represents a significant increase in efficiency of the delivery system with associated decreases in cost.

Fig. 2.5. Hose-suspended jetting tool cutting through steel drum.

The major differences between using the MPI™ system to treat shallow buried waste vs tank sludge is related mainly to the jetting pressure, which is the most significant factor influencing the ability of a mono-directional jet to cut gunite or steel. For shallow buried waste a jetting pressure of 11,000 psi was used. During tank applications, only half that pressure is currently used (about 6,000 psi). Knowledge of the physical characteristics of the tank sludge will dictate the actual pressure requirements for treatment of sludge, hardpan, or saltcake. This is why site reconnaissance of the tank sludge has been integrated into the MPI™ process.

Another important mechanism that controls the cutting efficiency of a mono-directional jet is the standoff distance. If the jets are more than approximately 20 in. away from the target (55-gal steel drum), then the jet stream has dispersed sufficiently so that the impact energy is not concentrated. No holes develop in the steel drum, even if very long jetting times are used (above 120 s).

The mixing of the tank sludge and solidification agents are greatly enhanced if the MPI™ jetting tools are placed along the perimeter wall of the tank. This location allows a large vortex flow to be generated, which helps erode the sludge from against the tank wall and mix it with the treatment agents. For jetting tools placed near the tank wall, highly eccentric jetting tools are used, which only direct the jet streams inward toward the sludge. No cutting of the tank wall will happen if the jetting tools are only directed toward the sludge. These high-eccentricity jetting tools have been successfully demonstrated (Fig. 2.2) during treatment of shallow buried waste and were also successfully used during the cold field demonstration (see Section 4).

For steel tank walls (¼-in. or greater), the MPI™ jets cannot cut through the steel even when operated at 11,000 psi, with a standoff distance of 1 in., for a duration of 300 s, and jetting cement-based grout. These observations were made in March 1995 after the techniques for the MPI™ process were perfected. Steel plates can be cut if sand and bentonite gel are used as the jetting medium.

Knowledge of the fluid mechanics of jetting allows control over where and when the MPI™ jets cut a material or do not cut. It is an obvious advantage for the MPI™ process to be able to cut hard material, such as saltcake or hardpan, in underground storage tanks. Because the major operating parameter that needs to be changed is merely the pump pressure, the MPI™ system can be converted from a mixing process to a cutting process by merely increasing the pump pressure. Halliburton can easily provide any pressure and flow rate required for operating the MPI™ system. If accelerated cutting of saltcake is needed, Halliburton can also inject a bentonite gel with sand through their pumping equipment and into the MPI™ jetting tools. The decision to cut saltcake can be made while remediation is occurring, because the quantity of saltcake may not be well know until the tank sludge is disturbed. The mixing and cutting potential of the MPI™ process allows extension of the MPI™ system to perform both exhumation of weak tank sludge in addition to in-tank treatment of residual heel material, such as zeolite, hardpan, and saltcake.

2.2 PRELIMINARY TESTS TO FORM HOMOGENOUS LOW-CONDUCTIVITY MONOLITHS

The following sections present photographic documentation on the variety of waste forms that have been converted into low-conductivity monoliths. These earlier successes in the treatment of B-25 box waste and shallow buried waste paved the way for the successful cold demonstration of the MPI™ system inside a simulated underground storage tanks (which is discussed in Sections 4 and 5).

2.2.1 Solidification of B-25 Box Waste

Fig. 2.6. Photograph of shallow buried waste.

The reduction to practice required to prove the ability of the MPI™ system to convert miscellaneous shallow buried waste into low-conductivity monoliths was performed in Duncan, Oklahoma, in March 1995. The data collected during the reduction to practice are documented in U.S. Patent 5,645,377 with other patents pending. The B-25 boxes used during the MPI™ injection were 5 ft wide by 10 ft long by 3 ft deep and filled with shallow buried waste similar to that pictured in Fig. 2.6. Two 4-in.-diameter PVC plastic casings were installed within the waste at about a 5-ft spacing along the center line of the waste. Because the MPI™ system treats waste in an incremental, plate-like fashion it was of interest to measure the hydraulic conductivity of the solidified waste over very thin intervals, in the range of 3 to 6 in. Furthermore, partially saturated hydraulic conductivity measurements on cemented waste required an appropriate interpretation technique. The methodology developed at the University of Guelph, Toronto, Canada, was selected for use, along with their Guelph permeameter to perform the actual flow measurements on the cemented waste. The conductivity tests were conducted in three core holes and involved coring through the solidified waste for a limited distance, performing a conductivity test (typically 2-day test), and then coring a deeper hole into the waste and performing another conductivity test. Although this incremental procedure is very time-consuming, it allows a specific zone of solidified waste to be tested.

Conductivity tests were performed at the bottom, middle, and top of each core hole. The measured data for the nine conductivity tests performed on the B-25 box monolith are listed in Table 2.1 (level a corresponds to the uppermost level, level b is intermediate in depth, and level c is near the bottom of the monolith). The first tests were typically done at about a 19 in. depth. The data in Table 2.1 indicate that at two locations (32a, 33a) the conductivity was around 1×10^{-6} cm/s. The conductivity measured at borehole location 31a was greater (more pervious). The reason for this higher measurement is related to stopping the MPI™ injection. The other conductivity data listed in Table 2.1 indicate that the monolith was of relatively low conductivity with 8 of the 9 conductivity values being between 1 to 10×10^{-7} cm/s. Only ordinary cement grout was used with a water to cement ratio of 1:1.

The low values of hydraulic conductivity are further supported by the visual appearance of the internal core structure of the dissected solidified waste. A concrete saw was used to cut the block along the transverse direction (3-ft × 5-ft cross section) about 1/3 of the way from the edge (3 ft in from edge of treatment).

The photograph of the dissected block, shown in Fig. 2.7 reveals two well-cemented blocks of waste. The portion of the block on the left side of the photograph represents the interior of the B-25 box monolith. The overall appearance of the inside and outside of the block is similar to that of cast concrete.

Table 2.1. Hydraulic conductivity values measured on municipal waste solidified using the multi-point injection (MPI™) process in Tank 3, Duncan, Oklahoma (1994)

Hole ID	Test depth (in.)	Hydraulic conductivity (cm/s)
31a	19	1.9×10^{-4}
31b	26	1.0×10^{-6}
31c	32	4.2×10^{-7}
32a	19	1.7×10^{-6}
32b	27	1.3×10^{-6}
32c	31	6.2×10^{-7}
33a	16	1.4×10^{-6}
33b	23	1.2×10^{-7}
33c	30	2.7×10^{-6}

2.2.2 Shallow Buried Waste in Pits

The solidification performed inside the steel B-25 boxes has an advantage in that the steel shell of the box helps keep all the jetting (mixing) energy confined inside the box. This is also the situation for underground storage tanks, such as the GAAT. For shallow buried waste, the DOE (Oak Ridge Y-12 Plant) was interested in examining the capability of the MPI™ process to homogenize shallow buried waste deposited into pits dug in the ground. Shallow pits 8 ft × 10 ft × 4 ft deep were filled with the highly containerized waste previously pictured in Fig. 2.6. Several MPI™ injectors were used to inject an ordinary water cement grout (W:C = 1:1) at an inter-axis spacing in the range of 60 to 72 in. After the injection, core samples, constant-head Guelph permeameter tests, and exhumation of the solidified pit waste were performed. Most of the conductivity data collected indicated that the MPI™ system transformed the buried waste into a low-conductivity (1 to 10 × 10^{-7} cm/s) monolith. The observation that the waste pit was turned into a monolith is confirmed by the excavation of the treated waste. It is obvious from the visual inspection of the photograph in Fig. 2.8, that the waste pictured in Fig. 2.6 was converted into a large concrete block.

Fig. 2.7. Dissected block of cemented shallow buried waste.

Fig. 2.8. Excavated monolith of cemented buried waste.

3. 1996 BENCH-SCALE DEVELOPMENT OF GROUTS FOR GAAT TANK SLUDGE

The best management practices for in-tank treatment of tank sludge requires an integrated approach to develop appropriate solidification agents that can be safely delivered and mixed uniformly with sludge in the tank. It is unacceptable to formulate grouts that can immobilize the sludge contaminants of concern and then merely pour them atop the tank sludge with little quality control to assure intimate mixing. Deploying a robust injection system to distribute grouts that are incapable of immobilizing the tank sludge is also a poor management practice.

The bench-scale study at ORNL to develop GAAT tank sludge treatment agents was a collaborative effort between ORNL and GES, developers of the MPI™ process. ORNL provided its expertise and understanding on formulating robust grouts for treating tank sludge. GES provided its knowledge of the MPI™ process to help assure that the grout and delivery system were compatible and capable of producing a homogeneous monolith of treated tank sludge. The major questions answered during the ORNL bench-scale study focused on whether a slag–fly ash grout could be used to treat a GAAT tank surrogate to

- Produce leach-resistant treatment for radionuclides (especially, strontium and cesium),
- Stabilize the RCRA metals (mercury, lead, chromium) within TCLP limits,
- Uniformly suspend zeolite-sized particles (0.5- to 0.8-mm) within a 2-ft column of liquid grout to help assure formation of uniform, monolithic treatment,
- Produce little or no free water upon setting, and
- Result in compression strengths that would support the tank shell yet leave treated waste inside the tank that could be exhumed in the future (if required).

Issues related to the pumpability of the slag–fly ash grout could only be partially resolved during the ORNL bench-scale tests because of the limitations of the laboratory mixing equipment. Although most of the slag and fly ash were added to the surrogates in the grout water, a small portion of the slag and fly ash had to be added to the surrogates as dry material. This concept was to increase the solids content of the treated sludge as much as possible to provide the greatest treatment possible. It was planned to mechanically stow the dry slag and fly ash onto the sludge through openings in the top of the tank. This two-step delivery of the solidification agents complicates the remediation of the tank sludge. However, it was later shown that the oil-field grout-mixing equipment provided by Halliburton Energy Services could mix and deliver all dry-blend components that were required in the ORNL grout formulation. Halliburton’s equipment eliminated the need for the mechanical stowing of slag and fly ash and thus simplified the sludge treatment. This situation points to the difficulty of extending bench-scale solidification studies to full-scale field operations.

The surrogate used during the bench-scale tests, along with the grout formulation developed and results from the TCLP and ANS 16.1 diffusion tests are summarized below. A more comprehensive discussion is presented in the ORNL Technical Memoranda ORNL/TM-13389 written by Spence and Kauschinger (1997).

3.1 GAAT SURROGATE

A GAAT sludge surrogate for bench-scale testing was developed based upon the characterization data reports and measured sludge mass in GAAT tanks W-3, W-4, W-5, W-6, W-7, W-8, W-9, W-10, and TH-4. The weighted average composition of tank sludge listed in Table 3.1 was obtained by summing the products of the concentrations for each tank and obtaining a weighting factor. The weighted average composition was the basis for the proposed surrogate GAAT sludge. The “bad actors” referred to in Table 3.1 are those compounds that have an affect on the setting and leach-resistance properties of the grouted waste. These “bad actors” include RCRA components, sulfates, phosphates, carbonates, and halides. The tank sludges have proven characteristically hazardous by TCLP for mercury only, so mercury was included in the surrogate. Lead and chromium were also included in the surrogate because of their high concentrations relative to the TCLP standards. The mercury was added as a very mobile salt ($HgCl_2$), the lead as PbO, and the chromium(VI) as $Na_2Cr_2O_7$.

Numerical analysis was performed to estimate the potential waste loading attributable to treating the mass of sludge deposited in each gunite tank. Most mass balance calculations indicated that the waste loading would be low, usually less than 15% by weight. However, for Tank TH-4 there was only 4 ft of freeboard above the estimated 30 in. of sludge (MAC Technical Services Co. 1996). This freeboard restriction requires mixing the TH-4 sludge at a waste loading of about 35%. Therefore, all surrogate testing was performed near this target value. Also the primary constituents of the TH-4 sludge were uranium and thorium. Therefore, the GAAT surrogate contained uranyl nitrate and thorium nitrate, which created a large excess of nitrate in the surrogate compared with the nitrate measured in the tank sludge. Table 3.2 lists the elemental and ionic composition of this surrogate and compares the surrogate concentrations with the weighted average and maximum tank average concentrations.

3.2 ORNL GAAT GROUT DEVELOPMENT

Based upon previous experience with solidifying the tank sludges, a four-component grout was selected for the GAAT sludge. The dry components consisted of granulated blast furnace slag, fly ash, illite clay (Indian Red Pottery Clay: IRPC), and Portland Type I Cement. A short description of the selection of dry blend additives is attached in Appendix B of this report.

In order to create a uniform monolith of Gunite tank sludge, it was deemed important that the solidification agent be able to suspend certain sized particles. Zeolite particle sizes in the range of 0.5 mm to 0.85 mm were chosen because zeolite and zeolite-type particulates commonly remain as residual contamination (heel) after exhumation of tank sludges. It is common knowledge that bentonite has very good gel strength characteristics and is a fluid-loss control agent. However, bentonite also can change the rheology of the grout significantly, which may cause problems with the pumpability of the grout. Several different tests were conducted using various percentages of bentonite clay, either in dry form or pre-hydrated with the grout mix water. The key to keeping zeolite-sized particles uniformly suspended in a fluid grout mixture was related to pre-hydration of the bentonite clay prior to mixing with the other dry materials. Grout mix water when prepared as a 3% bentonite gel has sufficient thixotropic properties to uniformly suspend a 2-ft high sand/grout mixture column containing 35% sand particles (0.50 to 0.85 mm). The 3% gel corresponded to 3% dry bentonite when it is added to the other components of the best grout formulation developed during the ORNL bench-scale study (see Table 3.3). This grout formulation was used during the sensitivity testing with the GAAT tank surrogate sludge used during the 1996 studies.

Table 3.1. Summary of surrogate GAAT sludge design

Compound	Weighted average	Uncorrected surrogate: weighted average + maximum bad actors	Target surrogate after correction
Concentration in wet sludge (mg/kg)			
$HgCl_2$	177	305	281
PbO	1,032	3,749	3,458
$Al(OH)_3$	35,809	35,809	33,029
$Ca(OH)_3$	17,305	17,305	15,962
Fe_2O_3	10,094	10,094	9,310
K_2CO_3	4,209	4,209	3,882
$Mg(OH)_2$	5,455	5,455	5,031
NaOH	4,820	0	0
$Th(NO_3)_4{\cdot}4H_2O$	56,649	56,649	52,252
$UO_2(NO_3)_2{\cdot}6H_2O$	83,657	83,657	77,162
$Na_2Cr_2O_7$	1,140	3,435	3,168
NaCl	1,258	4,530	4,178
NaF	3,562	13,135	12,115
Na_3PO_4	4,129	10,927	10,079
Na_2SO_4	7,643	15,822	14,593
Na_2CO_3	38,585	38,585	35,589
TPB[a]	7,816	12,385	11,424
Weight percentage			
Solids	28.3	31.6	29.2
Water	70.8	70.8	70.8
Mass balance	99.1	102.4	100.0
Unknown	0.9	12.4	0.0

[a]Tributyl phosphate, used to simulate the total organic carbon + 100 ppm calcium oxalate.

Table 3.2. Summary of target surrogate elemental and ionic concentrations compared with the weighted average and the maximum tank average concentrations

Species	Target surrogate concentration	Ration of surrogate to weighted average	Radio of surrogate to maximum tank average
	Cations (mg/kg)		
Hg	208	1.59	0.92
Pb	3,210	3.35	0.92
Al	11,424	0.92	0.37
Ca	8,634	0.92	0.30
Fe	6,512	0.92	0.37
K	3,002	0.92	0.30
Mg	2,082	0.92	0.28
Na	35,001	1.33	0.71
Th	21,960	0.92	0.14
UO_2	41,495	0.92	0.30
Subtotal	**133,528**	**1.02**	**0.30**
	Anions (mg/kg)		
Cr_2O_7	2,612	2.78	0.92
Chloride	2,535	3.32	0.92
Fluoride	5,482	3.40	0.92
Nitrate	42,528	3.38	1.18
Phosphate	5,839	2.44	0.92
Sulfate	9,869	1.91	0.92
Carbonate	22,454	0.92	0.46
Hydroxides (estimated)	36,155	N/A	N/A
Subtotal	**127,474**	**2.67**	**1.13**
Total	**261,001**	**1.46**	**0.47**

Table 3.3. Compilation of constituents required in ORNL solidification formulation

Material type in monolith	Dry blend grout (%)	Grout (lb/gal)	Total material tank TH-4 (lb)	Dry blend tank TH-4 (%)	ORNL formula tank TH-4 (%)
I. Injected grout dry blend					
Slag	35	2.2	16,760	25.2	9.3
Fly ash	35	2.1	15,829	23.8	8.8
Cement	17	1.0	7,915	11.9	4.4
IRPC	10	0.6	4,656	7.0	2.6
Bentonite	3	0.2	1,397	2.1	0.8
Dry blend in grout	100	6.1	46,557		
II. Dry blend stowed into tank					
Slag stowed	50		10,000	15.0	5.5
Fly ash stowed	50		10,000	15.0	5.5
Total dry blend in tank TH-4			66,556	100.0	36.9
III. Injected grout water					
		6.0	46,556		25.8
Total grout weight		12.1			
IV. Surrogate quantities					
Wet sludge			62,227		34.5
Supernatant (6 in. in tank TH-4)			5,160		2.8
Total weight of monolith (lb)			180,499		100
Total injection time (min)			17.3		
Total volume grout injected (gal)			7700		

When the grout formula listed in Table 3.3 is intermixed with the GAAT tank surrogate at 35% waste loading, the breakdown of the individual components in the ORNL monolith is summarized in the right-most column of Table 3.3. The total amount of slag and fly ash injected with the grout and added by stowing are about equal, totaling nearly 15% for the slag and 15% for the fly ash. The composition of the individual components in the grout surrogate mixture in Table 3.3 indicate that about 10% of the slag and fly ash were added with the jetting slurry and the remaining 5% was introduced as dry stowed material. Even though the grout injection water, wet sludge, and supernatant in the mixture accounted for nearly 63% of the total weight, the mixture consolidated to a soft mass within 12 h. Just as important, there was no free water released from the mixture. Also the consolidated mass does not start to harden for about 48 h. This allowed time for sieving sand particles (zeolite-sized) from the mixture for purposes of examining the particle distribution over a 2-ft column. The measurements proved that the grout formulation could uniformly suspend the particles over a 2-ft thickness and keep them suspended until the mixture achieved a soft, semisolid state. This observation also held true for the much larger monolith formed during the cold field demonstrations (15 ft diameter × 40 in. thick with a total weight of 32 tons).

3.3 GAAT GROUT SENSITIVITY TESTING

The grout/surrogate mixture presented in Table 3.3 (right-most column) is analogous to the constituents that would be in the monolith created in GAAT TH-4. It was of interest to examine the strength, leachability, and diffusion characteristics of this mixture, along with potential variations in the grout injection process. This sensitivity testing produced a total of five grout formulations that were subjected to the aforementioned tests. Two other formulations were tested to examine the effect of the minimum and maximum water expected within the GAAT tank farm. This water variation was to examine an extreme of water conditions in the entire GAAT tank farm.

The variation of the solidification agents, wet sludge content, and quantity of supernatant examined during the sensitivity study are summarized in Table 3.4. The wet sludge containing the contaminants of concern varied from about 32% for sample 3 up to a maximum of 37% waste loading for sample 2. The sample with the highest waste loading (37%) had the lowest percentage of solidification agents (32.2%), whereas the sample with the lowest waste loading had the greatest amount of solidification agents (41.5%) (i.e., approximately 10% variation in the total amount of solidification agents in the grout/surrogate mixture).

3.3.1 Compression Strength

The results from measuring the physical properties for each of the seven grout/GAAT surrogate samples are contained in Table 3.5. In general, the 28-day unconfined compression strengths varied from a low of 177 psi to a maximum of 496 psi. These monolith strengths are sufficient to support any external lateral

Table 3.4. Grout compositions for testing sensitivity of the in situ grout formulation for the GAAT sludges to variations in composition

Component		Composition in the final grout (wt %)				
		1[a]	2	3	4	5
Jetting slurry	IRPC	2.6	2.3	2.9	2.7	2.5
	Bentonite[b]	0.8	0.7	0.9	0.8	0.7
	Fly ash	8.8	7.7	9.9	9.1	8.4
	Slag	9.3	8.1	10.5	7.9	10.9
	Cement	4.4	3.8	4.9	3.7	5.1
	Injection water	25.8	27.7	23.9	26.8	24.8
Preadded additives[c]	Fly ash	5.5	4.8	6.2	5.7	5.3
	Slag	5.5	4.8	6.2	4.7	6.5
Surrogate tank contents	Wet sludge	34.5	37.0	31.9	35.7	33.1
	Supernate water	2.9	3.1	2.6	3.0	2.7
Total		100.0	100.0	100.0	100.0	100.0

[a]Standard grout selected for sensitivity testing.
[b]Prehydrated in mixing water before mixing with other dry blend components.
[c]Stabilizing additives dumped on surrogate tank contents before grout mixing.

Table 3.5. Results of performance testing of sensitivity of in situ GAAT grouts

Surrogate	Grout	Fann™ reading at 600 rpm[a]	Mixture density (g/mL)	Volume ratio of grout to sludge[b]	28-day free water (vol %)	28-day unconfined compressive strength (psi)				
						Sample 1	Sample 2	Sample 3	Average	Standard deviation
Standard	1	138	1.29	2.75	0.0	449	332	513	432	75
	2	75	1.27	2.61	0.0	155	117	131	134	16
	3	231	1.35	2.84	0.0	508	511	534	517	12
	4	114	1.26	2.72	0.0	142	212	177	177	29
	5	169	1.33	2.78	0.0	504	474	510	496	16
Maximum water	1	143	1.20	2.94	0.0	218	218	206	218	9
Minimum water	1	163	1.39	2.54	0.0	514	467	375	452	58

[a]Fann™ viscometer reading of the jetting slurry at a rotation rate of 600 rpm.
[b]Calculated from the measured wet surrogate sludge density of 1.22 g/mL, the measured grout density, and the wet sludge loading in the grout (see Table 3.4).

loading applied to the tank shell. Furthermore, these material strengths are sufficiently low that treated waste could be easily exhumed using a conventional backhoe or clamshell bucket.

3.3.2 Leachability and Diffusion Characteristics

The data measured from TCLP and ANS 16.1 diffusion tests are summarized in Table 3.6. It is evident from Table 3.6 that untreated surrogate was characteristically hazardous for both mercury (8.38 mg/L) and chromium (46.4 mg/L) by TCLP. Yet all seven grout formulations listed in Table 3.4 were able to successfully treat the wet sludge to meet land disposal restriction (LDR) and universal treatment standards (UTS) standards. The treated GAAT surrogate sludge had TCLP extract concentrations that were more than a factor of 60,000, 30, and 100 lower for mercury, lead, and chromium, respectively, when compared with the untreated surrogate sludge. In addition, the TCLP extract concentration of uranium decreased from 4,198 to <0.089 mg/L, a reduction factor of more than 40,000. The extract uranium concentration is undoubtedly related to the final extract pH of 10 for the grout/surrogate mixtures. Lastly, the leachability indices determined from ANS 16.1 diffusion tests are listed in Table 3.6. The average leachability index for strontium is above 10, while the leachability index for cesium was an order of magnitude higher. The leachability indices are the negative logarithm of the effective diffusion coefficient. For instance a diffusion coefficient of 1×10^{-10} cm^2/s has a leachability index of 10.

Table 3.6. Results of leach testing of sensitivity of in situ GAAT grouts

Surrogate	Grout	TCLP extract concentration (mg/L)[a]				Leachability index	
		Hg	Pb	Cr	U	^{85}Sr[b]	^{137}Cs[c]
Standard	1	0.00007	<0.009	0.023	<0.089	10.4	11.1
	2	0.00005	<0.009	0.07	<0.089	10.3	11.1
	3	<0.00001	<0.009	0.13	<0.089	10.6	11.6
	4	0.00004	<0.009	0.108	<0.089	10.7	11.3
	5	0.00006	<0.009	0.092	<0.089	10.5	11.4
Maximum water	1	0.00012	<0.009	0.079	<0.089	10.4	10.9
Minimum water	1	<0.00001	<0.009	0.39	<0.089	10.3	11.2
Wet surrogate sludge		8.38	0.275	46.4	4,198		
TCLP characteristics limit		0.2	5	5	NA[d]		
TCLP LDR limit		0.2	5	5	NA		
TCLP UTS limit		0.025	0.37	0.86	NA		

[a]All of the grout samples were extracted with TCLP extraction fluid number 1, and the final extract pH was about 10; the wet surrogate sludge was extracted with TCLP fluid number 2, and the final extract pH was about 6.

[b]This index was measured to be 9.5 for the standard MVST grout and 11.9 for the MVST grout with crystalline silicotitanate (CST) replacing IRPC.

[c]This index was measured to be 9.9 for the standard MVST grout and 11.4 for the MVST grout with CST replacing IRPC.

[d]Not applicable.

Note: TCLP = Toxicity Characteristics Leaching Procedure; MVST = Melton Valley Storage Tanks; IRPC = Indian Red Pottery Clay.

3.4 CONCLUSIONS FROM BENCH-SCALE STUDY

It is evident from the bench-scale studies that the ORNL slag–fly ash grout successfully stabilized GAAT tank surrogate at wet sludge loadings of 37% or less. The treated monoliths' strength (200 to 500 psi) is sufficiently strong to support the tank walls yet allow future exhumation of the treated waste, if necessary. The grout selected for sensitivity testing decreased the concentrations of mercury, lead, and chromium in the TCLP extract by orders of magnitude, which produced waste forms that were acceptable for land disposal (leachates with RCRA component concentrations significantly below LDR or UTS). Despite the high water content, these grouts exhibited excellent diffusion resistance, with strontium-85 and cesium-137 leachability indices in excess of 10. None of the properties of this grout proved sensitive to the variations in grout and surrogate sludge compositions tested, except the pumpability of the jetting slurry. The grout resisted settling of zeolite-sized particles.

3.4.1 Grout Formulation Used During Full-Scale Cold Demonstration

Direct injection of all the dry solidification agents in the ORNL formulation (Table 3.3, second column from the right) requires the mixing of the dry blend components given in Table 3.7.

Table 3.7. Dry blend solidification agents used in ORNL formulation

Agent	Percentage
Granulated blast furnace slag	40
Class F fly ash	40
Indian Red Pottery Clay	7
Portland Type I cement	10
Bentonite (prehydrated with grout mixing water)	3

The formulation in Table 3.7 for the slag and fly ash was obtained by adding the contributions from the jetting slurry and dry material added by stowing. A one-to-one ratio of slag to fly ash was established to make blending of bulk material easier for field applications. The ORNL formulation requires a water-to-solids ratio of the grout to be about 0.70, as indicated by the ratio of the injected grout water (25.8%) to total dry solidification agents (36.9%) listed in Table 3.3. It is reemphasized here that the bench-scale mixing equipment could not blend this grout in the lab because of the extreme viscous nature of the grout. However, Halliburton's full-scale oil-field equipment was able to mix this very viscous grout.

The percentages of the dry-blend material given in Table 3.7 were used to make the grout injected during the cold field demonstration of the MPI™ process. However, the water-to-(dry-blend)-solid ratio (W:S) was reduced to about 0.48 by the addition of a minor amount (0.4%) of a dispersant recommended by Halliburton's oil-field cementing services engineers. For the same conditions used to calculate the treated sludge constituents listed in Table 3.3, the cold field demonstration grout was higher in solids (41.1% vs 36.9% and required lower injected grout water (20.5% vs 25.8%). Obviously, both are more attractive grout characteristics especially if the grout can be pumped in the field.

4. FULL-SCALE COLD FIELD TEST DEMONSTRATION OF MPI™: TRIAL FIELD DETAILS

The cold field demonstration of the application of the MPI™ technology for in situ disposal of tank waste was conducted in December 1997 at the field test facility of Halliburton Energy Services, in Duncan, Oklahoma. The major performance criteria established for determining a successful demonstration were the following:

1. Pump the ORNL grout formulation under high pressure.

2. Use the MPI™ process to homogeneously intermix the ORNL grout with a physical surrogate, with both cohesive strength (clay pods) and rapid sedimentation properties (uniform sand).

3. The near full-scale monolith should have the percent constituents similar to those of the ORNL bench-scale study for tank TH-4 (see Table 3.3).

4. Create a homogeneous monolith.

The following discussion of the cold field demonstration will reflect all the field activities anticipated being used in the MPI™ system to treat actual GAAT TH-4 sludge. The equipment layout, injection procedures, and workers' location will be very similar at ORNL. The results and observations from near-full-scale mock-up of the MPI™ system also allow health physicists to better evaluate potential exposure paths and make suggestions for improvements to the field operations specialists. The only major activities not demonstrated during the cold test were the drilling of holes into the dome of the GAAT tank and the insertion of the plastic casing and jetting tools into the sludge. The issues related to conducting these site-preparation activities for the actual remediation of tank TH-4 are discussed in Section 7.

The following subsections discuss the logistics and site setup used during the cold field demonstration. Section 5 of this report presents a summary of the analytical results, which documented the formation of the homogeneous monolith during the trial field operation.

4.1 SITE LOGISTICS: EQUIPMENT AND TEST TANK

Five major pieces of equipment were used during the MPI™ cold field demonstration, as illustrated in the equipment lay-down plan view in Fig. 4.1. The grout-mixing operation consisted of the three pieces of equipment (water tank, bulk cement storage, RCM) shown on the righthand side of the figure. The total volume of grout prepared to perform the demonstration was approximately 4000 gal. All grout was prepared prior to injection. This allowed very precise control over the final density of the grout (14.5 lb_m/gal), which was measured using nuclear densometers.

The grout flowed from the RCM through a manifold that supplied the intake side of three tractor-mounted twin HT-400 high-pressure oil-field pumps, which were each driven by a Cummins V-12 diesel engine. The HT-400 pumps were arranged in parallel so that up to 6 pumps could be simultaneously used to pump grout at 500 gal/min and 6,000 psi.

The test tank was located about 200 ft away from the equipment lay-down area. The pressurized grout was delivered to the test tank via high-pressure hard-line piping. For safety in viewing the high-pressure

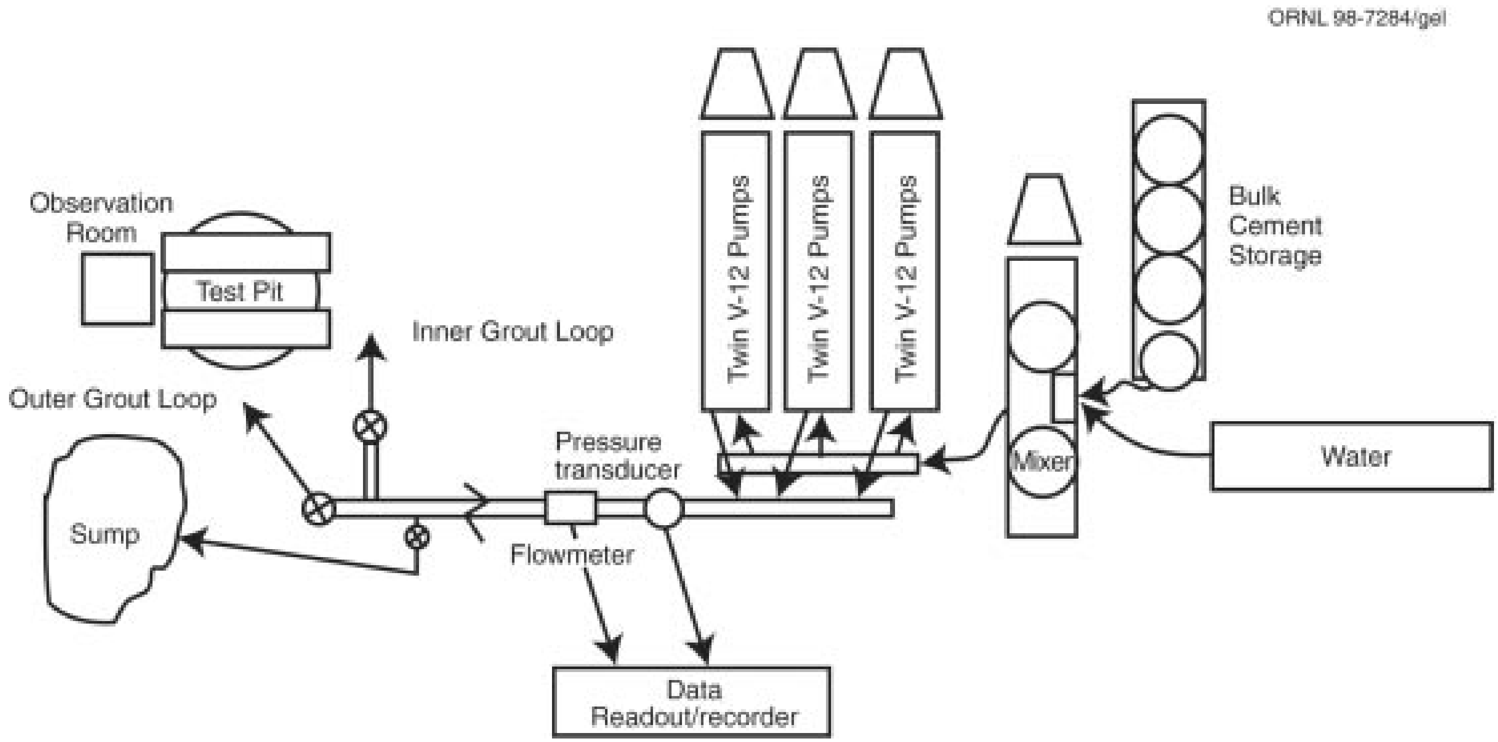

Fig. 4.1. Layout of in situ grouting equipment used in cold field demonstration.

grout injection, an observation room was positioned close to the edge of the open-top test tank. The photograph in Fig. 4.2 presents a general view of the test setup within the tank (note Halliburton's equipment in the background). All plastic pipe and steel jetting rods were supported above the top of the tank to simulate the points of fixity under actual site conditions (see close-up photograph in Fig. 4.3 depicting vertical steel stanchions driven into the ground and steel bands used to secure PVC casings and jetting rods).

A 15-ft-diameter × 8-ft-deep tank was used as the test container for performing the cold demonstration. The bottom of the tank floor, shown in the illustration in Fig. 4.4, was lined with 6 in. of 3,000 psi concrete. Nine pieces of PVC plastic pipe were arranged within the tank and later used as entry points for the MPI™ jetting tools. Once the PVC casings were in place approximately 11 tons (183 cubic ft) of a uniformly fine Ottawa sand (20 to 40 mesh) was spread over the bottom of the tank. The average sand thickness spread across the tank floor was about 12 in.

Fig. 4.2. Test setup used in the cold field demonstrations at the Halliburton test facilities.

4.2 PHYSICAL SURROGATE: FINE SAND AND COHESIVE CLAY PODS

Fine sand was used as the physical surrogate for zeolite-sized particles. The sand also served as a tracer, which allowed determination of how uniformly the MPI™ system could intermix the slag–fly ash grout with the sand. The grain-size distribution of the zeolite (sand) surrogate used during the demonstration is displayed in Fig. 4.5. Note that 100% of the sand is coarser than an ASTM 100-mesh sieve. Once the monolith was formed four foot-long steel tubes were driven through the entire thickness of the monolith to retrieve a continuous sample. The steel tubes were cut into approximately 6-in.-long pieces. The sand was washed over an ASTM 100-mesh sieve, which would capture the sand but allow all traces of the slag–fly ash grout to be washed through the sieve. Laboratory work at ORNL indicated that all the grout could be removed from the sand if the mechanical sieving were performed within 24 h of mixing the grout and sand. Obviously, as time increases there is a tendency for the sand and grout to harden, which makes it more difficult to physically separate the two materials.

Fig. 4.3. Close-up of vertical steel stanchions used to secure the PVC casings and jetting tools.

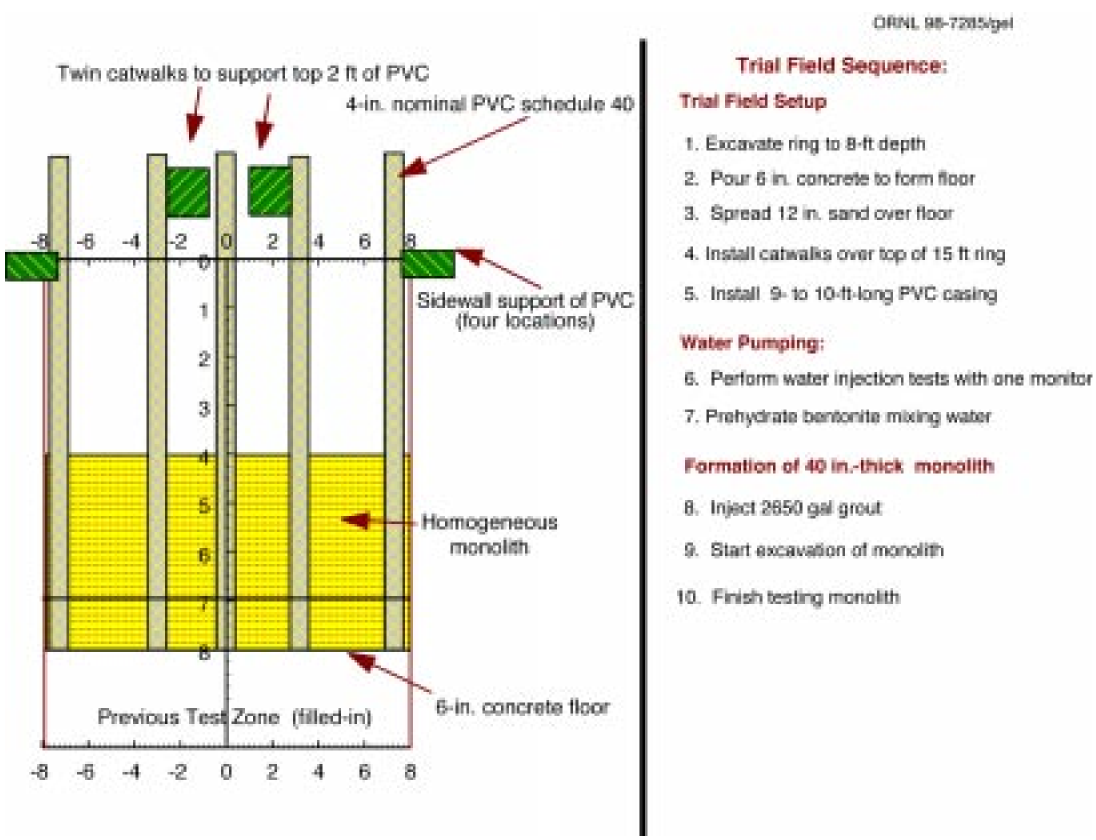

Fig. 4.4. Elevation view of 15-ft-diameter steel ring, used in the cold field demonstration at the Halliburton test facilities.

ORNL 98-7286/gel

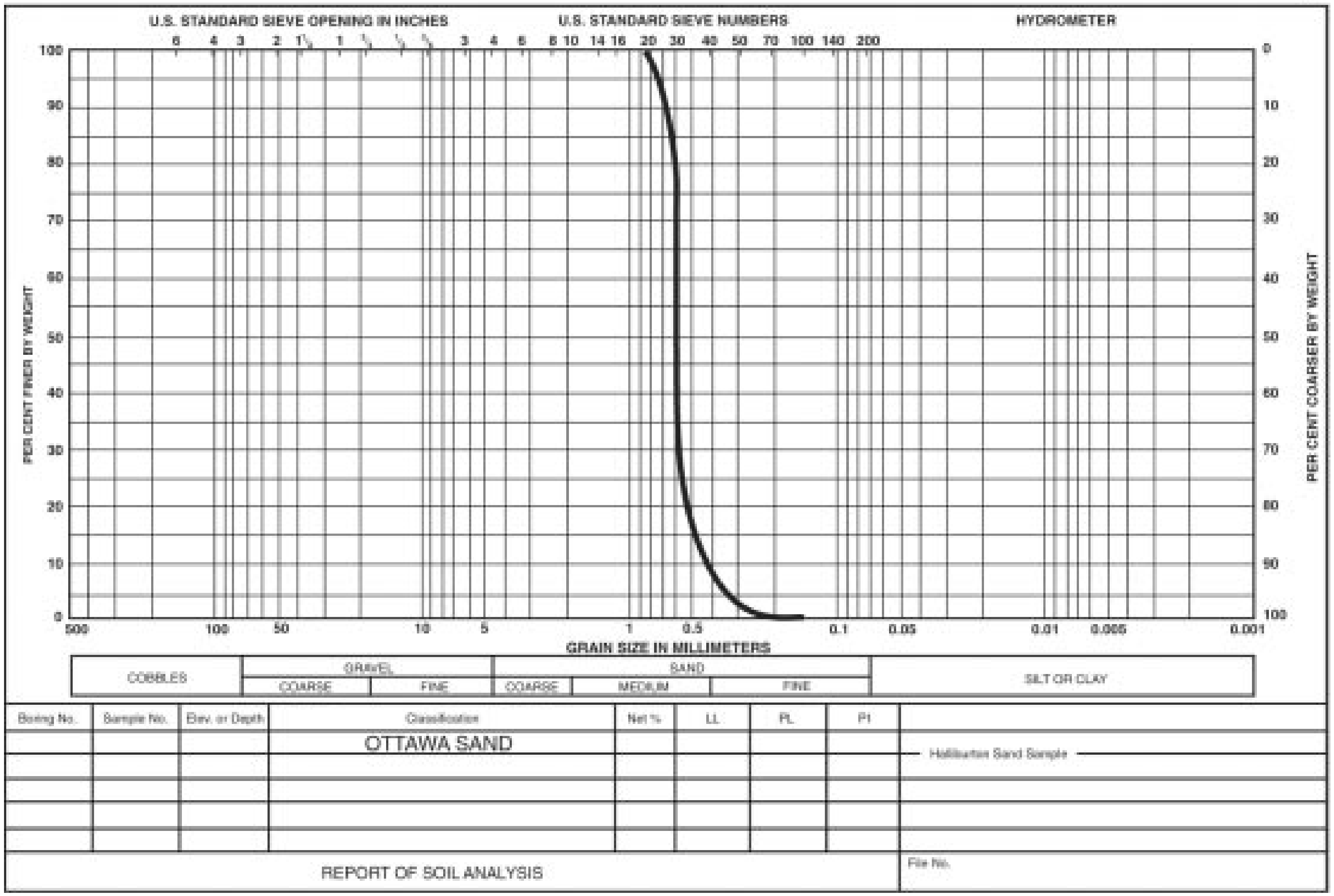

Fig. 4.5. Particle-size distribution for Ottawa sand used in the cold field demonstrations at the Halliburton test facilities.

Actual samples of waste taken from GAAT TH-4 indicate that the sludge appears to have some cohesive nature. As an attempt to include cohesive-type sludge simulants in the cold field demonstration, a clay–water surrogate was formulated that had physical properties (gravimetric water content, cohesive consistency) similar to those of the sludge in GAAT TH-4. The clay–water–dye tracer used as a cohesive simulant in the cold test had the following properties:

Indian Red Clay	=	93 lb_m
Water	=	60 lb_m
¾ in. stone	=	11 lb_m
Red dye	=	2.3 lb_m

Representatives from Hanford wanted to use a more cohesive surrogate and decided to add an additional 52 lb of clay to the above recipe. The photograph in Fig. 4.6 is illustrative of the consistency and placement of the Hanford clay pod near the center of the test tank. Laboratory vane shear tests on the Hanford mixture produced shear strength values of around 15,000 dynes per cm^2. The location of the five red dye tracer pods is shown in Fig. 4.7. The total volume of the five clay pods was about 10 ft^3 and represented a total of about 1000 pounds of cohesive surrogate.

4.3 TRAINING

None of the Halliburton operators had ever performed MPI™ injection. The use of the high-pressure pumps for the MPI™ system was very different from the normal operations in oil-field hydrofracturing or conventional jet grouting. MPI™ requires a very rapid increase in pump pressure and flow rate followed by a rapid decrease after about 40 s. The pressure–time curves nearly resemble an impulse function. Therefore, a limited amount of training had to be conducted to enable the crew to operate the

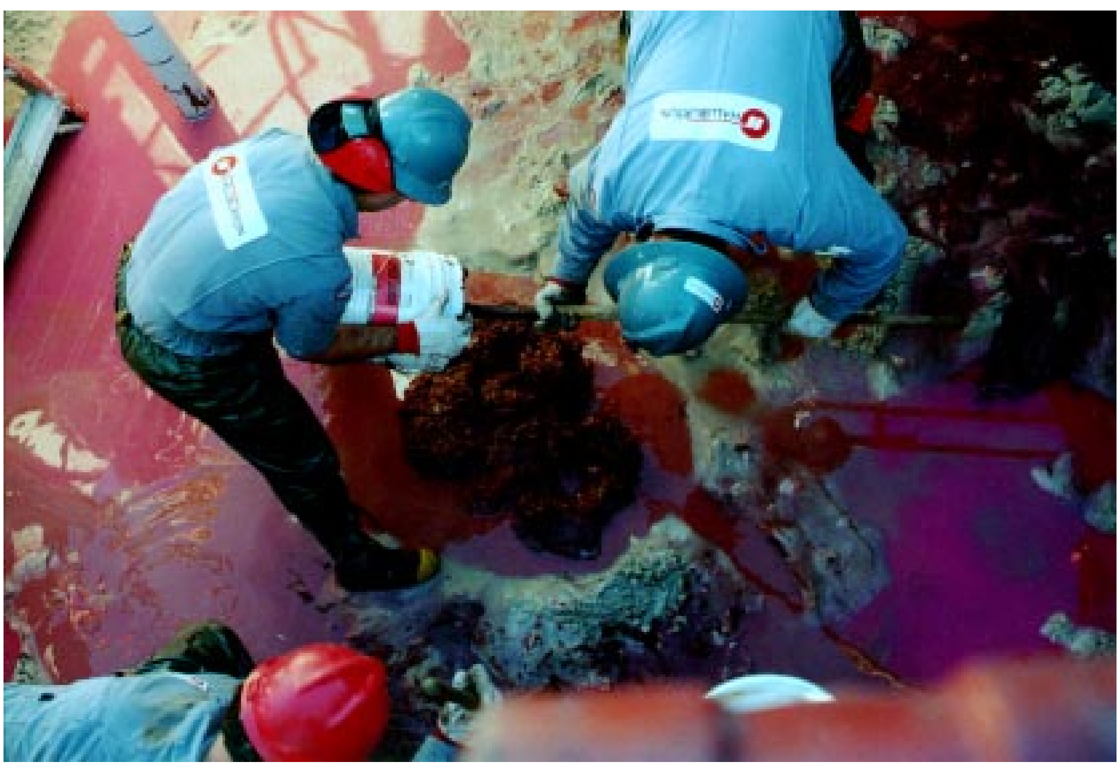

Fig. 4.6. Photograph of placement of clay pod.

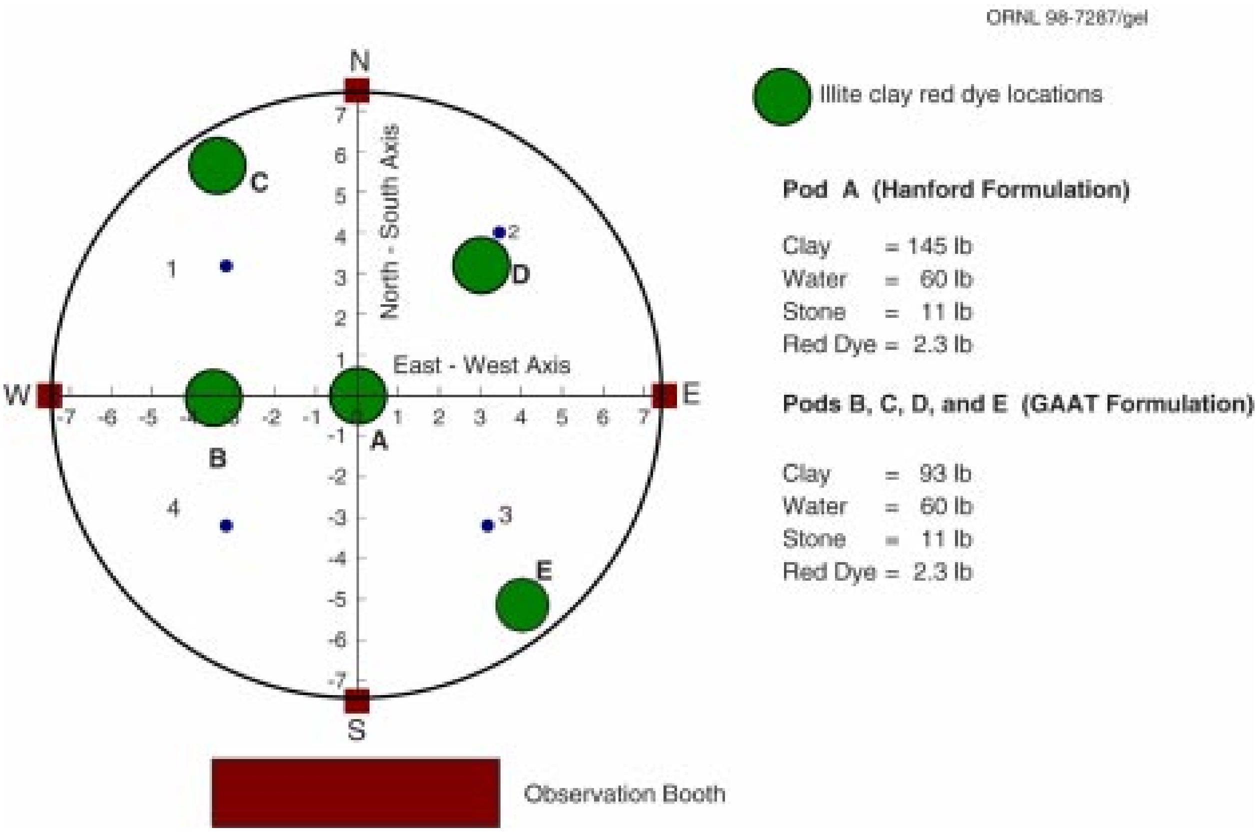

Fig. 4.7. Location of five clay/red dye tracer pods.

equipment to achieve full pressure and flow rate in a very short period of time (500 gal/min at 6,000 psi within 5 s). Water-pumping tests were used for the crew to set up their equipment and coordinate the grout mixer with throttling of the HT-400’s. In order to provide visual feedback to help train the crew, four MPI™ jetting tools inside of PVC plastic pipes were laid on the ground. Observation of the water spray in the air allowed the crew to evaluate how quickly they were coordinating their pumping operations. The photograph in Fig. 4.8 illustrates the level of turbulence and jet-stream arrangement of the MPI™ tools to be placed along the perimeter of the tank. The jet spray (airborne mist) is not indicative of the jetting process inside of the tank for a submerged set of jetting tools.

The entire crew training process took about 1 h.

4.4 SINGLE-POINT INJECTION

Part of the crew training required activation of a single MPI™ jetting tool placed at the center of the tank. The other purpose of this activity was to demonstrate that a single-injection point could not be used to form a homogeneous monolith. The photograph in Fig. 4.9 is illustrative of the jet pattern as it cuts through the PVC plastic casing. The photograph in Fig. 4.10 shows the pattern of the jet close to the PVC casing as it cut into the sand. The photograph in Fig. 4.11 shows that the jets push the sand near the center of the tank outward toward the tank wall and create sand heaps. The sand heaps resemble pie-shaped segments with water-filled gaps created as the jet streams cut into the sand. The thickest part of

Fig. 4.8. Turbulent jet streams produced by MPI™ jetting tool during operator training.

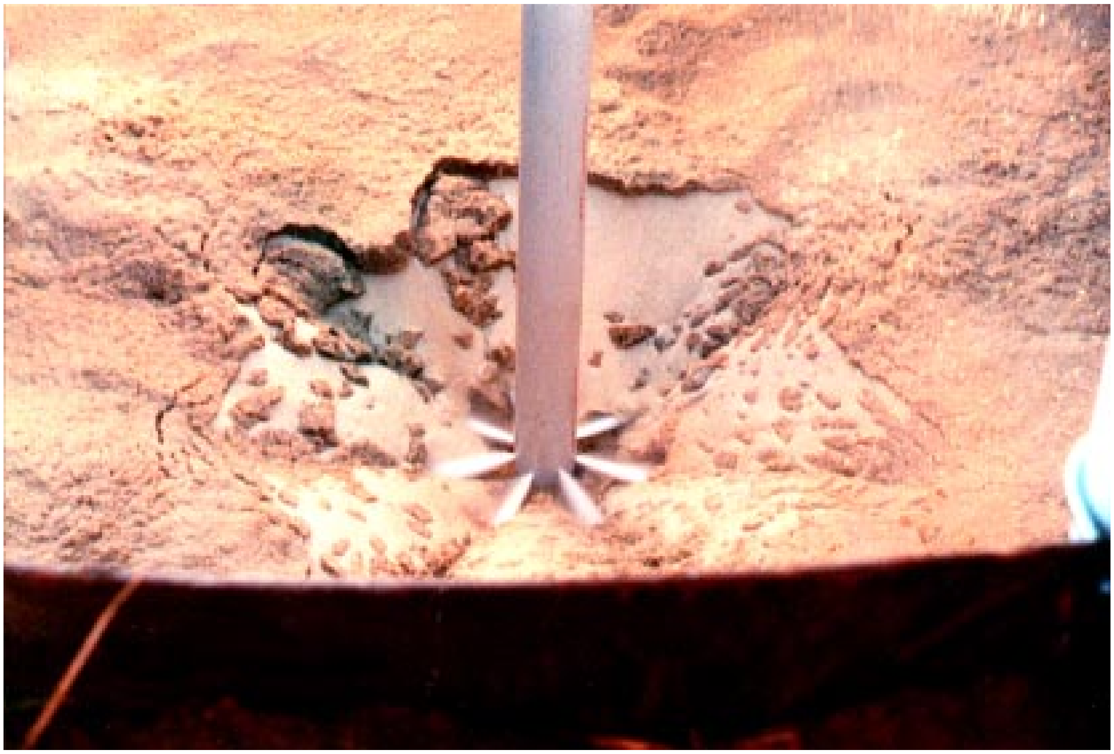

Fig. 4.9. High-pressure jets from single-injection tool cutting through PVC casing.

Fig. 4.10. High-pressure jet pattern in sand from single-injection tool.

Fig. 4.11. High-pressure jet pattern near tank wall from single-injection tool.

the pie segments is closest to the tank wall, that is, the jet stream tends to push sand up against wall. This is the least desirable location for the sand, because the tank wall is the last line of defense against contaminant transport. Note that the monodirectional MPI™ jetting tools were reoriented slightly to provide several horizontal axis of treatment and 360 degrees of coverage by the monodirectional jets on the jetting tool. Therefore, rotation of a single centrally located injector would not produce the desired result of homogenization, because more of the pie-shaped sand heaps would be pushed up against the tank wall.

4.5 MPI™ INJECTION SEQUENCE

A plan view location of the jetting tools used during the MPI™ cold test demonstration is shown in Fig. 4.12. The arrows emanating from each injection point indicate the vector direction of the MPI™ jet streams. The orientation of the jet nozzles was chosen to create maximum mixing efficiency with the cohesive clay pods and zeolite surrogates. The jetting tool configuration along the tank wall projected all the jets inward toward the physical surrogate. This would protect the gunite tank walls from any damage by the jets. All information presented in Fig. 4.12 is considered limited rights data, the sole intellectual property of Dr. Joseph L. Kauschinger and protected by U.S. patent 5,645,377 with several other patents pending. The demonstration of the MPI™ process was conducted under a limited license to Lockheed Martin, which expired on January 30, 1998. There was no transfer of technology, either implied or by consent of Ground Environmental Services, Inc.

4.5.1 Injection Sequence

The injection sequence for the inner and outer set of MPI™ injectors is summarized along the righthand side of Fig. 4.12. Initially, the inner four injection rods were activated. A total of 32 2.4-mm nozzles were pressurized to approximately 6,000 psi, which developed a theoretical grout flow rate of about 400 gal/min. This requires a nearly 2000-hp engine to drive the system, which was provided by four HT-400 pumps (two additional HT-400 pumps on standby). After about 40 s of jetting, the injection from the inner grouting loop was stopped. The second stage of grouting immediately commenced with the opening of the valve on the manifold and the supply of grout flow to the outer four injection lances.

The jetting tools for the outer grout loop contained 32 2.4-mm nozzles, which were pressurized to about 6,000 psi for a duration of nearly 40 s. Prior to the start of the next round of inner and outer injection, all eight jetting rods were reorientated by about 20 degrees. This allowed the monodirectional jets to be pointed along a slightly different path than the previous injection. However, during activation all jetting tools are held stationary. The reorientation of the jetting rods can be done remotely for GAAT TH-4 and, therefore, minimize any risk of exposure to the workers. Furthermore, if there are any lapses in the field to correctly orient the jetting tools (especially along the tank walls), the jetting tools can be easily repositioned to the correct orientation.

The sequence of incremental injection (inner and outer loops) was repeated until all the required grout was injected into the tank. It was estimated that about 2,500 gal of grout would be required to produce a wet surrogate waste loading of about 35% to 37% [i.e., 2,500 gal were needed to create a monolith with constituents similar to those of the monolith tested during the ORNL bench-scale study (see Table 3.3)]. The pressure, flow rates, and injection times measured for each stage of the MPI™ grout injection are summarized in Table 4.1. A total of 12 injection stages were required to inject a total of 2,647 gal of grout. The injection times for each of the 12 stages listed in Table 4.1 varied from a low of 35 s to a maximum of 46 s, with an average injection time of 40.7 s. This precision to inject high flow rates (400 gal/min) at high pressures (6,000 psi) is indicative of the good communications and coordination

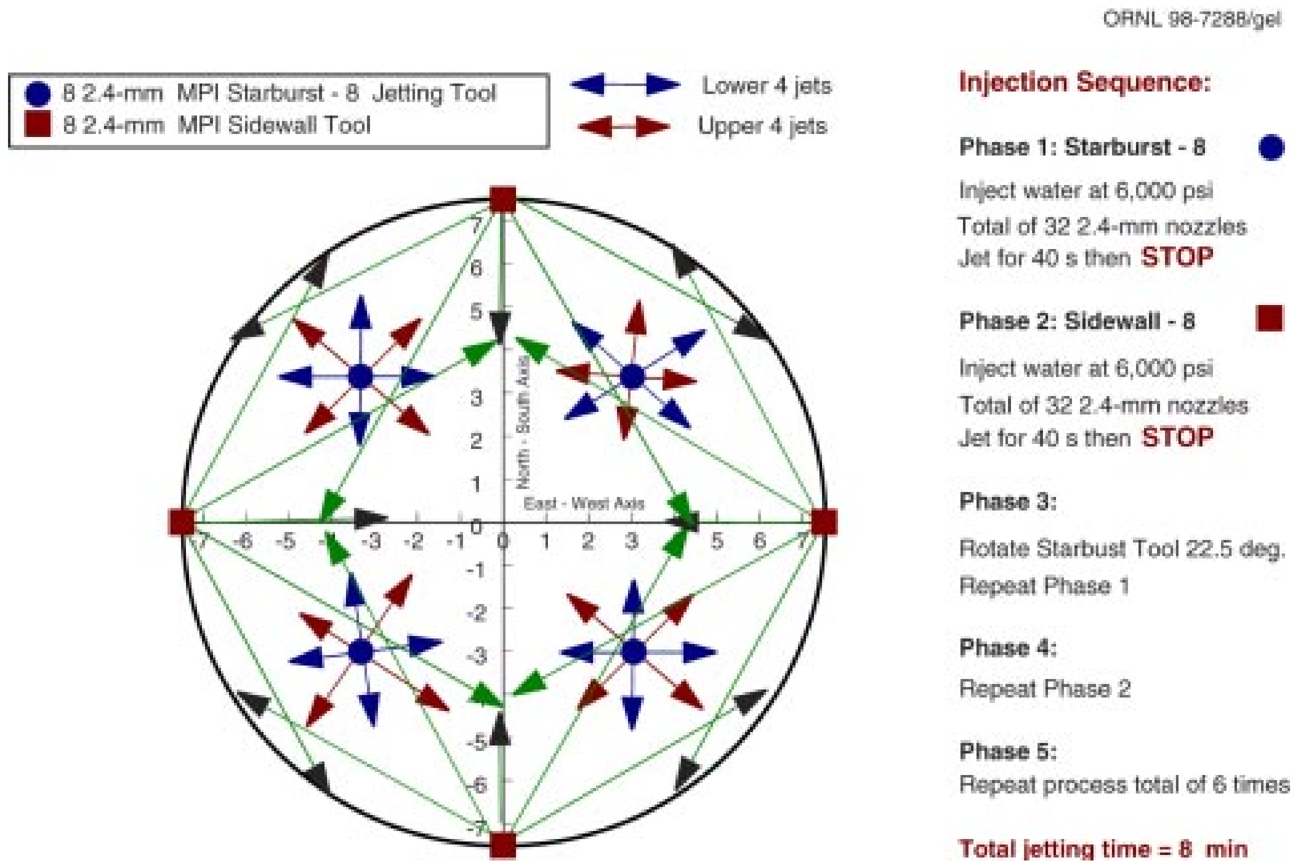

Fig. 4.12. Schematic plan view of MPI™ injection tool layout and jetting configuration used in the cold field demonstration at the Halliburton test facilities. (U.S. Patent 5,645,377 and Patents Pending.) GES Copyright 1998.

Table 4.1. Compilation of jetting data measured during MPI™ Duncan, Oklahoma, cold field demonstration (1997)

Injection no.	Clock time	Injection stage time (min:s)	Measured at injection stage			Theoretical calculations[a]		Theoretical measurement		Estimated number of plugged jets	Grout loop ID
			Pressure (psi)	Volume[b] (gal)	Rate (gal/min)	Volume (gal)	Rate (gal/min)	Delta Q (gal/min)	Difference (%)		
1	16:00	00:40.0	7000	262	393	291	436	43	9.9	3	Inner
2	16:04	00:40.0	5600	209	314	260	390	77	19.6	6	Outer
3	16:13	00:36.0	6200	239	398	246	410	12	2.8	1	Inner
4	16:14	00:43.0	6100	273	381	292	407	26	6.4	2	Outer
5	16:25	00:40.0	6100	242	363	271	407	44	10.8	3	Inner
6	16:26	00:40.0	6100	279	419	271	407	–12	–2.8	0	Outer
7	16:32	00:43.0	6100	209	292	292	407	115	28.3	9	Inner
8	16:34	00:42.0	6100	245	350	285	407	57	14.0	4	Outer
9	16:37	00:46.0	6100	207	270	312	407	137	33.7	11	Inner
10	16:38	00:35.0	6100	156	267	237	407	140	34.3	11	Outer
11[c]	16:44	00:42.0	6100	170	243	285	407	164	40.3	13	Inner
12[d]	16:46	00:41.0	6100	156	228	278	407	179	43.9	14	Outer
Total		08:08.0		2647		3320					
Average		00:40.7	6142	221	326	277	408				

[a]Theoretical calculations based upon 32 2.4-mm diameter jets with an efficiency of 0.80.
[b]Batched 4000 gal of grout at average unit weight of 14.5 lb/gal.
[c]After Stage 11, measured 14 of 32 clogged jets for inner grout loop vs 13 calculated.
[d]After Stage 12, measured 16 of 32 clogged jets for outer grout loop vs 14 calculated.

between the pump and grout plant operators with the grout control center, which was monitoring the injection in real time. This type of communication and coordination is essential for proper operation of the MPI™ system. The comparison between the individual constituents used to create the 15-ft-diameter × 40-in.-thick monolith and ORNL formulation is summarized in Table 4.2. It is obvious that all the required dry-blend material was correctly injected. This would imply that the performance of the monolith would be similar to that observed during the bench-scale testing (see Table 3.6) for results from TCLP and ANS 16.1 diffusion tests. Furthermore, this was accomplished during the cold demonstration using significantly less grout water (19.4% of monolith) than that used in the ORNL bench-scale study (25.8%). The waste loading for the cold demonstration and used during the 1996 ORNL bench-scale studies were both about 35%.

4.5.2 Material Volumes and Rates

The cold field demonstration produced a monolith that weighed about 63,000 lb. This means that the MPI™ process was able to homogeneously intermix nearly 32 tons of material in about 8 min (4 tons/min). The entire MPI™ process took about 45 min from start to finish. This includes the time to open and close valves, to reorient the jetting tools, to calculate the constituents injected into the tank, and

Table 4.2. Compilation of monolith constituents injected during the MPI™ cold field demonstration vs material requirements for ORNL monolith formation

Material type in monolith	Dry blend (%)	Grout (lb/gal)	Total material (lb)	Monolith composition	
				Cold demo (%)	ORNL formula (%)
I. Injected grout formulation					
Slag	39.8	3.85	10,197	16.1	14.8
Fly ash	39.8	3.85	10,197	16.1	14.3
Cement	10.0	0.96	2,549	4.0	4.4
IRPC	7.0	0.67	1,784	2.8	2.6
Bentonite	3.0	0.29	765	1.2	0.8
CFR-3	0.4	0.04	115	0.2	0.0
Grout water		4.62	12,236	19.4	25.8
Total grout weight (calculated)[a]		14.30	37,843	59.9	62.7
W:S ratio		0.48			
II. Surrogate quantities					
Zeolite surrogate (20- to 40-mesh quartz sand)			17,772		
Pore water			4,798		
Wet sand surrogate				35.7	34.5
Supernatant (3 in. water)			2,757	4.4	2.8
Total weight of monolith (lb)			63,170	100	100
Total injection time (min)			8.13		
Total vol grout injected (gal)			2,647		

[a]Note: Measured grout density = 14.5 lb_m/gal.

to inject 2647 gal of grout. A total of 4,000 gal of grout having a unit weight of about 14.5 lb_m/gal was prepared for the cold test demonstration.

Although the injection was conducted in a smooth and uninterrupted manner, a significant number (about 40%) of the jet nozzles became clogged with debris released from inside either the pumps or grout plant. The following subsection addresses the issues related to nozzle clogging and procedures to minimize clogs.

4.5.3 Clogged Nozzle Issues

During the grout injection it was decided not to remove any jetting tools from inside the tank to clean clogged nozzles on the jetting tools. This approach tested the robustness of the MPI™ process to create a homogeneous monolith under an ALARA constraint. Keeping the jetting tools inside the tank during active remediation will help ensure that no workers are exposed to contaminated tools when solidifying sludge in tank TH-4. All tools are planned to be abandoned in place.

A single 2.4-mm-diameter jet delivers approximately 13 to 15 gal/min of grout for the range of pressures, grout density, and estimated hydraulic efficiency for the carbide jets used (e = 0.8). A nozzle clog can be determined by comparing the total measured flow with estimated theoretical flow rates. The difference between the two is indicative of a nozzle clogging. The actual number of clogged jets can be estimated by dividing the difference between theoretical and measured flow rates by the flow rate of a single jet. The difference between the theoretical and measured flow rates was obtained for each of the 12 injection stages and is listed in column 9 in Table 4.1. A positive difference indicates a potentially clogged nozzle because the measured values are less than the theoretical. During the first 2 injection stages there were a few jets that clogged but then passed the obstruction through the jet during subsequent stages. It was not until injection number 7 that the inner set of injection lances began to have multiple clogs, estimated 9 of 32 jets (28%). Subsequent injection stages produced additional clogged jets, until the last two stages, at which point the inner set of jetting tools had 13 of 32 jets clogged and the outer jetting tools had about 14 jets clogged. These numbers were physically confirmed by examining all the jetting tools after the equipment was pulled from the test tank. Even though 45% of the injectors had clogged there was sufficient redundancy in the MPI™ jetting tools to ensure that the correct amount of grout was injected into the tank, as supported by the comparisons in Table 4.2.

The following are two simple methods to decrease the number of clogged nozzles to a more reasonable number (0 to 10% of total):

1. Install a low-pass filter between the grout plant and high-pressure pumps to ensure that the grout plant does not introduce debris into the fresh grout. Install a high-pass filter in line with the manifold between the high-pressure pumps and the data acquisition system used to monitor the injection. This will help ensure that debris does not clog the nozzles and also ensure that the in-line instrumentation does not become fouled. Installation of high- and low-pass filters is normally done. However, because of the tight schedule for the cold demonstration, there was not enough time to acquire the filters capable of handling a grout flow rate of 400 gal/min and 6,000 psi. It is emphasized that the procurement for the test setup, execution, and documentation of the cold field demonstration was all accomplished within the month of December 1997.

2. Use multiple grout circulation loops, in which individual HT-400 pumps are attached to only two injection lances per pump. This will permit using more conventional low-flow-rate filters and smaller diameter supply lines.

The real issues concerning the effect of clogged jets are related to the outcome of the cold demonstration. These issues focus on (1) the sufficiency of the QA/QC controls in the field to ensure that the monolith formed in the test tank contained the prescribed quantities of ORNL solidification agents and (2) the uniformity of distribution of the grout and surrogate throughout the monolith.

The data previously presented in Table 4.2 show that there was excellent QA/QC in the field and that the correct amount of grout was injected to form a mixture with the required gross amount of constituents. The clogging of the nozzles had no impact on the end product produced. This only proves that the MPI™ process is extremely robust and has sufficient redundancy to overcome problems that arise when actually performing remediation activities in the field. Data have been presented that show that the gross amount of constituents were correctly injected into the tank. The following sections discuss the analytical data gathered to examine the spatial variation of the monolith components. It will be shown that the MPI™ process was able to create a homogeneous 32-ton monolith in about 8 min. The monoliths approximate dimensions were 15 ft in diameter × 40 in. thick.

5. FULL-SCALE COLD FIELD DEMONSTRATION OF MPI™: ANALYTICAL RESULTS

The 32-ton grout/sand/water mixture produced from the MPI™ cold field demonstration was allowed to consolidate overnight for a period of about 12 h. The next morning the monolith was solid enough to walk upon. The top of the monolith was completely level and did not have any free water at the surface. In a few locations there were surface cracks about 1/8 in. wide and 1/8 in. deep. This was the result of the clay-rich surface (hydrated bentonite) of the monolith being exposed overnight to cold temperatures (see Section 5.4). Cold and freezing are drying processes and, therefore, desiccate the bentonite gel at the surface. This will not be the case for a monolith formed inside of an underground storage tank.

The photograph in Fig. 5.1 is illustrative of the surface of the monolith after 12 h of consolidation. The photograph also depicts the backhoe used to push sampling tubes through the 40-in. thickness of the monolith. The backhoe was also used to dig a 40-in. deep trench across the entire 15-ft tank diameter. The shallow trench exposed the entire inner core of the monolith, especially at the interface with the tank's concrete floor.

The following sections describe the location of the samples and the laboratory test program and results used to measure the distribution of the sand surrogate throughout the entire volume of the monolith. It should be emphasized that although the surface of the monolith had consolidated, the solidification agents in the grout had not achieved an initial set after 12 h. Therefore, the sand surrogate could be mechanically sieved (separated) from the dry-blend constituents of the grout. The sand particles act as tracer elements that allow examination of how uniformly the surrogate was mixed within the monolith.

Fig. 5.1. Surface of monolith after 12 h of consolidation.

5.1 LOCATION OF TEST SAMPLES AND TRENCH EXCAVATION

One of the primary goals of the MPI™ demonstration was to show (by analytical results) that the process could deliver a very viscous grout and uniformly intermix the grout with a zeolite-type (fine sand) physical surrogate with rapid sedimentation properties. Continuous samples were retrieved from the monolith to determine the vertical distribution of sand. Nine locations were randomly selected for extracting continuous samples from the monolith over its entire thickness (approximately 40 in. long). The sample plan locations are depicted in Fig. 5.2.

The photograph in Fig. 5.3 shows the backhoe digging the test trench to expose the inner core of the monolith. The test trench also allowed extraction of the steel sample tubes over their entire length (i.e., no sample was lost even at the contact with the concrete mat). The close-up photograph in Fig. 5.4 shows the imprint left after the careful removal of two sampling tubes from the sidewalls of the monolith. Bag samples of the interface of the monolith and tank floor were also taken.

The sedimentation rate of the sand surrogate was very rapid (a few seconds for 100% of 0.5- to 0.8-mm particles to fall out of solution). Therefore, it was of interest to examine the amount of sand that resided in direct contact with the concrete mat. The sidewalls of the test trench were prepared by using a shovel to remove any loose material from the interface of the monolith and tank floor (see photograph in Fig. 5.5). Thereafter, 3in.-diameter × 6-in.-long cylinders were driven into the monolith's wall at the contact with the concrete floor (i.e., samples taken within 3 in. of the bottom of the floor). The four samples extracted from various locations along the tank floor are identified as W, X, Y, and Z in the plan location map in Fig. 5.2.

Several compression test cylinders were taken from various locations in the monolith and tested after 3, 7, and 28 days of curing. Cube samples of fresh grout prior to mixing with surrogate waste were also taken and tested in unconfined compression at the same cure times.

Two testing firms were used for the mechanical separation of the grout and sand. Halliburton's Cement Grouting Division was given sampling tubes S3 and S7 (Fig. 5.2). The mechanical sieving and washing of these samples all occurred within 24 h of the final injection. PSI, Inc., from Oklahoma City, was selected as the independent testing firm, because it was the largest material-testing firm within a 50-mile radius of the test site. PSI was given continuous test samples S1, S4, S8, and S9. The large number of samples processed by PSI required about 4 days of cutting the steel tubes, sieving the sand from the monolith mixture and drying in an oven.

5.2 UNCONFINED COMPRESSION STRENGTH

The unconfined compression strengths for the cylinders extracted from the monolith are summarized in Table 5.1. In general, the strengths vary from about 50 psi after 3 days to 400 to 500 psi after 28 days.

The slag–fly ash-grout cube strengths measured after 3, 7, and 28 days are summarized in Table 5.2. The grout strength after 3 days was typically 25 psi. After 28 days of curing the unconfined compression strength was about 2,000 psi. This is quite remarkable considering the small amount of cement (10%) in the grout formulation. This is a testament to the low water content that could be pumped using Halliburton's equipment.

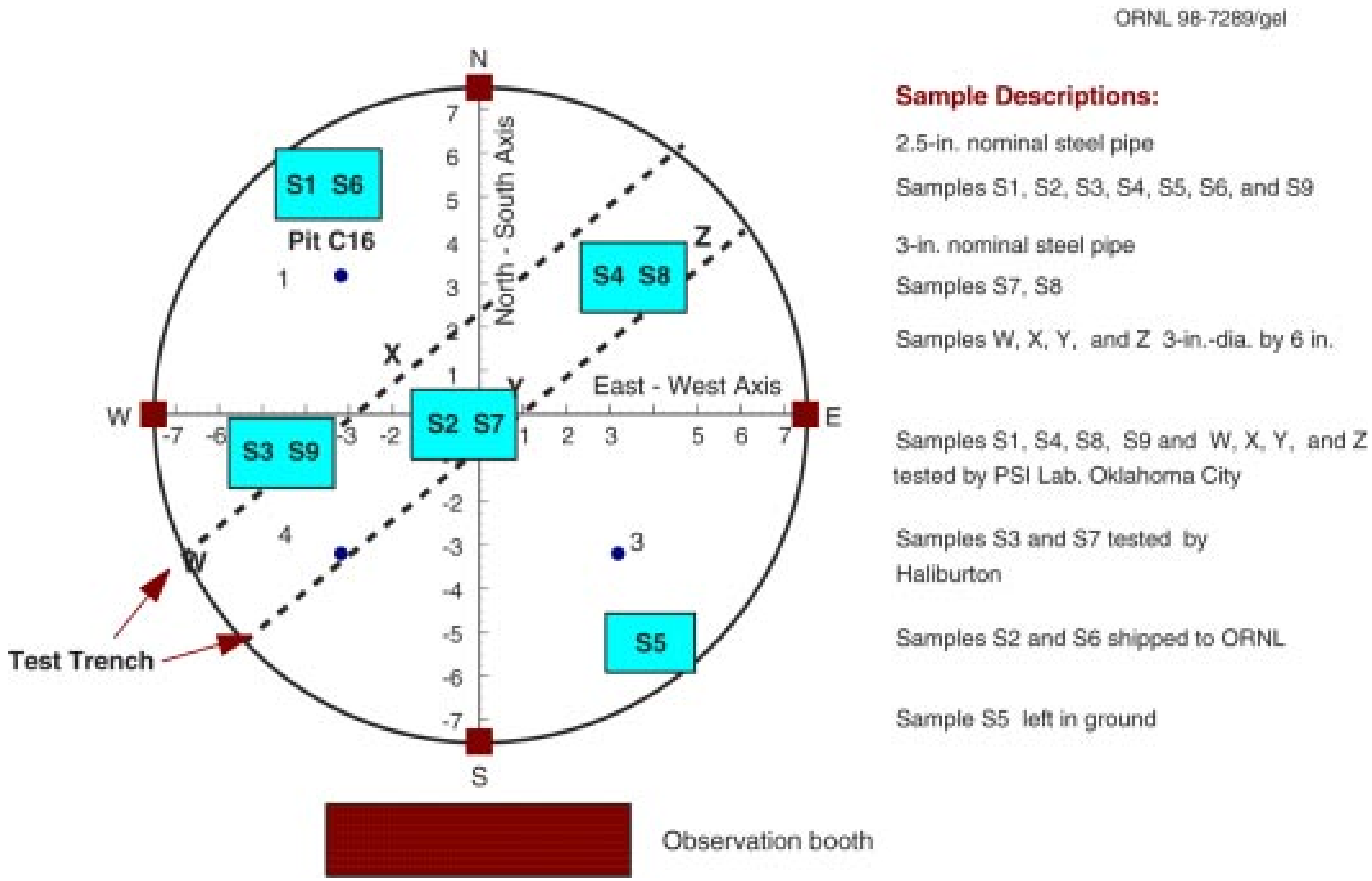

Fig. 5.2. Location of test trench, 3-in. cylinders, and steel tube samples.

Fig. 5.3. Backhoe digging test trench.

Fig. 5.4. Sample tube imprint after extraction of steel sample tubes.

Fig. 5.5. Removal of loose material from side walls of test trench.

Table 5.1. Compilation of unconfined compression test on samples taken from MPI™ grouted monolith; Duncan, Oklahoma, cold field demonstration (1997)

Sample ID	Location	Unconfined compression strength (psi)		
		Day 3	Day 7	Day 28
C16	Top	21		
C16	Top	44	62	
C16	Middle	44	47	380
C16	Middle	47		
C16	Bottom	55	63	450
C16	Bottom	54	72	510
C27	Middle			370
C27	Middle		74	210
C27	Bottom	69		
C48	Top		49	420
C48	Top	51		420

Table 5.2. Compilation of unconfined compression test on fresh grout samples taken from Halliburton grout plant MPI™ cold field demonstration (1997)

Sample ID	Location	Unconfined compression strength (psi)		
		Day 3	Day 7	Day 28
Grout	Cube	27		
		25		
			56	2340
Grout	Cube		122	2370
			105	2340
			145	2020
			143	1980
Grout	Cube		142	2040

5.3 EQUIVALENT SAND DENSITY VS MONOLITH THICKNESS

The sample tubes given to Halliburton Energy Services were taken on December 16, 1997, to their laboratory in Duncan, Oklahoma, and the steel tubes were cut into 6-in. sections. The sand–grout mixture was washed through a 100-mesh sieve (ASTM), which retained 100% of the sand particles (see Fig. 4.5 for sand particle size distribution). Thereafter, the wet sand extracted from the mixture was dried in an oven overnight and the weight of dry sand determined. The weight of sand from each incremental volume was used to calculate an average concentration of sand per total control volume (represented by the volume of the 6-in.-long steel tube). This is termed equivalent sand density in the plots discussed in the text that follows. The range of values for the equivalent sand density vary between 120 lb_m/ft^3 (pure sand in sample) to 0 lb_m/ft^3 for only clay in the sample (i.e., all material was washed through the 100-mesh sieve). The total amount of fine sand placed into the test cell was about 183 ft^3 (nearly 11 tons). When uniformly distributed over the approximately 40-in.-thick monolith, the average theoretical uniform sand density of the monolith would be about 38 lb_m/ft^3.

The results from the mechanical sieving/washing of the monolith performed by Halliburton produced an exceptionally uniform distribution of sand over the 40-in. thickness of the monolith. For both samples S3 and S7 the sand concentration is about equal to 30 lb_m/ft^3 (Fig. 5.6). The sand concentration measured by PSI at sample point WXYZ is also drawn in Fig. 5.6 for comparative purposes. For each of the four samples at contact with the tank floor, the sand density varied from 40 to 50 lb_m/ft^3. This compares very well to the average theoretical value of 38 lb_m/ft^3. It should be noted that test samples S3, S7, and WXYZ were all washed and sieved on the same date (December 16, 1997), which is within 24 h of the formation of the monolith.

5.3.1 PSI Sand Density Data

Four continuous sampling tubes, S1, S4, S8, and S9, were taken to the Oklahoma City testing facility of PSI. The distribution of the sand density over the 40-in.-thick monolith as determined from these samples is illustrated in Fig. 5.7. In general, for each individual test sample the vertical distribution of sand is very uniform, with essentially the same sand concentration at the top of the monolith as at the tank bottom.

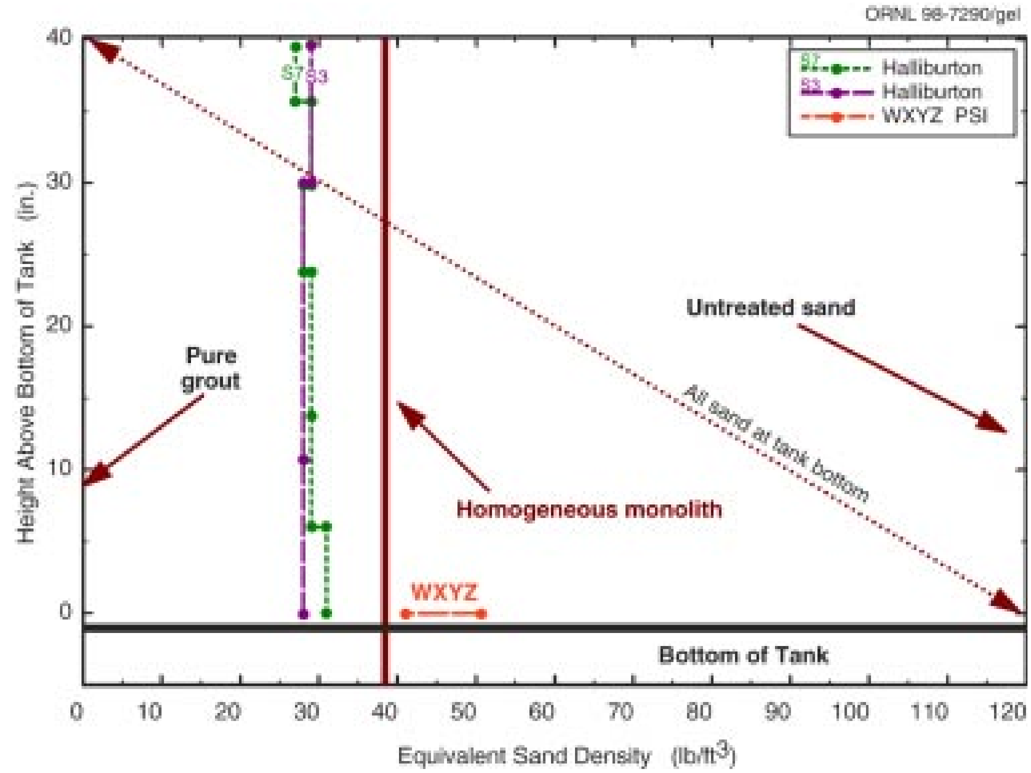

Fig. 5.6. Compilation of sand distribution within grouted monolith; Halliburton data and WXYZ samples measured by PSI within 24 h.

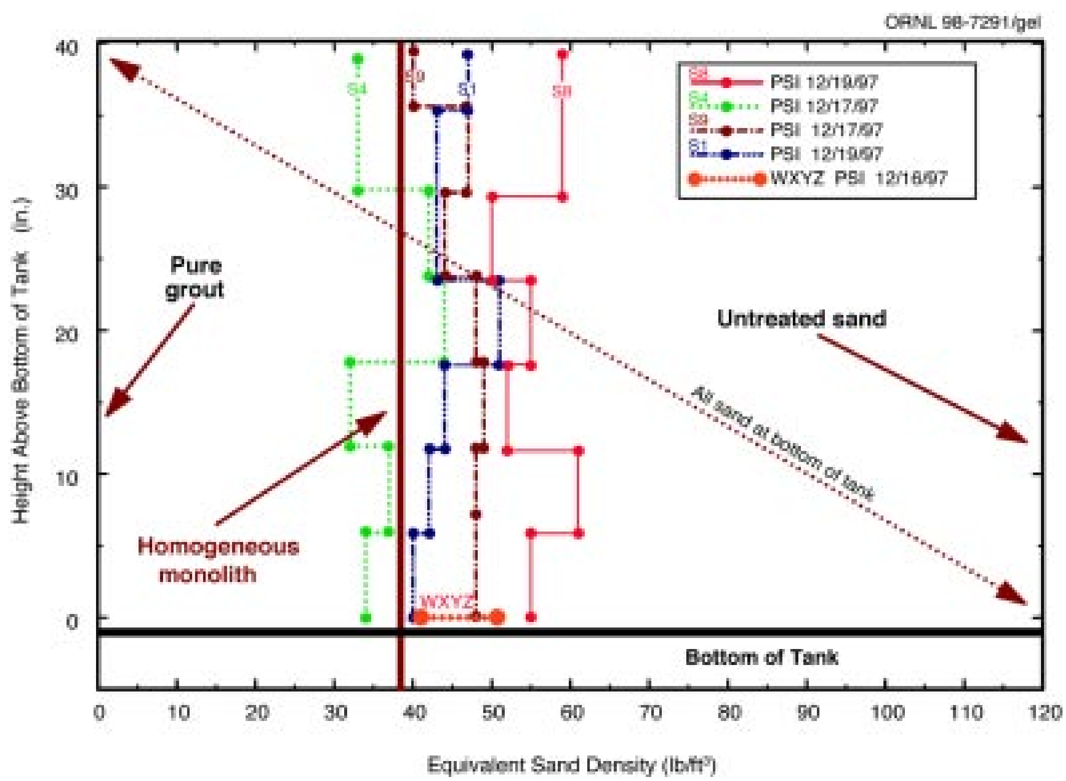

Fig. 5.7. Compilation of PSI sand distribution data within grouted monolith.

This is quite remarkable because the sand sedimentation characteristics are very rapid and the monolith was injected without lifting any of the MPI™ jetting tools.

When examining the spatial distribution of the sand in each test sample (Fig. 5.7), there is added complexity to the interpretation because the samples were washed and sieved at different times, as summarized below:

Sample ID	Date tested	Days after monolith formation
S1	December 19, 1997	4 days
S4	December 17, 1997	2 days
S8	December 19, 1997	4 days
S9	December 17, 1997	2 days

The impact of testing continuous samples at different dates can be ascertained by comparing the distribution curves measured for samples S4 and S8. These two samples were taken within a few inches of each other (see plan location in Fig. 5.2). Therefore, the distribution of sand should be very similar, if they were tested on the same date. Samples S4 and S8 were given to the PSI in order to evaluate the reproducibility of PSI testing procedure. The sand distribution measured on sample S4 (Fig. 5.7) varies closely around the overall average for the monolith (38 lb_m/ft^3). However, the distribution for sample S8 has the highest sand density with most data points at about 55 to 60 lb_m/ft^3. The unconfined compression data on samples extracted from the monolith indicate that the 3-day unconfined strength for the monolith should be equal to about 50 psi. Therefore, some cementation occurred. The wet sieving of the sand and grout was probably impacted by the grout curing (i.e., slag–fly ash cement grout and sand hardened into particle sizes larger than the 100-mesh size). It is believed that the difference between sand distributions for S4 and S8 is the result solely of the grout hardening and thus preventing the hardened sample from being sieved through the 100-mesh sieve.

Similar logic can be used when comparing the distribution of PSI sample S9 with that measured by Halliburton for sample S3. Both samples were obtained within a few inches of each other. The laboratory testing procedure was standardized between each laboratory, with the only major difference being the time of testing. Sample S9 was tested about 24 h later than Halliburton's sample S3. The difference between the two distribution curves is believed to be the result of the effects of cementation and inability to wash the hardened grout through a 100-mesh sieve.

PSI sample S1 was tested 4 days after the injection. However, there was no corresponding sample to compare the results from S1 (i.e., sample S6 was shipped to ORNL for possible testing of the red dye distribution). It is believed that after 4 days the equivalent sand density in sample S1 is higher than the measurements indicate.

5.3.2 Most Probable Monolith Uniformity Distribution

From the discussion in Section 5.3.1 it appears that the sand distribution measured for samples S1 and S8 had sieving problems related to curing of the grout (4 days of curing). The most probable sand distribution within the 15-ft-diameter monolith is depicted in Fig. 5.8. The analytical data presented in this section strongly support the statements that the

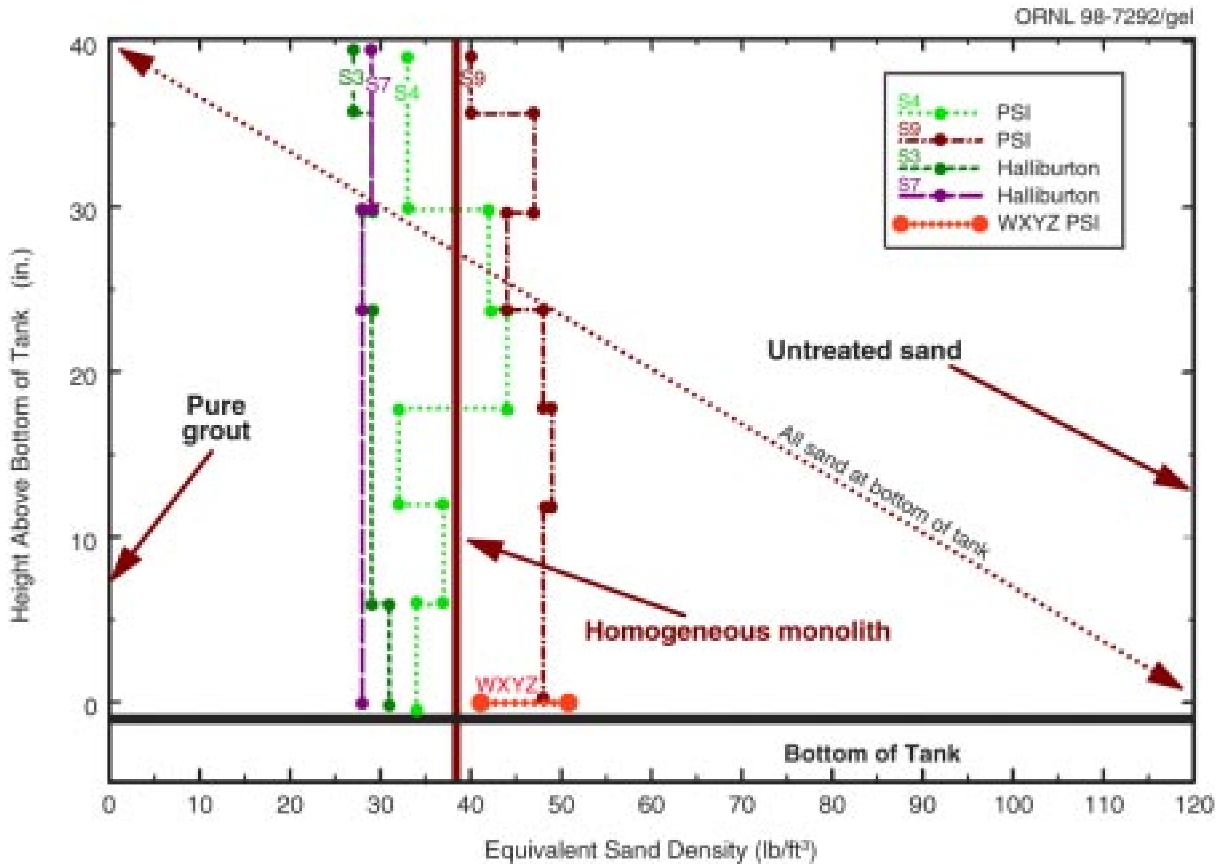

Fig. 5.8. Most probable sand distribution within 15-ft-diameter grouted monolith formed using the MPI™ process.

- MPI™ process successfully delivered the correct gross amount of treatment agents required in the ORNL formulation, and

- Formed near homogeneous monolith with physical surrogates that possessed both rapidly settling characteristics (zeolite-type particles) and pockets of cohesive material similar to Hanford type sludge.

The quantitative data cited above for the near homogeneous monolith are further supported by visual evidence gathered in the test trench. The photographs previously shown in Figs. 5.3, 5.4, and 5.5 are indicative of the uniform nature of the inner core of the 40-in.-thick monolith. There were no signs of untreated white quartz sand at the contact of the monolith across the 15-ft-length of concrete floor exposed at the bottom of the monolith.

5.4 TEMPERATURE OF MONOLITH OVER TIME

As part of the field monitoring of the monolith several thermistor-type temperature probes were placed into the core of the monolith to monitor the temperature changes as the monolith cured. A baseline temperature of the dry sand surrogate was obtained and measured at about 50°F. The final MPI™ injection was completed at about 16:45 on December 15, 1997. A temperature probe was placed at the central mid-height of the 40-in.-thick monolith, and a temperature of 74°F was measured immediately after the last injection. During the night the air temperature dropped to a low of 38°F. In the morning at 8:00 a.m. (14 h after final injection), the monolith's core temperature had increased to about 86°F. The surface of the monolith had been exposed to the night air temperature. After the internal core of the monolith had been excavated and examined, all the excavated material was placed back into the open trench and the surface of the monolith was covered with plastic (to keep moisture constant). Finally, 4 ft of soil fill was placed over the plastic liner and monolith. Temperature readings were taken once a day until the maximum temperature was measured, which occurred 48 h later on December 17, 1997, and was about 100°F. Thereafter, the monolith slowly cooled. On December 24, 1997, the temperature was 97°F, and on December 31, 1997, the core temperature had dropped to 79°F. The final temperature reading of 72°F was taken on June 5, 1998.

5.5 CONCLUSIONS AND RECOMMENDATIONS

The MPI™ cold-field demonstration successfully demonstrated the following items, which correspond to the performance criteria established as requirements at the start of the demonstration:

1. The MPI™ system delivered a very viscous slag–fly ash grout that was proven to immobilize RCRA metals and radioactive nuclides of concern in the GAAT.

2. The field QA/QC was able to ensure gross injection of the grout constituents which ORNL has proven could effectively treat GAAT sludge.

3. The MPI™ system could be used to uniformly intermix a rapidly settling sand surrogate, cut into cohesive clay pods, and uniformly intermix these two surrogate types to create a uniform solidified monolith over a thickness of 40 in. and tank diameter of 15 ft. About 32 tons of material were uniformly mixed in ~8 min.

Although there were no strength criteria established, the unconfined compression strength of the monolith is strong enough to fully restrain the tank shell. Yet the monolith formed could be easily excavated by a backhoe. Future exhumation (if required) can be done with minimal volume increase. The maximum measured temperature of the inner core of the monolith was about 100°F.

Further demonstration work is required for installation of the MPI™ lances, especially though hardpan and/or saltcake-type material. There is a potential of encountering these hardened sludges in some GAAT and other underground storage tanks in the DOE Complex. Hardpan and saltcake should not present a problem for installation of the MPI™ injection tools because percussion installation of the MPI™ tools has been proven through steel drums, wooden pallets, and construction debris. It is not clear at this point if only percussion installation is required or a combination of percussion and jet cutting is needed for efficient installation of the MPI™ injection tools.

5.5.1 Lessons Learned from Cold Test for Application to Tank TH-4 Remediation

The MPI™ system successfully injected the ORNL grout formulation and created a near homogeneous monolith, with dimensions similar to tank TH-4. The equipment and injection system demonstrated during the cold test will be the same used to remediate Tank TH-4 with the following improvements:

- A low-pass filter will be used on the distribution pipeline between Halliburton's RCM grout mixer and the intake side of the high-pressure pumps.

- A separate valve is needed for opening and closing the grout supply to each of the eight MPI™ injection lances. This will allow flexibility for mixing high and low spots of sludge within tank TH-4. The sand surrogate was initially perfectly level during the cold demonstration. This may not be the case for the actual sludge in tank TH-4.

- A high-pass filter will be installed between the high-pressure pumps and data acquisition systems used to monitor the injection in real time. These high-pass filters will help to minimize the potential for nozzle clogging.

- Use an improved grout circulation loop. Two inner and two outer grouting loops are suggested. An individual HT-400 pump should directly drive two jetting tools, approximately 16 nozzles. This will allow small-diameter pipelines to be used, which will fill with grout and pressurize more quickly. This will help the MPI™ jets to achieve a higher velocity more quickly and cut through the plastic casings faster.

- Utilize lexan plastic casing instead of PVC. The clear plastic casing will allow use of borehole cameras to examine layers/structure of tank TH-4 sludge. The camera will also allow video documentation of mixing of TH-4 sludge and ORNL treatment agents and may be able to detect separation of grout and waste particles.

- A piping/manifold system for interconnecting the plastic casing at the surface needs to be designed. This will allow direct connection to a HEPA filter and other air exchange handling equipment. This type of system was used during the MPI™ shallow buried waste demonstration. The white PVC pipe shown in Fig. 2.4 should be replaced with clear PVC. This will allow visual confirmation that no fluid has been ejected up the plastic pipe and captured by the surface piping.

- There is a need to develop a material specification for the granulated blast furnace slag and Indian Red Pottery Clay. There were several candidate slags available from Lone Star Cement, but there are no guidance documents nor criteria for selecting the “best” slag.

The cold field demonstration successfully proved that the MPI™ process can be safely used to form a uniform monolith with the correct amount of constituents which would create a leach-resistant treatment of tank sludge. It is of interest to examine the chemical properties of the 38 tons of bulk dry-blended material mixed by Halliburton for the cold field demonstration. During the 1996 bench-scale studies only kilogram-sized samples were mixed in the laboratory. Obviously, bulk blended material would be more representative of the ORNL grout needed during actual remediation of GAAT TH-4. The following chapter discusses the results from the 1998 bench-scale testing of the bulk blended material. The bench-scale tests were conducted using a GAAT TH-4 surrogate sludge and actual “hot” sludge taken from tank TH-4.

6. 1998 BENCH-SCALE DEVELOPMENT OF GROUTS FOR GAAT TH-4 SLUDGE

The bench-scale testing of the ORNL grout formulation performed in 1996 (Section 3) was conducted using a two-prong strategy for placing the slag–fly ash solidification agents into a GAAT tank. Seventy percent of the dry-blended material (see Table 3.3) were injected as a grout, with a water-to-solids (W:S) ratio of 1:1. The remaining dry-blend (30%), consisting of equal portions of slag and fly ash were to be placed into the GAAT tank via mechanical stowing techniques. Although this two-step approach complicated the field activities, and could have caused unnecessary risk of exposure to remediation workers, at the time it represented the best effort for the GAAT tank remediation based upon the results from the initial bench-scale experiments.

The robustness of the Halliburton oil-field pumping and mixing equipment was able to overcome the limitations of the laboratory test equipment. All the dry blend materials required in the ORNL grout formulation (Table 3.3) were able to be mixed with the grout water. Furthermore, with small amounts (0.4%) of a dispersant (CFC-3) commonly used by Halliburton, the W:S ratio used during the cold field demonstration could be drastically reduced from 1:1 to a W:S ratio of about 0.48 (Table 4.2). This low W:S ratio corresponded to a grout density of approximately 14.5 lb_m/gal, which was measured on the 4,000 gal of grout used during the cold field demonstration.

Another major distinction between the 1998 and 1996 bench-scale studies was related to the following:

- Halliburton's bulk plant was used to blend 38 tons of dry material during the cold field demonstration. This bulk-blended material was used during some of the 1998 bench-scale studies as opposed to the less than kilogram quantities of blended samples used in the 1996 laboratory studies. When performing full-scale in-tank treatment much larger portions of dry blend must be blended. Issues related to quality control and handling procedures of the dry blend become another important implementation issue. The bulk-blended material prepared by Halliburton performed very well during strength and leach-resistance tests using TH-4 surrogate sludge.

- All the dry blend materials used in 1998 bench-scale studies were from different suppliers that those used in the 1996 bench-scale study.

The following sections present the results from the 1998 bench-scale studies used to examine the leach resistance of the bulk-blended formulation used in the cold field demonstration. The unconfined compression strength and leach resistance of the grout to the RCRA metals (Hg, Cr, Pb) were examined for wet sludge loadings of 35%, 50%, and 65%. Additionally, nine different grout formulations were examined to evaluate the sensitivity of the individual grout components to resist leaching and diffusion of a surrogate sludge similar to GAAT TH-4 sludge. Leachability and ANS 16.1 diffusion test results indicate that the RCRA metals and radionuclides could be immobilized for the nine formulations examined. Compressive strength and leachability tests performed on actual hot sludge taken from GAAT TH-4 indicated that the strength of the treated sludge was about 1,400 psi after 28 days. All TCLP leach results for RCRA metals were below universal treatment standards (UTS).

6.1 GAAT TH-4 SLUDGE SURROGATE USED IN THE 1998 TEST PROGRAM

In 1996 emphasis was placed upon developing a robust grout that could be used to treat sludges representative of the entire GAAT tank farm (Tables 3.1 and 3.2). The rationale for this approach was related to the GAAT waste-retrieval campaign that was removing sludge from a variety of tanks and mixing the exhumed waste in a consolidation tank prior to transfer to the Melton Valley Storage Tanks (MVST). During fiscal year 1998, emphasis was placed on developing a grout that could be used to specifically treat GAAT TH-4 waste. The primary reason for the in-tank remediation of TH-4 was related to its small size (20-ft diameter, 6.5-ft vertical walls) not being able to accommodate the robotic arm used to retrieve the wastes from the larger gunite tanks.

The comparison among the ionic concentrations of the hot TH-4 sludge sample extracted from GAAT TH-4 and the GAAT surrogates used in 1996 and 1998 studies are listed in Table 6.1. In general, the hot sludge is not characteristically hazardous, whereas the surrogates used in 1996 and 1998 are both hazardous for chromium and mercury. The surrogate used in 1996 typically contains a higher concentration of the RCRA metals when compared with the TH-4 surrogate used in 1998. However, there is considerably more thorium in the 1998 surrogate.

The chemical composition of the individual RCRA metals used to make the GAAT TH-4 surrogate are listed in Table 6.2. A highly mobile form of mercury ($HgCl_2$) was used, along with sodium di-chromate for the chromium(VI) source ($Na_2Cr_2O_7$), and lead oxide (PbO) for lead. The RCRA metals are slightly less concentrated than the GAAT-tank-farm sludge surrogate used in 1996 (see Table 3.1). Tributyl phosphate (TBP) was used in both surrogates to simulate the total organic carbon content of the sludge, which was about 11,000 mg/kg in both the 1996 and 1998 surrogate sludges.

The chemical analysis of the actual hot TH-4 sludge is contained in Table 6.3.

6.2 PROPERTIES OF BULK DRY BLEND USED DURING THE COLD FIELD DEMONSTRATION

When the 38 tons of dry blend used in the cold field demonstration were mixed at the Halliburton bulk plant in Duncan, Oklahoma, several 10-lb samples were taken, at various times, from the pneumatic supply lines connected to the truck bins, which transported the dry blend to the test facility. It was of interest to prepare the bulk-blended dry blend at the same density and W:S ratio as used during the cold field demonstration. This grout would be representative of the formulation that would be injected into GAAT TH-4. A limited study was conducted to measure the mechanical properties and grout leachability resistance for the RCRA metals contained in the GAAT TH-4 surrogate sludge (Tables 6.1 and 6.2).

The combination of dry blend, water, and bentonite used during these studies is listed in Table 6.4. The 1.85% bentonite was prehydrated with the grout mix water (30.88%) to form a 6% bentonite gel. This is the bentonite slurry concentration used during the cold field demonstration. The water-to-total solids (W:S) ratio of 0.45 (total solids of 67% + 1.85% bentonite) produced a grout that has a total unit weight of about 14.5 lb_m/gal. This was the measured density obtained as an average for the 4,000 gal of grout prepared for the demonstration. This basic grout formulation was then combined with the GAAT TH-4 surrogate sludge at three different waste loadings. The 35% loading is the best estimate for the sludge concentration for the planned in-tank remediation of GAAT TH-4. The 50% and 65% waste loadings are extremes for any possible eventuality in the field. It is reemphasized here that the field controls implemented during the MPI™ cold field demonstration were able to ensure that the correct gross amount of solidification agents were injected and that the total volume in the test tank produced a waste loading of 35.7% (see Table 4.2). This is the current target value for the actual in-tank remediation of tank TH-4.

Table 6.1. Composition of TH-4 sludge sample and GAAT surrogates

Ions[a]	TH-4 sludge sample (mg/kg)	FY 96 GAAT surrogate[b] (mg/kg)	FY 98 TH-4 surrogate sludge (mg/kg)
Ag	13.4		
As	<1.67		
Hg	<0.00668	207.6	145.9
Pb	<6.03	3209.8	2255.9
Al	2630	11424.4	1848.4
B	37.6		
Ba	9.54		
Be	68.1		
Ca	1250	8634.1	878.5
Cd	<5.72		
Co	9.62		
Cu	31		
Fe	3300	6511.9	2319.3
K	762	3002.4	535.5
Mg	<1.68	2081.6	224.0
Mn	28.7		
Na	29900	35000.5	45742.0
Ni	21.8		
Se	<1.67		
Sb	<27.2		
Si	13900		9769.2
Sr	8.55		
Th	75200	21959.7	52852.1
Tl	<1.67		
U	36900	36577.6	25934.1
V	<0.61		
Zn	<13.4		
Zr	3770		
Cr	208	1257.6	883.8
Chloride	723	2534.7	508.1
Fluoride	1010	5481.6	709.8
Nitrate	13600	42528.5	70003.0
Nitrite	281		197.5
Phosphate	34400	5838.6	24177.0
Sulfate	10900	9869.4	7660.7
TIC (carbonate)	<1000	4494.3 (22454.2)	6852.5
TOC (TBP)	8730	6182.6 (11423.9)	6135.6
Ca oxalate		100	70.3
Water content	66.20%	73.90%	66.20%
pH	10		

[a]TIC = total inorganic carbon; TOC = total organic carbon; TBP = tri-butylphosphate.
[b]Weight average plus maximum bad actors.

Table 6.2. Composition of the surrogate TH-4 sludge used in the 1998 bench-scale studies

Compound	Concentration (mg/kg)
$HgCl_2$	197.4
PbO	2430.2
$Al(OH)_3$	5343.8
$Ca(OH)_2$	1588.5
Fe_2O_3	3316.0
K_2CO_3	1087.7
$Mg(OH)_2$	537.4
SiO_2	20899.4
$Th(NO_3)_4 \cdot 4H_2O$	125758.1
$UO_2(NO_3)_2 \cdot 6H_2O$	54707.5
$Na_2Cr_2O_7 \cdot 2H_2O$	2532.7
NaCl	752.6
NaF	1568.8
$NaNO_2$	296.2
Na_3PO_4	34755.9
Na_2SO_4	11327.5
Na_2CO_3	59493.0
Total salts (mg/kg) wt%	326592.7 32.66%
TBP (mg/kg) wt%	11337.0 1.13%
$CaC_2O_4 \cdot H_2O$ (mg/kg) wt%	70.3 0.01%
Water wt%	66.20%
Mass balance wt%	100.00%

[a]Tri-butylphosphate.

Table 6.3. Chemical analysis of sludge sample from GAAT TH-4

Nonradioactive component	μg/g	Nonradioactive component	μg/g	Radionuclide[a]	Bq/g
Ag	1.34×10^{1}	Na	2.99×10^{4}	Am-241	$<7.3 \times 10^{1}$
Al	2.63×10^{3}	Ni	2.18×10^{1}	Co-60	$<5.1 \times 10^{1}$
B	3.76×10^{1}	NO_2	2.81×10^{2}	Cs-134	$<3.7 \times 10^{1}$
Ba	9.54	NO_3	1.36×10^{4}	Cs-137	5.20×10^{2}
Be	6.81×10^{1}	P (microwave)	3.44×10^{4}	Eu-152	$<2.5 \times 10^{2}$
Br	<4.94	P (fusion)	4.92×10^{3}	Eu-154	$<1.5 \times 10^{2}$
Ca	1.25×10^{3}	Pb	<6.03	Eu-155	$<8.4 \times 10^{1}$
Cd	<5.72	PO_4	4.89×10^{3}	G-alpha	3.30×10^{3}
Cl	108	S as SO_4 (microwave)	1.09×10^{4}	Total-act	1.10×10^{4}
Cl (fusion)	723	S as SO_4 (fusion)	9.76×10^{3}	Total rad-Sr	2.40×10^{4}
Co	9.62	Sb	$<2.72 \times 10^{1}$		
Cr	2.08×10^{2}	Si (HF)	1.39×10^{4}		
Cu	3.10×10^{1}	SO_4	8.64×10^{3}	Other	
F	5.79×10^{2}	Sr	8.55		
F (fusion)	1.01×10^{3}	Th	7.52×10^{4}	Density	1.38 g/mL
Fe	2.06×10^{3}	U	3.69×10^{4}	Moisture	66.20%
K	7.62×10^{2}	V	$<6.10 \times 10^{-1}$	pH	10.09
Li	<1.53	Zn	$<1.34 \times 10^{1}$	TIC	<0.1%
Mg	<1.68	Zr	3.77×10^{3}	TOC	0.87%
Mn	2.87×10^{1}			Total carbon	0.87%

[a]Total act = total activity; total rad = total radioactivity; TIC = total inorganic carbon; TOC = total organic carbon.

Table 6.4. Grout composition for screening tests with surrogate TH-4 sludge

ID no.	Jetting slurry (wt %)				Grout (wt %)			Comments
	Bentonite gel slurry (%)		Field preblend (%)	Total (%)	Wet sludge (%)	Jetting slurry (%)	Total (%)	
	Bentonite	Water						
1DB	1.85	30.88	67.27	100.00	35.00	65.00	100.00	Good consistency, whitish tan color
2DB	1.85	30.86	67.29	100.00	50.00	50.00	100.00	Thicker and still slightly soupy, burnt orange brown
3DB	1.85	30.90	67.25	100.00	64.97	35.03	100.00	Wet and pourable

6.2.1 Unit Weight and Free Water

The treated TH-4 surrogate had a density that varied from 1.5 g/cm^3 for 35% waste loading to 1.36 g/cm^3 for the 65% waste loading. The 65% waste loading was the only sample that produced any free water, which was 1.2% of the total volume after 7 days of curing. Typically, ordinary cement grouts have a free-water ratio of about 25% after only several hours of curing.

6.2.2 Unconfined Compression Strength

There were no criteria established for the unconfined compression strength of the treated tank sludge. The approach taken for the remediation was to provide the maximum amount of dry chemicals that would provide maximum treatment of the sludge. This is the main reason why large amounts of slag and fly ash were used in the ORNL grout formulation, as opposed to Portland cement. Furthermore, compared with slag, cement tends to cause the generation of larger amounts of heat during curing, which can be deleterious to the grout. Ordinary water:cement grout would reach a temperature of over 175°F for the same conditions as the cold field demonstration, wherein a maximum temperature of 100°F was measured (see Section 5.4).

The compression strengths measured on the 35% surrogate waste loading samples after 7 days had an average value of 824 psi with a standard deviation of 38 psi. After 40 days, the strength nearly doubled to an average of 1,788 psi (105 psi standard deviation).

As the waste loading increases the strength typically decreases. For the 50% surrogate waste loading, the measured unconfined compression strength had an average value of about 209 psi after 40 days, with a standard deviation of 29 psi. The minimum strength measured for any sample was 172 psi. This strength is much more than that required to support the walls of the GAAT but can allow easy exhumation of the solidified sludge in the future, if necessary.

At a waste loading of 65% there was no initial set (cementation) of the sample after 40 days. The samples had formed a consolidated solid. Furthermore, the treated sludge at the 65% waste loading was able to immobilize the RCRA metals of concern, as discussed in the following section.

6.2.3 TCLP Extract for Chromium, Lead, and Mercury

The surrogate GAAT TH-4 sludge listed in Tables 6.1 and 6.2 is characteristically hazardous for the RCRA metals mercury and chromium. The extract concentrations leached from untreated surrogate are listed in Table 6.5. The chromium concentration (104 ppm) is about 120 times more concentrated than the UTS limit of 0.86 ppm. The untreated sludge releases mercury over 625 times higher than the UTS limit of 0.025 ppm.

Table 6.5. TCLP extract concentrations for screening tests with surrogate TH-4 sludge

ID no.	Waste loading (%)	TCLP extract concentration[a] (mg/L)		
		Cr	Pb	Hg
Surrogate sludge		104.27	0.51	15.6
1DB	35	0.14	<0.014	0.000045
2DB	50	0.082	0.029	0.00078
3DB	65	1.794	0.066	0.000512
UTS[b]		0.86	0.37	0.025

[a]TCLP = Toxicity Characteristic Leaching Procedure.
[b]UTS = universal treatment standard.

There was a significant reduction in the total concentration released for the three RCRA metals of concern at all waste loadings listed in Table 6.5. Below 50% waste loading, all the RCRA metals are immobilized below their respective UTS limits. At a 65% waste loading, the chromium (1.79 ppm) in sample 3DB is slightly above the UTS limit but is below the old land LDR value of 5 ppm.

6.2.4 Conclusions on Bulk-Blended Grout Used During Cold Field Demonstration

The 38-ton bulk dry blend formulation was sufficiently blended in the field to formulate a grout that should be able to successfully treat the hazardous components of GAAT TH-4 sludge to UTS limits. The grout performed exceptionally well even at waste loadings of 65%. There was little to no free water released, and at 50% waste loading and less the treated waste had good mechanical properties. Although the 65% waste loading did not set after 40 days of curing, the grout and sludge formed a consolidated mass with a unit weight of 1.36 g/cm^3 (85 lb$_m$/ft^3). The consolidated mass was able to immobilize mercury and lead below UTS and significantly reduce the di-chromate compounds ($Na_2Cr_2O_7$) to significantly below the LDR for chromium. The addition of 0.4% dispersant (CFR-3) had no influence upon the strength gain or leach resistance of the treated TH-4 surrogate.

6.3 SENSITIVITY TESTING

A comprehensive understanding of the treatment capabilities of the ORNL grout formulation required more extensive testing of the grout. Sensitivity testing allows a rational decision to be made as to the variability of the chemical and physical properties of the tank sludge. The analysis of the sensitivity test data allows more confidence in the likelihood of success of the in-tank remediation process.

The bulk dry blend formulation prepared by Halliburton discussed in Section 6.2 was sufficiently robust to treat GAAT TH-4 sludge loadings up to 65%. The tests conducted during the sensitivity study used the same TH-4 surrogate sludge (Tables 6.1 and 6.2) as discussed in Section 6.1. The individual constituents (slag, fly ash, IRPC, cement, and bentonite) used to make the bulk dry blend used in the cold field demonstration at the Halliburton facilities in Duncan, Oklahoma, were obtained. Although the same fly ash, IRPC, bentonite, and cement used in the cold demonstration bulk dry blend were used during the sensitivity study, the slag was replaced by a slag manufactured by Holnam Inc.

6.3.1 Grout Mixes

A total of nine combinations of grout formulations and sludge loadings were examined during sensitivity testing. The precise combination of ingredients used during the sensitivity tests is listed in Table 6.6. The calculated values in Table 6.6 are discussed in Section 6.4. The data listed in the first 10 columns represents the components in the grout. The percentages in each column are based upon the total grout weight (solids plus water). The W:S ratio data (column 2) are the proportions of the water to the total amount of solids in the grout. The W:S ratio is directly controlled in the field and represents a key QA/QC factor. The actual value used during the cold field demonstration was W:S = 0.45. The maximum value of W:S used during the sensitivity testing was 0.69, which is more than 50% higher than that used in the field. The likelihood of this variation of W:S ratio occurring in the field is extremely remote. Real-time field controls are in place that are designed to prevent this occurrence (for example, “Mix large volume of grout prior to injection to assure grout W:S = 0.45” and “use real-time monitoring of grout density during injection”).

The grout mix water (column 3, in Table 6.6) was combined with the bentonite (column 4) and allowed to hydrate for several hours, which is precisely what is done in the field. During the sensitivity study there was essentially no variation in the bentonite gel concentration, which remained at about 5 to 6% for all tests performed. The hydrated bentonite gel is more related to the water-control aspects of the final mixture and also provides thixotropic qualities of the grout (needed to suspend particles).

The first eight blends (1S and 8S) listed in Table 6.6 have dry blend constituents that typically varied from about +5% to as low as –20% of the standard formulation injected during the cold field demonstration. This standard grout formulation is represented by test number 1DB at the bottom of Table 6.6. Sensitivity test 9S was mixed without any fly ash, and therefore, the slag represented about half of the entire grout formulation.

6.3.2 GAAT TH-4 Surrogate Variation

Most of the GAAT TH-4 surrogate used during the sensitivity testing was representative of the most probable sludge in Tank TH-4. The waste loading of 35% was based upon current sludge thickness (~30 in.) in the tank and a maximum freeboard of about 48 in. The volumetric water content (66%) of the sludge was based upon measurements of actual sludge taken from GAAT TH-4. The variation of the waste loading and volumetric water content of the sludge listed in Table 6.6 can be examined by reviewing the data plotted in Fig. 6.1. Most sludge data (8 of 12 tests) are clustered around a single point at 35% waste loading and a volumetric water content of 66%. This is the most likely sludge condition in tank TH-4. Four extreme sludge types were examined during the sensitivity studies:

- Sample 6S at 35% waste loading and 85% water content was selected to represent the highest water content sludge ever measured for a GAAT tank farm sludge sample. This sludge represents a diluted sludge when compared with the actual TH-4 surrogate sludge.

- Sample 7S is at the lowest water content of 35% and 35% waste loading. This represents a sludge with concentrated solids at the extreme for the entire GAAT tank farm.

Table 6.6. Grout mix water, dry blend, and TH-4 surrogate used during 1998 bench-scale study

Grout mix water composition					Dry-blend constituents in grout						TH-4 surrogate waste		
Test ID[a]	W:S ratio	Grout mix water (%)	Bentonite clay (%)	Bentonite gel (%)	Cement (%)	Slag (%)	Fly ash (%)	IRPC clay (%)	CFR-3 (%)	Grout density (lb_m/gal)	Water content (%)	Waste loading (%)	Supernatant (%)
1S	0.54	35.1	1.7	5.0	6.5	25.9	25.9	4.5	0.3		66	35.0	2.4
Calc.	0.54	35.1	1.9	5.6	6.5	26.0	26.0	4.5	0.0	13.9	67	34.9	2.4
2S	0.66	39.8	1.6	4.0	6.0	24.0	24.0	4.2	0.3		66	37.8	2.7
Calc.	0.66	39.8	1.8	4.5	6.0	24.1	24.1	4.2	0.0	13.2	67	37.8	2.8
3S	0.44	30.7	1.9	6.1	6.9	27.7	27.7	4.9	0.3		66	32.1	2.3
Calc.	0.44	30.6	1.9	6.2	7.0	27.9	27.9	4.9	0.0	14.5	67	32.1	2.3
4S	0.60	37.3	1.8	4.9	5.6	22.5	27.6	4.8	0.3		66	36.3	2.5
Calc.	0.60	37.5	1.9	5.1	5.7	22.7	27.1	5.1	0.0	13.5	67	36.3	2.6
5S	0.49	32.7	1.6	4.9	7.4	29.5	24.2	4.2	0.3		66	33.5	2.3
Calc.	0.49	32.9	1.7	5.1	7.3	29.0	24.4	4.7	0.0	14.2	67	33.5	2.4
6S	0.54	35.1	1.7	5.0	6.5	25.9	26.0	4.5	0.3		85	35.0	2.5
Calc.	0.54	35.1	1.8	5.0	6.5	26.1	26.1	4.6	0.0	13.9	85	34.9	2.4
7S	0.54	35.2	1.7	4.9	6.5	25.9	25.9	4.5	0.3		35	35.1	2.2
Calc.	0.54	35.1	1.8	5.0	6.5	26.1	26.1	4.6	0.0	13.9	35	35.4	2.2
8S	0.69	40.7	1.6	3.9	5.9	23.7	23.7	4.2	0.3		66	50.0	2.2
Calc.	0.69	40.8	1.6	3.9	5.9	23.7	23.7	4.2	0.0	13.1	67	50.8	2.1
9S	0.54	35.1	1.7	5.0	6.5	51.8	0.0	4.5	0.3		66	35.0	2.4
Calc.	0.54	35.1	1.7	5.0	6.5	51.8	0.3	4.5	0.0	14.3	67	35.2	2.4
1DB	0.44	30.9	1.9	6.0	6.7	28.0	28.0	4.7	0.3		66	35.0	0.0
Calc.	0.45	31.0	1.9	6.0	6.9	27.7	27.7	4.8	0.0	14.5	67	35.0	0.0
2DB	0.44	30.9	1.9	6.0	6.7	28.0	28.0	4.7	0.3		66	50.0	0.0
Calc.	0.45	31.0	1.9	6.0	6.9	27.7	27.7	4.8	0.0	14.5	67	50.0	0.0
3DB	0.44	30.9	1.9	6.0	6.7	28.0	28.0	4.7	0.3		66	65.0	0.0
Calc.	0.45	31.0	1.9	6.0	6.9	27.7	27.7	4.8	0.0	14.5	67	65.0	0.0

[a]Calc. = calculated values.

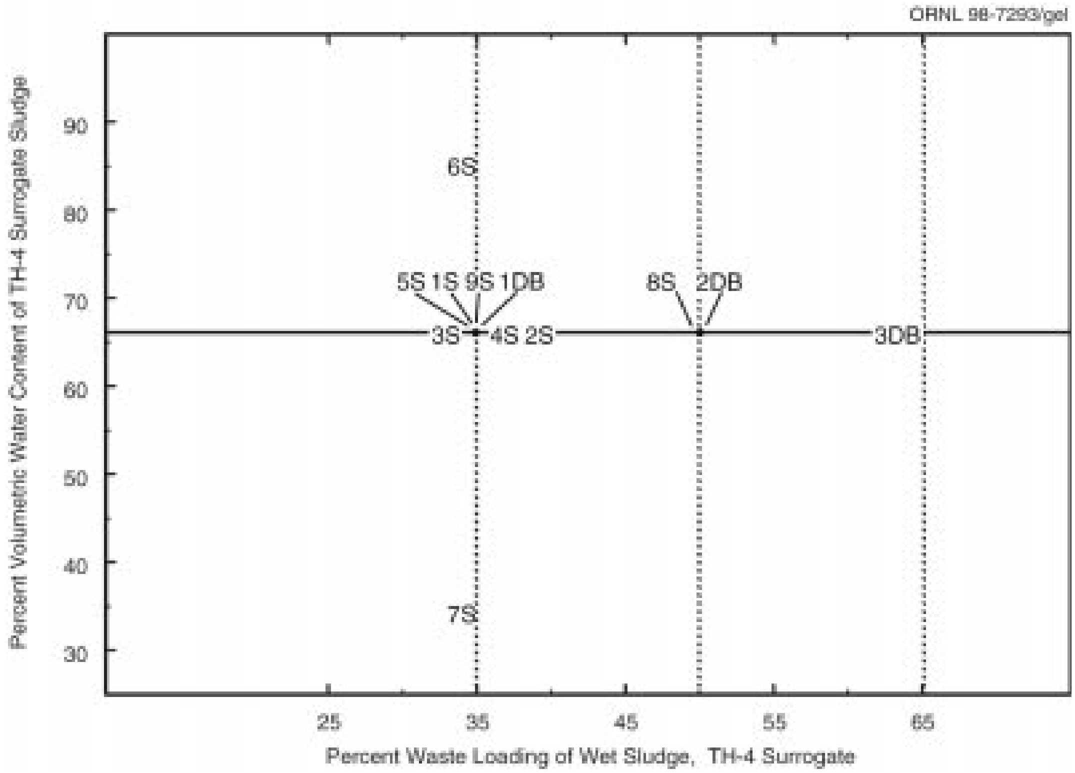

Fig. 6.1. Volumetric water content vs percent waste loading of wet sludge used in 1998 bench-scale tests with GAAT tank TH-4 surrogates.

- Sample 8S and 2DB are superimposed over each other in Fig. 6.1 at a water content of 66% and waste loading of 50%. These sludge waste loadings would occur if there was less freeboard in tank TH-4 or there was a major failure in the field pumping equipment. Both situations are easily controlled or verifiable in the field, and therefore, are a remote possibility.

- Sample 3DB represents the highest waste loading attempted during the 1998 bench-scale study, 65% waste loading and 66% water content.

The other difference between the nine sensitivity test samples (1S and 9S) and the specimens made with the Halliburton bulk dry blend (1DB, 2DB, and 3DB) is that there was a small amount of supernatant water introduced into the sensitivity test samples.

6.4 SENSITIVITY TESTING: DATA ANALYSIS

The percentages of grout mix water, dry blend, and surrogate sludge listed in Table 6.6 need to be combined into a single uniform mixture in order to evaluate the influence that the variation of the 12 mixtures have upon the properties of the treated sludge. Mass balance calculations were performed in order to obtain the composition of the final mixture (treated sludge). The data listed in Table 6.6 have calculated values beneath each of the measured data points. The calculated values represent back-calculated data obtained from the mass balance calculations. The back-calculated values and measured data for each of the 12 tests listed in Table 6.6 are within a few tenths of a percent of each other. The agreement between the back-calculated data and actual data provides a check of the accuracy of the calculations of the final composition of the mixture.

The leach resistance and mechanical properties of the treated waste are strongly linked to three main factors:

1. Type of waste, including items such as waste loading, concentration of dry sludge particles, and volume of the liquid phase of the waste

2. The amount of water in the final monolithic structure which comes from grout injected water, pore water in the sludge, and supernatant

3. The amount of treatment agents (slag, fly ash, and cement)

The data in Table 6.7 have been grouped into quantities that control the characteristics of the monolith.

- The clay portion in column 4 is indicative of the amount of IRPC and bentonite in the final monolith. The calculated variation in composition is small and ranges between 2.4 to 4.4% of the entire monolith. This small clay portion was able to control any free-water release. Samples 1S, 3S, 5S, 7S, 9S, 1DB, and 2DB had 0% free-water release after 2 days. Samples 8S and 3DB had the maximum water release of 1.2% after 2 days.

- The total water quantities in column 5 represent the contributions from the grout water, pore water within the sludge, and any supernatant. The values vary from 37.2 to 46.1%. This represents about a 25% variation in monolith water content.

- The dry sludge column represents the best estimate of the concentration of the solid phase of the surrogate within the entire monolith. The highest solids concentrations occur for samples 3DB (33%) and 2DB, 7S, and 8S (26%).

- The pozzolan fraction (column 7) represents the concentration of the slag, fly ash, and cement in the final monolith. These materials are directly related to the level of treatment of the sludge.

6.4.1 Dry Sludge and Levels of Treatment in TH-4 Monolith

The percentage of dry sludge in each of the 12 mixtures presented in Table 6.7 was plotted in Fig. 6.2 vs the water-to-pozzolan (W:P) ratio. The W:P ratio was selected because it represents the concentration of the treatment agents within the monolith. A low W:P ratio (below 1.0) indicates more concentrated treatment agents in the monolith compared with a high value (above 1.75).

Because the behavior of treated sludge is strongly influenced by the concentration of the contaminants and level of treatment, a clearer analysis of the data can be performed if the samples are grouped into categories with similar sludge loading and treatment. Examination of the data in Fig. 6.2 produced the following four groupings:

1. Most probable sludge solids and most probable level of treatment
2. Most probable sludge solids and lower degree of treatment
3. Concentrated sludge solids and lower degree of treatment
4. Concentrated sludge solids and lowest degree of treatment

A detailed discussion of these groupings follows.

Table 6.7. Composition of final mixtures, measured strength and leach resistance, TH-4 surrogate sensitivity tests 1998

	Estimated composition of final monolith							Measured strength and leach resistance					
								TCLP extract results				ANS16.1 diffusion[b]	
Test ID[a]	Monolith density (g/cm³)	Grout vol (gal)	Clay (%)	Total water (%)	Dry sludge (%)	Pozzolan fraction (%)	Water to pozzolan ratio	Strength (psi)	Cr (ppm)	Pb (ppm)	Hg (ppm)	Sr-85	Cs-137
1S	1.43							580	0.01	0.0140	0.0003	9.2	10.9
Calc.	1.53	8,400	4.1	41.4	17.9	36.6	1.13						
2S	1.36							45	0.071	0.0820	0.0065	8.9	10.4
Calc.	1.48	7,700	3.6	44.8	19.4	32.2	1.39						
3S	1.47							841	0.01	0.0140	0.0009	9.1	11.0
Calc.	1.58	9,100	4.4	38.0	16.5	41.1	0.92						
4S	1.37							20	0.02	0.0140	0.0003	8.7	10.1
Calc.	1.50	8,100	4.2	43.2	18.6	33.9	1.28						
5S	1.46							800	0.01	0.0140	0.0001	9.3	11.0
Calc.	1.56	8,750	4.1	39.8	17.2	38.9	1.02						
6S	1.27							355	0.01	0.0140	0.0001	8.7	10.5
Calc.	1.53	8,350	4.0	46.1	13.2	36.7	1.26						
7S	1.62							0	0.02	0.0400	0.0008	9.5	10.0
Calc.	1.53	8,350	3.9	33.0	26.4	36.6	0.90						
8S	1.33							0	0.163	0.0300	0.0007	ND	ND
Calc.	1.45	4,600	2.7	46.1	26.1	25.1	1.83						
9S	1.65							1370	0.01	0.0140	0.0002	9.4	11.2
Calc.	1.56	8,100	3.9	41.4	18.0	36.6	1.13						
1DB	1.50							1788	0.014	0.014	0.0005		
Calc.	1.59	8,350	4.4	37.2	17.9	40.5	0.92						
2DB	1.40							209	0.082	0.029	0.0007		
Calc.	1.53	4,450	3.4	39.9	25.6	31.1	1.28						
3DB	1.36							0	1.794	0.066	0.0000		
Calc.	1.48	3,000	2.4	42.5	33.3	21.8	1.95						
									0.86	0.37	0.025		

[a]Calc. = calculated values.
[b]ND = not determined.

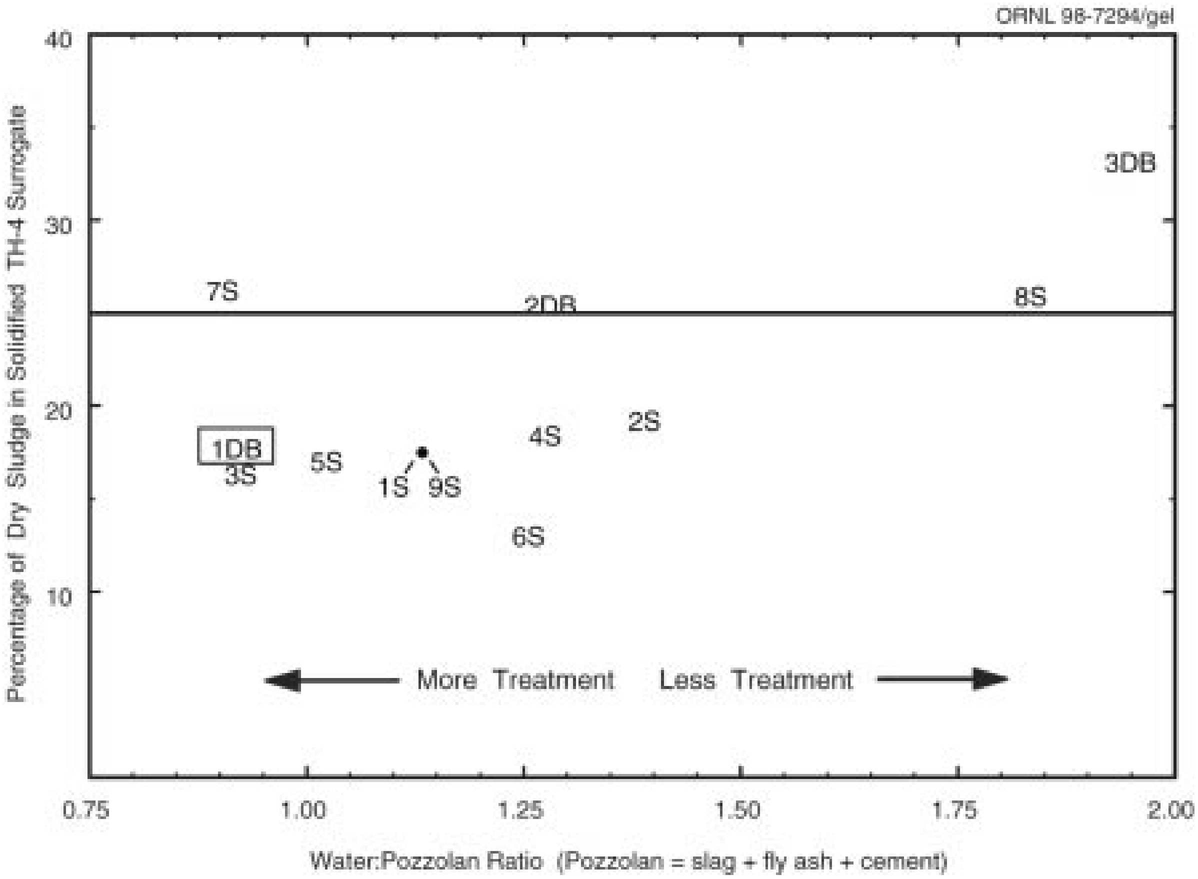

Fig. 6.2. Comparison between percentage of TH-4 surrogate dry sludge and water: pozzolan ratio in final monolith.

6.4.1.1 Most probable sludge solids and most probable level of treatment

The data in Fig. 6.2 for sample number 1DB represents the most likely combination of dry sludge solids (18%) and concentration of treatment (W:P = 0.90) to be formed in GAAT TH-4. Sample 3S is essentially the same as 1DB with the exception of the type of slag used in the preparation. Sample 1DB was made from the bulk-blended dry blend prepared by Halliburton during the cold field demonstration. Sample 3S was prepared with ORNL's Holnam slag.

Samples 1DB and 3S represent the most probable situation for GAAT TH-4. This grouping of formulations eliminated many uncertainties in the in situ treatment process as indicated by the following:

- GAAT TH-4 sludge surrogate contains more concentrated contaminants of concern than the actual tank sludge (see Table 6.1)
- Measured volumetric water content was obtained on actual samples, as was depth of supernatant
- Sludge loading of 35% is assured because the freeboard in the tank is known, and field controls on the MPI™ injection will assure that gross levels of treatment agents are uniformly intermixed with the sludge

Although a sensitivity study usually examines a potential range around the most likely field situation, this could not be done in this case. The ability to mix the viscous grout at more concentrated levels than 1DB and 3S was not possible with the available laboratory equipment. Furthermore, the most concentrated grout was injected in the field and proved to be a successful formulation. The only variability that could be examined during the sensitivity study was having a more concentrated sludge at lower degrees of treatment

6.4.1.2 Most probable sludge solids and lower degree of treatment

Eight out of twelve samples (1S, 2S, 3S, 4S, 5S, 6S, 9S, and 1DB) plotted in Fig. 6.2 contained about 18% dry sludge solids. Six of the samples had less treatment within the final mixture when compared with sample 1DB, whereas sample 3S was nearly identical to 1DB. Therefore, when evaluating the performance of all eight samples, the influence of the sludge solids can be eliminated as a variable. Any difference in the treated sludge’s properties can be directly linked to the level of treatment or type of slag used.

6.4.1.3 Concentrated sludge solids and lower degree of treatment

Two samples were prepared at about 25% dry sludge solids, 7S and 2DB. The treatment level for sample 7S is comparable to that for samples 1DB and 3S, whereas the concentration of pozzolan in the monolith is lower for sample 2DB. It should be anticipated that the level of treatment in sample 7S would provide for better performance than that represented by sample 2DB. Again, the other difference between 7S and 2DB is the type of slag used. Sample 7S was prepared with the Holnam slag, whereas sample 2DB was prepared with the slag purchased by Halliburton from Lone Star Cement (i.e., the cold field demonstration slag).

6.4.1.4 Concentrated sludge solids and lowest degree of treatment

The concentration of the dry sludge solids and high W:P ratio (lowest degree of treatment) for samples 8S and 3DB plot at the most extreme levels for any data shown in Fig. 6.2. These two samples represent 25 to 33% sludge solids at low treatment levels (W:P of about 1.90). This is about twice as much sludge solids with half as much treatment when compared with sample 1DB, which is the most probable situation expected in GAAT TH-4. Samples 8S and 3DB should have the lowest performance in terms of mechanical properties. It will be shown that the mixtures for samples 8S and 3DB could immobilize the RCRA metals below TCLP treatment standards. Therefore, mechanical strength alone is not a good precursor for leach resistance.

6.4.2 Percentage of Pozzolan in Monolith

The above groupings only provide a qualitative indication of the levels of treatment within the various grout/surrogate mixtures. The calculated percentage of pozzolan in the monolith will allow better quantification of the level of treatment to performance of the treated sludge. The percentages of pozzolan for the twelve mixtures are plotted in Fig. 6.3 vs the W:P ratio (these axes allow easier comparison between the two data sets in Figs. 6.2 and 6.3).

A linear relationship is shown in Fig. 6.3 between the percentage of pozzolan in the entire monolith and water to pozzolan concentration ratio in the monolith. The linear correlation factor is 0.96 for the data in Fig. 6.3. The greatest amount of pozzolans (40%) in the monolith at the most concentrated levels (W:P = 0.90) occurs for samples 1DB and 3S. These data represent the most likely situation for the actual GAAT TH-4.

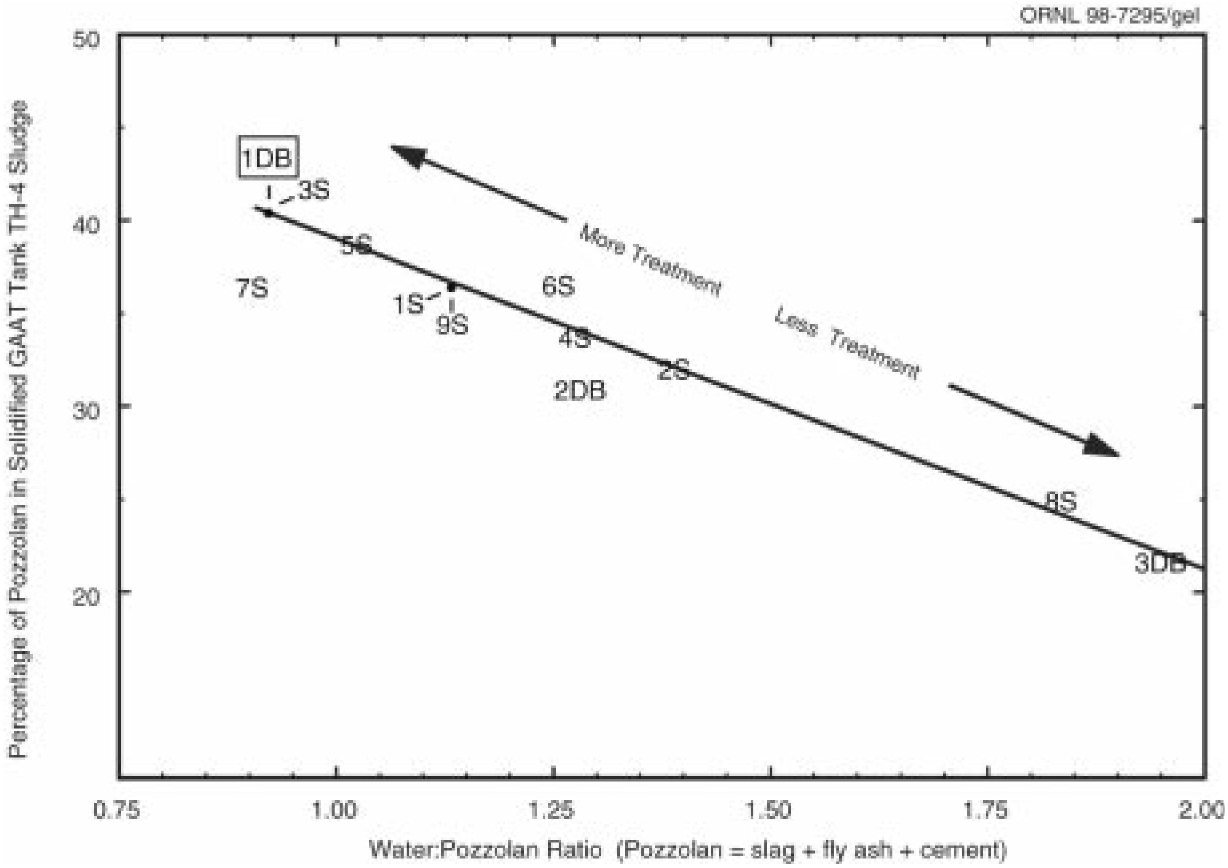

Fig. 6.3. Comparison between percentage of pozzolan and water:pozzolan ratio for various solidified TH-4 surrogate samples.

The remaining data in Fig. 6.3 occur below the data for samples 1DB and 3S. The other samples with the most probable sludge concentration (18%) vary in a decreasing order, as 5S, 9S, 1S, 6S, 4S, and 2S. It is anticipated that the mechanical strength of these samples will vary directly as listed, with the possible exception of sample 9S. This mixture was prepared with only slag, which should increase the strength over samples prepared with half slag and half fly ash.

The two samples with 25% sludge solids (7S, 2DB) contain slightly different levels of treatment with sample 7S having more pozzolan than 2DB, 37% vs 31%, respectively. The mixture represented by sample 7S should have a higher strength than sample 2DB.

6.5 MECHANICAL STRENGTH AND LEACH RESISTANCE OF TREATED TH-4 SURROGATE SLUDGE

The primary reason for performing treatment of the GAAT sludges is to prevent any future migration of the contaminants of concern out of the tank and into the environment. Established UTS for the various RCRA metals exist. Furthermore, mass transport studies performed at ORNL indicate that the strontium and cesium can be immobilized for at least four half-lives (suggested design life of treatment), if the diffusion coefficient is on the order of about 10 or higher.

Strength criteria for the grouted sludge have not been specified. A strength function of the monolith would be to resist any future inward movement of the gunite tank walls. However, this does not require any shear strength related to cementation of the treated sludge. Merely having a consolidated monolith of loose solids with a density above the unit weight of water should be adequate for long-term tank-wall stability issues. The unit weights for all the samples listed in Table 6.7 vary from a low of 1.27 g/cm^3 (79 lb_m/ft^3) to a high of 1.65 g/cm^3 (103 lb_m/ft^3), which is soil-like. Therefore, the tank walls should be structurally stable over the design life of the treatment.

The following sections present the results from measuring the unconfined compression strength, leachability of RCRA metals, and diffusion resistance of the treated sludge.

6.5.1 Unconfined Strength vs Levels of Treatment

The unconfined compression strength of the twelve grout/sludge mixtures was measured at various time intervals. The average values presented in Table 6.7 (column 9) were measured after 28 to 40 days of curing. The measured values of strength are plotted in Fig. 6.4 vs the W:P ratio. The discussion covering the mechanical properties of the various samples will follow the order of the groupings established above for the amount of sludge and treatment in the final mixture.

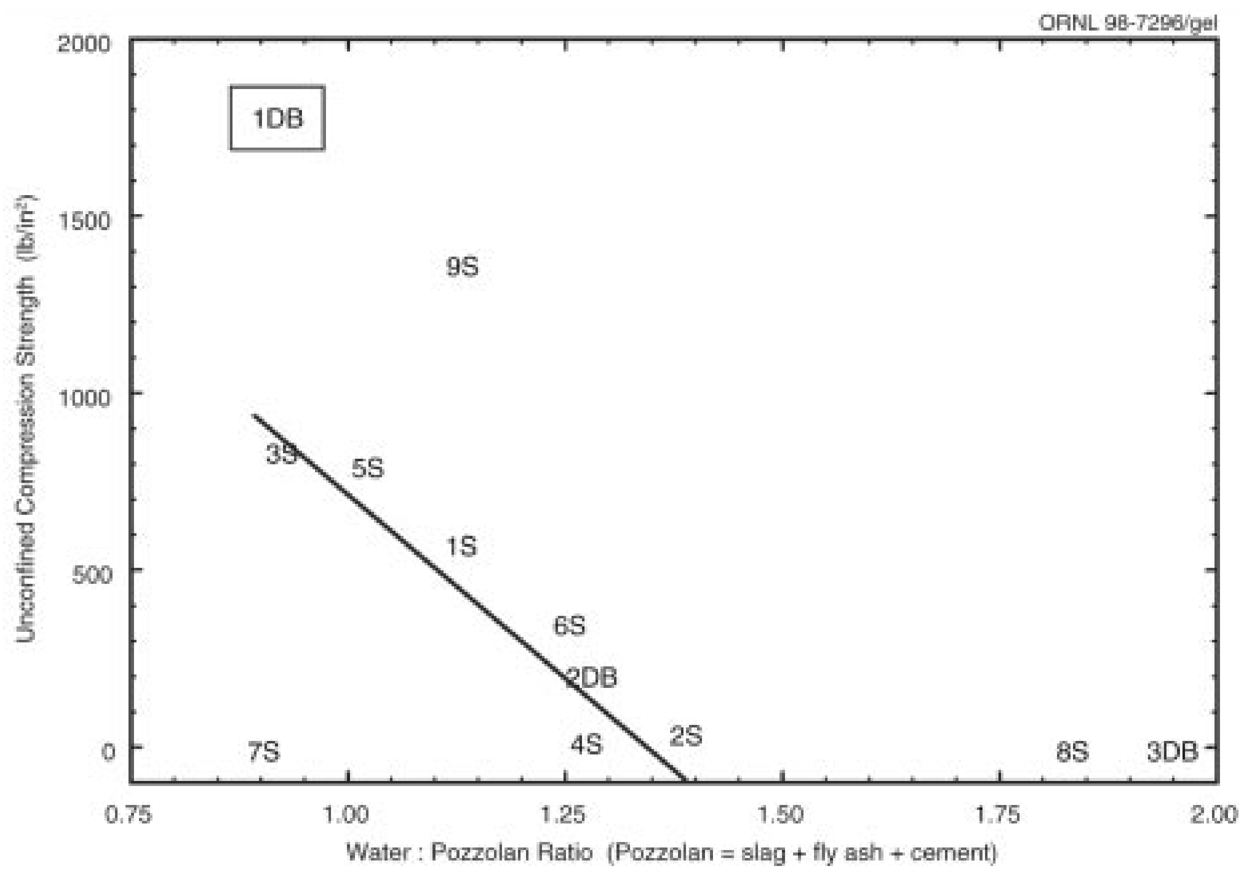

Fig. 6.4. Comparison between unconfined compression strength and water:pozzolan ratio in TH-4 solidified surrogate.

6.5.1.1 Most probable sludge solids and most probable level of treatment

The data point in Fig. 6.4 for sample 1DB (representing the cold field demonstration data) has the highest unconfined strength at about 1,800 psi. Sample 3S has a strength of about half this amount at 841 psi. The only major difference between these two samples was the type of slag used to prepare the specimens. The chemistry of these two slags was not examined during the 1998 bench-scale study but should be explored in the near future. A set of guidelines are needed for selecting the “most appropriate slag for use during full-scale production remediation.

6.5.1.2 Most probable sludge solids and lower degree of treatment

In Section 6.4.2, it was predicted that the rank ordering of the strengths of the samples with the 18% dry sludge solids would be 3S, 5S, 9S and 1S, followed by 6S, 4S, and 2S. The straight line drawn through these data points in Fig. 6.4 is inversely correlated at a high level $R = -0.95$). The only sample that falls outside the correlation line is sample 9S. Reference to Table 6.6 indicates that sample 9S was prepared with only slag and zero percent fly ash. The more typical ratio is to use equal amounts of slag and fly ash. The difference in mechanical strength between samples 1S and 9S is directly related to the increase in the slag in 9S. It appears that doubling the percentage of slag causes a doubling of the mechanical strength of the final mixture, from 580 psi (1S) to 1370 psi. (9S).

6.5.1.3 Concentrated sludge solids and lower degree of treatment

Because the relative amounts of dry solids for samples 7S and 2DB were similar (about 25%), it was believed that sample 7S would have a higher strength, because 7S had more treatment in the final mixture when compared with sample 2DB. The strength data for these two samples plotted in Fig. 6.4 do not hold for this prediction. Although sample 7S consolidated into a cohesive mass, it did not achieve any measurable unconfined compression strength after 42 days (i.e., 0 psi strength). There are several possibilities for this occurrence.

- There were mistakes in the laboratory during preparation of sample 7S

- There is a problem with the Holnam slag at 25% dry solids and above. However, the Lone Star Cement slag used by Halliburton during the cold field demonstration was able to achieve 200 psi strength (2DB), with less treatment (31% pozzolan) and more water (37%) in the final mixture than the corresponding values for sample 7S (see Table 6.7). The testing for sample 7S should be repeated with Holnam and Lone Star Cement slag to verify the results.

It will be shown in Section 6.6, that sample 7S was able to perform very well with respect to immobilizing the RCRA metals and producing a diffusion resistant mixture for strontium and cesium. The immobilization of the contaminants of concern are the key performance requirements for the treatment of the sludge. This can be accomplished by a soft consolidated mass with no cementation strength.

6.5.1.4 Concentrated sludge solids and lowest degree of treatment

After 42 days the two samples with the highest concentration of dry sludge solids and lowest amount of treatment (8S and 3DB) did not achieve an initial set. The data plotted in the lower right-hand side of Fig. 6.4 is at 0 psi for these two data points.

The causes for no cementation strength developing could be related to the following:

- Need for more time (above 42 days) because of the low concentration of solidification agents (20% to 25% of the monolith composition). This is believed to be the most likely cause and could be easily proved by extending the cure time of these samples above 42 days.

- There is insufficient pozzolans in the mixture to achieve an initial set. Two different types of slag were used and neither slag produced an initial set.

Although there was no initial set for samples 8S and 3DB, they were both able to produce mixtures with good leach resistance.

6.6 TCLP LEACH TESTS AND ANS 16.1 DIFFUSION MEASUREMENTS

Each of the twelve mixtures listed in Tables 6.6 and 6.7 were subjected to TCLP leach tests. The untreated TH-4 surrogate sludge was characteristically hazardous for chromium and mercury. The measured concentrations of these RCRA metals are listed in the box insert in Fig. 6.5. All samples displayed in the figure had TCLP measurements below the listed UTS for mercury and lead. There was a single data point for specimen 3DB in which chromium was slightly above the UTS limit of 0.86 ppm.

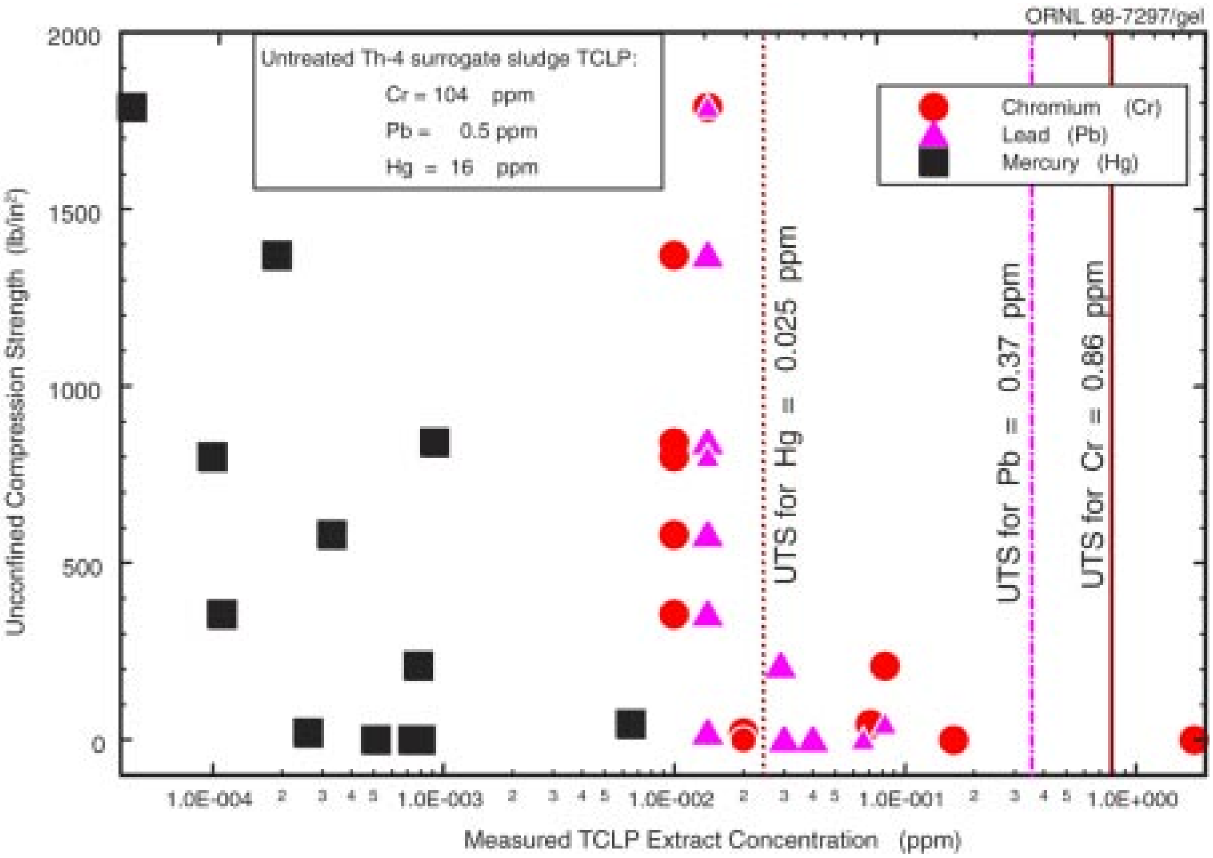

Fig. 6.5. Comparison between RCRA metal TCLP extract concentration and unconfined compression strength for the TH-4 surrogate sludge used in the 1998 ORNL studies.

The other observation that can be extracted from Fig. 6.5 is that there is not a strong correlation between the measured unconfined compression strength and leach resistance of the mixtures against chromium, lead, and mercury concentrations. Typical linear correlation factors were calculated at about 0.33 for leach resistance vs compression strength.

The level of treatment applied to a sludge is directly proportional to the amount of improvement in the performance of the treated sludge (i.e., better leach resistance). This is precisely the case when the TCLP extract data is plotted against the percentages of pozzolan in the final mixture. The data in Fig. 6.6 shows a linear relationship R = 0.8) for the reduction in chromium leaching vs the amount of treatment. Similar observations can be observed for lead (Fig. 6.7).

More scatter is observed in the data about the regression line drawn through the mercury TCLP data, as shown in Fig. 6.8. However, all mixtures were able to immobilize the mercury below the UTS of 0.025 ppm. Furthermore, all the soft samples (7S, 8S, 3DB) had mercury leach resistance comparable to that of sample 3S, which had nearly twice as much pozzolan (3S = 40% pozzolan in final monolith). The unconfined strength for sample 3S was 841 psi, whereas samples 7S, 8S, and 3DB were soft, consolidated masses with 0 psi unconfined strength (no cementation after 42 days).

6.6.1 Diffusion Resistance from ANS 16.1 Tests

The leachability indices for strontium-85 measured during ANS16.1 tests are summarized in Fig. 6.9 vs the percentage of pozzolan contained in the specimens prepared for the sensitivity study. All the samples shown in Fig. 6.9 had leachability indices between about 8.7 and 9.7. The most leach-resistant (D = 9.7) sample occurs for specimen 9S, which contained 50% slag in the grout (0% fly ash). Sample 9S had a strength of about 1370 psi. Sample 7S, which had zero unconfined compression strength, had a measured

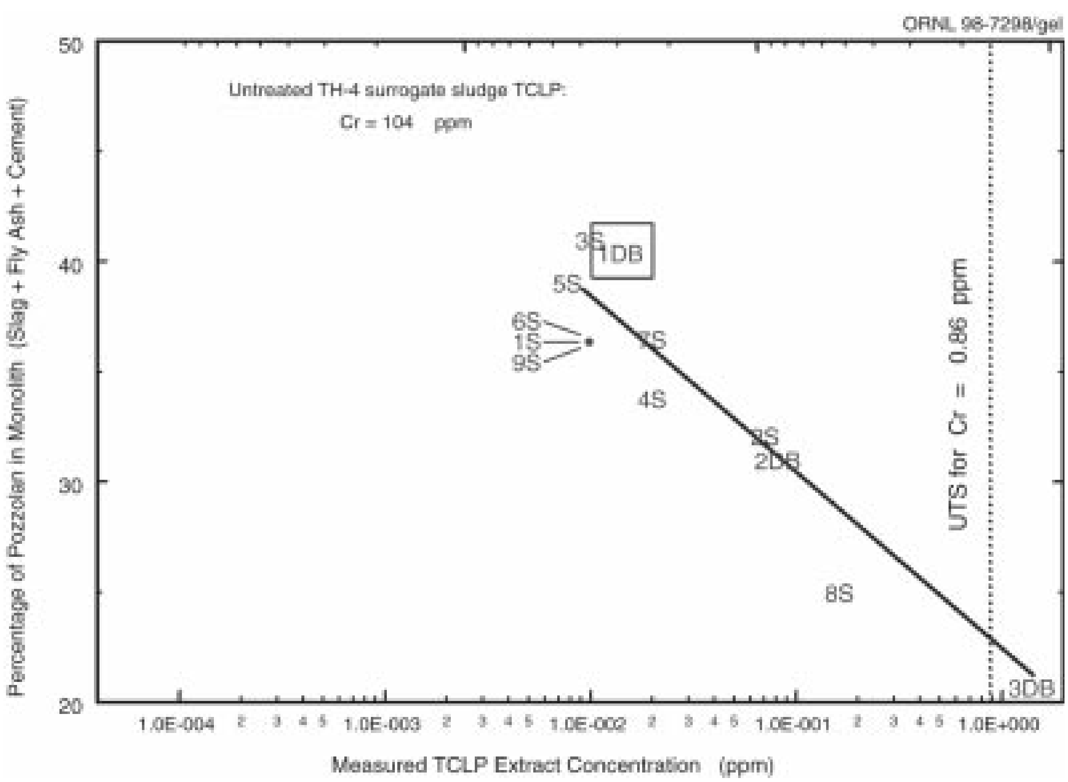

Fig. 6.6. Comparison between chromium TCLP extract and percentage of pozzolan in final mixture for the TH-4 surrogate sludge used in the 1998 ORNL studies.

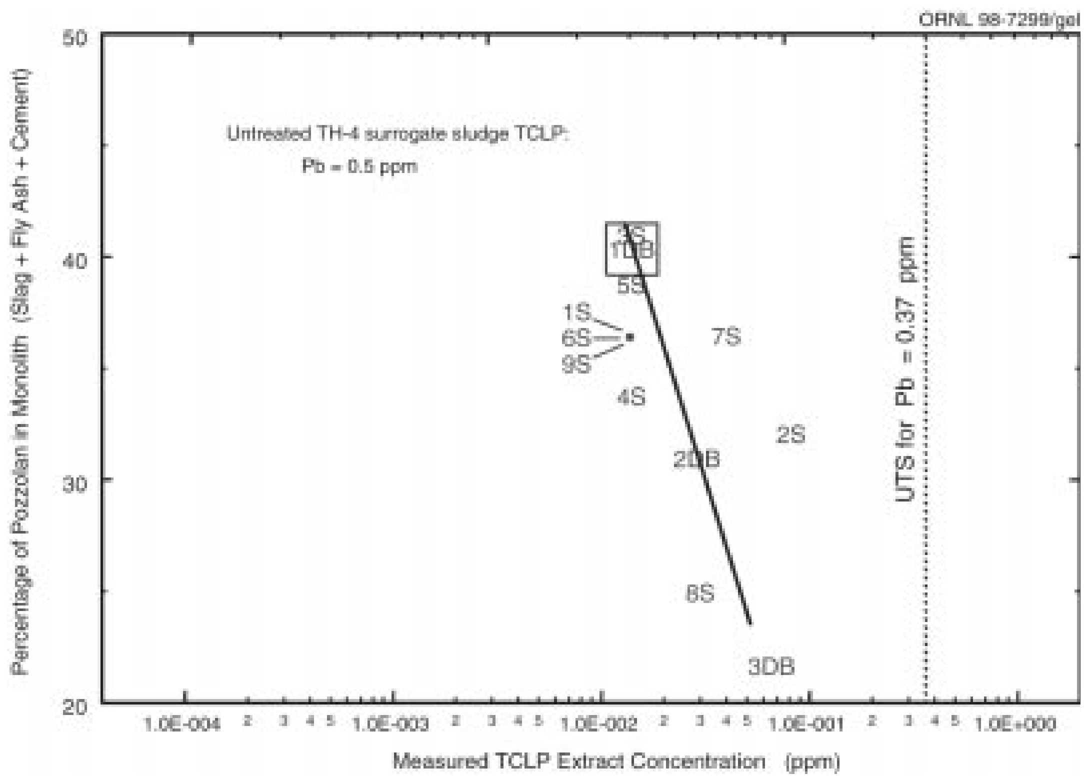

Fig. 6.7. Comparison between lead TCLP extract and percentage of pozzolan in final mixture for the TH-4 surrogate sludge used in the 1998 ORNL studies.

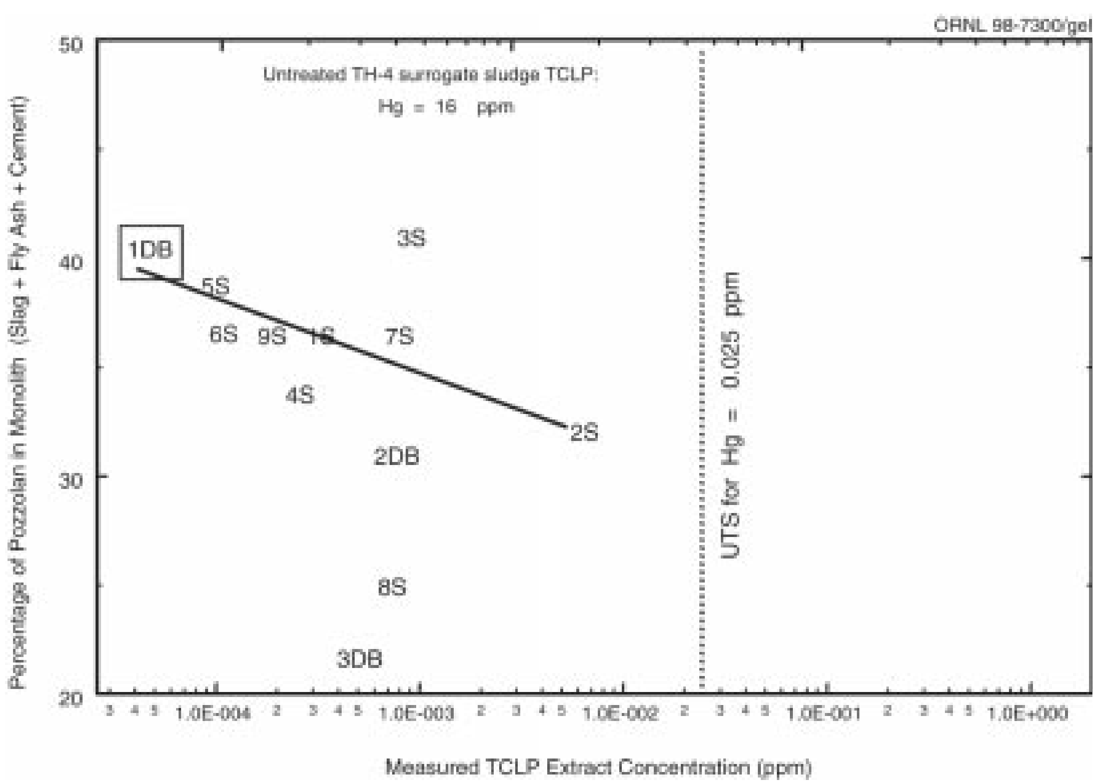

Fig. 6.8. Comparison between mercury TCLP extract and percentage of pozzolan in final mixture for the TH-4 surrogate sludge used in the 1998 ORNL studies.

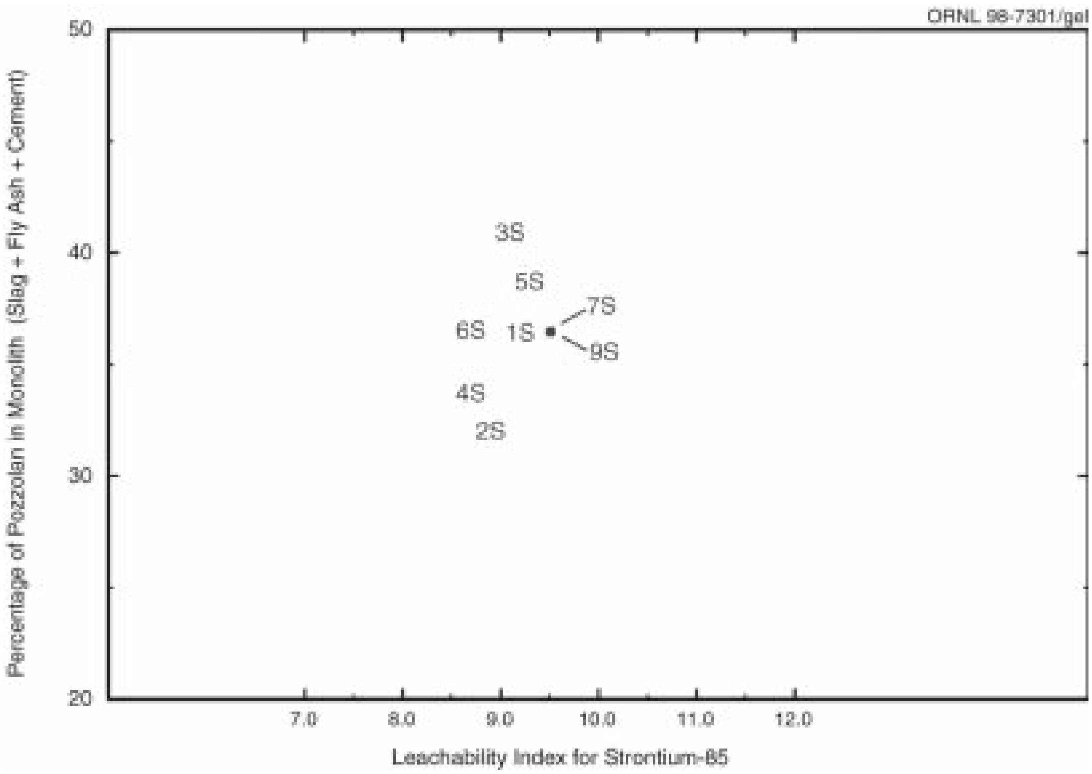

Fig. 6.9. Leachability index for strontium-85 in ANS 16.1 test and percentage of pozzolan in final mixture for the TH-4 surrogate used in the 1998 ORNL studies.

leachability index (D = 9.5) nearly the same as 9S. Sample 8S could not be formed into a cylinder for diffusion testing. No ANS 16.1 diffusion tests were performed on samples 1DB, 2DB, or 3DB.

The leach resistance for cesium-137 is plotted in Fig. 6.10 vs the amount of pozzolan in the final mixture. All leachability indices were above 10. The leach resistance of the specimens against the release of cesium-137 is dictated by the amount of IRPC clay in the mixture. All specimens plotted in Fig. 6.10 had IRPC contents of about 4% in the final mixture. Also, as the percentage of pozzolan increases from 33% to above 40% there is an increase in leach resistance.

6.7 HOT TESTING OF ACTUAL TH-4 SLUDGE SAMPLES

The real test of how well the ORNL grout formulation works was revealed when the actual sludge from GAAT TH-4 was treated with the ORNL grout formulation. The dry blend mixed at the Halliburton bulk plant was used for the hot testing of the TH-4 sludge samples.

The results from the strength testing indicated that the grouted hot TH-4 sludge achieved an unconfined compression strength of 1365 psi after 28 days (see Table 6.8). The preliminary results from TCLP extract analysis indicated that all RCRA metals (listed in Table 6.9) were below the UTS standards for the treated sludge.

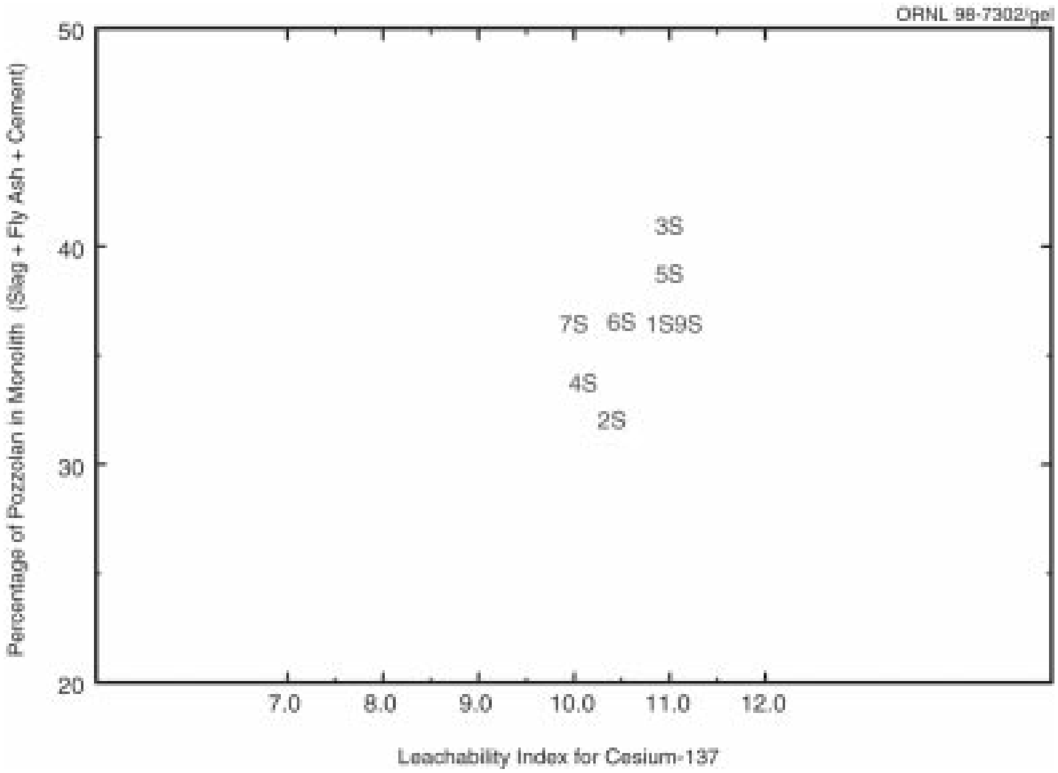

Fig. 6.10. Leachability index for cesium-137 in ANS 16.1 test vs percentage of pozzolan in the TH-4 surrogate used in the 1998 ORNL studies.

Table 6.8. Density, penetration resistance, and compressive strength of grout with TH-4 sludge (35 wt% hot test)

		Density[a]		
		267.1 g/169 mL = 1.58 g/mL		
Time (days)	Penetration resistance[b]			
	Test 1	Test 2	Test 3	Average
4	3 lb	2 lb	2 lb	2 lb
	120 psi	80 psi	80 psi	80 psi
7	68 lb	66 lb	57 lb	64 lb
	2720 psi	2640 psi	2280 psi	2560 psi
Time (days)	Compressive strength			
	Test 1	Test 2	Test 3	Average
7	889 lb	660 lb	776 lb	775 lb
	222 psi	165 psi	194 psi	194 psi
28	5650 lb	5250 lb	5480 lb	5460 lb
	1413 psi	1313 psi	1370 psi	1365 psi

[a]No free water.
[b]0.025 (1/40) square inch shaft.

Table 6.9. TCLP results for grouted and ungrouted GAAT TH-4 sludge sample

Component	GAAT TH-4 sludge sample (μg/mL)	Grout with TH-4 sludge (35 wt%) (μg/mL)	UTS[a] limits (μg/mL)
Ag	8.35×10^{-3}	1.34×10^{-1}	3.00×10^{-1}
As	$<8.35 \times 10^{-2}$	$<1.67 \times 10^{-2}$	5.00
Ba	1.34×10^{-1}	1.14×10^{-1}	7.60
Be	$<1.67 \times 10^{-3}$	$<1.67 \times 10^{-3}$	1.40×10^{-2}
Cd	$<1.25 \times 10^{-1}$	$<1.29 \times 10^{-1}$	1.90×10^{-1}
Cr	5.85×10^{-2}	$<4.51 \times 10^{-2}$	8.60×10^{-1}
Hg	$<3.34 \times 10^{-4}$	$<1.67 \times 10^{-2}$	2.50×10^{-2}
Ni	4.44×10^{-1}	$<9.02 \times 10^{-2}$	5.00
Pb	$<1.32 \times 10^{-1}$	$<1.67 \times 10^{-2}$	3.70×10^{-1}
Sb	$<5.95 \times 10^{-1}$	$<1.67 \times 10^{-2}$	2.10
Se	$<8.35 \times 10^{-2}$	$<1.67 \times 10^{-2}$	1.60×10^{-1}
Tl	$<8.35 \times 10^{-2}$	<1.40	7.80×10^{-2}

[a]UTS = universal treatment standards.

6.8 CONCLUSIONS

The sample formulation used during the cold field demonstration exhibited excellent waste immobilization and physical strength characteristics throughout all phases of the 1998 bench-scale tests. The small amount of CFR-3 dispersant had no impact on the strength, leachability, and diffusion resistance of the samples tested.

Large amounts (38 tons) of dry blend material can be mixed at a bulk-blending facility and produce a dry blend with qualities similar to those measured on laboratory-scale samples (i.e., can uniformly blend large bulk samples for use during production remediation of tank TH-4).

7. REMEDIATION OF GAAT TH-4 SLUDGE

Several of the major elements required for in situ remediation of GAAT TH-4 sludge have gone through extensive bench-scale testing and cold field demonstration. A robust grout formulation has been developed and shown to be effective for treating actual GAAT TH-4 sludge. The MPI™ system was able to safely deliver the grout and mix the solidification agents uniformly with a zeolite-type physical surrogate. This chapter will summarize all the activities that are required to implement the MPI™ system in the field for full-scale remediation of GAAT TH-4. A path forward is suggested for completing the remaining field activities required prior to actual deployment in GAAT TH-4.

Four primary construction stages are required for implementing the MPI™ process to remediate the 30 in. of sludge in GAAT TH-4. These stages correspond to the following items:

1. Preliminary site setup, which includes:
   - core drill initial penetrations into roof of tank and set steel casing
   - install plastic casing into tank sludge
   - visually inspect tank sludge using borehole camera prior to injection
   - reevaluate injection pattern based upon tank-specific observations

2. Field activities prior to mobilization of main equipment (pumps and grout plant)
   - lay down high-pressure piping
   - set up local containment
   - dry blend grout formulation and store in bulk facility on-site

3. Mobilization of high-pressure pumping equipment and grout plant:
   - connect pumps and grout plant to piping
   - run verification tests to check pumping equipment, piping, safety valves, and jetting tools
   - train operating crew for coordination to perform MPI™ process
   - finish installing any jetting tools into plastic casing not performed in Part 1
   - perform MPI™ injection

4. Demobilize site and dispose of grout not used during injection.

The activities required under Items 2, 3, and 4 have been successfully demonstrated during several cold demonstrations. The main work items that have not been demonstrated deal with the preliminary site setup, especially coring small-diameter holes in the roof of the gunite tank and installation of plastic casing and jetting tools. A closer examination of these items is required to obtain a clear understanding of any additional demonstration work that must be done prior to a hot deployment of the MPI™ system inside GAAT TH-4.

7.1 PENETRATIONS THROUGH GAAT TANK ROOF

The core drilling of the GAAT tank roofs and installation of tank riser pipes has previously been performed by MK Ferguson as part of the GAAT waste-retrieval efforts. A recent ALARA Workplan prepared by MK Ferguson (dated August 1997) has been attached in Appendix A of this report. Many of the activities listed in this workplan would be required for installation of the eight MPI™ injection lances through the roof of GAAT TH-4, as illustrated in Fig. 7.1. The major difference being that only

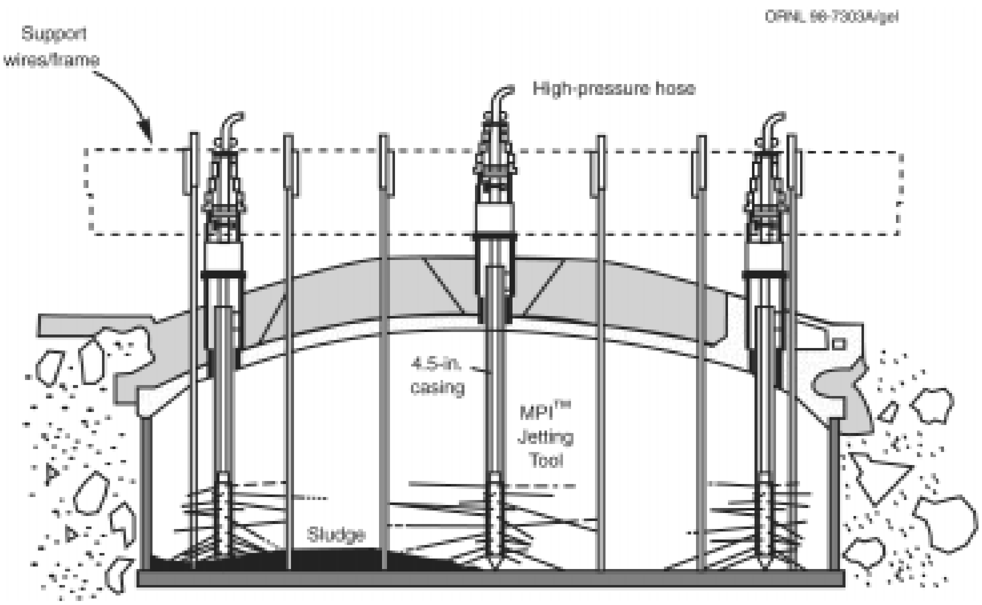

Fig. 7.1. Schematic of MPI™ jetting tool installation in a gunite tank.

6-in.-diameter core holes need to be drilled instead of the 31-in.-diameter hole required for the access for the robotic waste-retrieval systems.

The installation of a 31-in.-diameter hole currently requires a shallow excavation to be performed in which workers are down inside a shallow pit. The 6-in.-diameter access holes for the MPI™ system can be done using conventional core-hole-drilling techniques. Initially, a hollow-stem auger would be used to case the 6 ft of soil above the tank. This would generate significantly less spoil material when compared with the general excavation currently used to install holes in the GAAT tank roof. The auger would remain in the ground and act as the riser pipe to allow entry of the plastic casing used during the MPI™ process. Conventional rotary core drilling of the gunite tank roof would then be performed inside the hollow stem auger. The coring would be done dry, with no water or air for lubrication and removal of the drill cuttings. Drilling without water or air would help assure minimizing airborne releases of contamination and also minimize any secondary waste stream. Several drill bits may be consumed by this activity because the core bit will generate a significant amount of heat. The core bits would require disposal after use.

Once the core hole is drilled through the top of the gunite tank, the hollow-stem auger will be grouted into place to make a permanent seal between the tip of the auger and top of the GAAT tank. The plastic casing for the MPI™ process will be installed through the roof following the procedures discussed in the next section.

7.2 INSTALLATION OF PLASTIC CASING INTO SLUDGE

For the hot remediation work a lexan plastic casing will be used as the plastic liner for the borehole and guide tube for installation of the MPI™ jetting tools. This has advantages over the HDPE pipe currently used for shallow-buried-waste applications, because the lexan allows viewing of the tank sludge via a borehole camera. Some minor work must be done to adapt the drive system used for the HDPE plastic pipe to install lexan pipe. The drive shoe configuration used for the HDPE currently would place the jets at about 6 in. above the tank floor. The jetting tools used during the cold field demonstration have the lowest jets at 1.5 in. above the tank floor. The difference between the two distances (4.5 in.) is related to the current drive shoe used to advance the plastic casing through shallow buried waste.

The current drive system is a percussion system that hammers the plastic pipe into the waste. If the tank sludge does not contain saltcake, then the installation of the lexan should be relatively straightforward. A flat piece of plastic can be used for the drive shoe. Plastic is preferred because it is inexpensive and allows downward viewing by the borehole camera to visually confirm that the tip of the casing is in contact with the concrete tank floor. Furthermore, if severe resistance is encountered (e.g., saltcake layer), then the inner steel drive pipe can be hammered through the plastic shoe. This will assure that the jetting tools can be placed in contact with the tank floor. The steel drive pipe is also the MPI™ injection lance, which is abandoned inside the tank after remediation is completed.

A short series of tests to verify the redesign of the MPI™ drive shoe for tank application work is needed. It would be useful to verify the drive shoe's capabilities to be driven through zeolite-type material (sand), hardpan, and saltcake. Pacific Northwest National Laboratory (PNNL) has recommended various formulations to develop physical simulants for sludge, hardpan, and saltcake (Powell et al. 1997).

The importance of verifying the robustness of the drive shoe is related to the following:

1. Once the plastic casing is placed into contact with the tank floor, the tip of the casing provides some local restraint against movement of the jetting tool if nozzles clog or an eccentric jetting tool is used. Furthermore, if the drive shoe and plastic casing are driven intact, then the inner steel drive/jetting rod can be removed without fear of spreading contamination (plastic casing acts as a protective sheath covering the drive rod). It is reemphasized here that the current drive system with HDPE was driven 16 ft through miscellaneous shallow buried waste and experienced more than 1000 blows per foot from a 140-lb hammer dropped 30 in. Even after a total of 5000 blows of the hammer, the plastic casing and drive system were unaffected by the pounding. All the MPI™ tools could be installed through the plastic casing. The hammering of the plastic is similar to a standard penetration test that can be used to estimate the shear strength of the tank sludge prior to the injection.

2. After the lexan pipe is driven to contact the tank floor, the inner steel drive/jetting rods can be removed and replaced by a borehole camera. This would be used to perform an in-tank visual surveillance of the waste layering (structure, color variation, etc.) adjacent to the injection point. This information could help confirm and/or plan the strategy for installation of the other MPI™ injection points and also plan the MPI™ injection to be performed (selection of pressure, need for pretreatment, etc.). If extreme forces are required to drive in the plastic casing, and the casing is fractured, then the drive rod/jetting tool would not be removed in order to avoid exposing workers to potential contamination. Also, no borehole camera survey would be performed. Any force imbalance due to eccentric jetting configuration would have to be countered by a point of fixity above the tank roof. This fixity is easily achieved because there is about 6 ft of soil embedment above the GAAT tank roof. The cold field demonstration work proved that the jetting rods could be effectively supported in this manner.

The development of a drive shoe used to install the MPI™ injection lances through relatively thick sludge (30 in. in tank TH-4), would also benefit the use of the MPI™ system to treat residual heel material remaining inside a tank after bulk waste retrieval. A strategy for treating tank heel material is addressed in the following section.

7.3 MPI™ TREATMENT OF TANK HEEL MATERIAL

The ability of the MPI™ process to treat relatively thin layers (several inches) of residual material is related to the placement of the jet nozzles within a few inches of the tank floor. The jetting tools used during the Duncan, Oklahoma, cold field demonstration can be readily applied to this type of application because the jets are within 1.5 in. of the tank floor. The monodirectional jets can be used to disperse residual sludge, zeolite, saltcake, or hardpan. The cold field demonstration showed that waste with physical characteristics similar to zeolite can be kept in suspension and uniformly mixed into a uniform monolith. Test results reported by PNNL indicate that hardpan can have shear strengths upward of 150 kPA (20 psi). This is a relatively weak material that can be cut apart by the MPI™ monodirectional jets. Saltcake can have more concrete-like shear strengths (2,000 psi). This presents more of a challenge to cut and mix into the monolith. Although the MPI™ jetting technique can be used to cut and treat saltcake, the details of this application are beyond the scope of this technical memoranda.

The strategy for deploying the MPI™ jetting tools inside a tank containing residual heel material would take the following steps:

1. Evaluate video tapes of the bulk waste-retrieval process and estimate the physical characteristics of the heel material. This evaluation includes the review of mounded areas where there is locally concentrated contamination and rapidly settling material as well as determination of the general thickness of residual and general distribution of radioactivity.

2. Based upon the specific characteristics of the residual heel material remaining on the tank floor, design a layout of the MPI™ jetting tools to best cut, mix, and treat the residual waste. For the current discussion, the solidification agent of choice will be the ORNL slag–fly ash formulation because it has been proven to immobilize GAAT tank sludge at up to 37% waste loading. After bulk waste-retrieval, the waste loading of the residual heel material within the monolith will be significantly lower (5 to 10% range).

3. Because the volume of waste to be treated after exhumation is significantly less than that required for a whole-tank solidification campaign, it is consistent that less injection energy is required for uniform mixing of the grout and heel material. The results from the cold demonstration in which about 40% of the jet nozzles were clogged provides some insight. It is suggested that using low- and high-pass filters will totally eliminate nozzle clogging problems. The monolith could be effectively mixed using eight injection lances with only four jets each instead of eight per jetting tool. The only exception would be those jetting tools in which saltcake had to be pretreated. It is believed that these jetting tools would still require an eight-jet configuration.

4. Perform the MPI™ injection similar to that used during the cold field demonstration. In order to eliminate any aerosols as a result of jet spray in the air, a small amount of grout should be pumped into the tank prior to high-pressure injection. The level of the grout would only be a few inches, which is sufficient to submerge all the jet nozzles. The other modification from the cold field demonstration is that there may not be the need to use plastic casing. This would simplify the field activities and provide for a potentially safer working environment.

8. SUMMARY AND CONCLUSIONS

The bench-scale testing and cold field demonstration have paved the way for the hot deployment and remediation of GAAT TH-4. The combined efforts have helped to build confidence that the TH-4 sludge can be successfully remediated in situ. The bench-scale work discussed in this report showed that a wide variety of GAAT tank surrogate sludges and also actual sludge taken from GAAT TH-4 could be effectively treated at sludge loadings between 35 and 65%. Both RCRA metals and radioactive contaminants were effectively treated. The grout formulation used during the cold field demonstration performed at a superior level for all phases of the bench-scale tests. The small amount of CFR-3 dispersant mixed into the grout to improve the pumping characteristics of the viscous grout had no impact upon the strength, leachability, and diffusion resistance of the samples tested. The bulk blending (38 tons) of the ORNL dry blend had chemical qualities equivalent to those measured on small-scale laboratory samples prepared from individual constituents.

The cold field demonstration of the MPI™ process proved that it is a very robust jet delivery system that could form a uniform 32-ton monolith in about 8 min. Analytical data showed that a zeolite-type physical surrogate was uniformly mixed over the 40-in.-thick monolith without lifting the jetting tools off the tank floor. The other physical surrogates used in the cold field demonstration had cohesive characteristics with consistency similar to both GAAT TH-4 and Hanford sludge. Both cohesive surrogates were easily intermixed into the monolith. The grout formulation exhibited good thermal properties as indicated by the maximum internal core temperature of the monolith of about 100°F.

The simplicity of the MPI™ process allowed the treatment of the physical surrogates to be done remotely with all capital equipment and workers in the safety of a work zone about 200 ft away from the test tank. The field quality controls implemented during the MPI™ cold field demonstration showed that the formulation specified in the ORNL laboratory could be reproduced accurately in the field. The bulk-blended grout used during the cold demonstration had chemical properties that were shown to be effective in treating GAAT surrogate sludge and also actual sludge taken from GAAT TH-4.

The only remaining element needed for demonstration is the modification to the MPI™ drive shoes required for installation of the plastic casing used during the MPI™ process. This redesign should go smoothly because it is based upon a current design that has been used very successfully for shallow buried waste applications.

9. REFERENCES

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APPENDIX A

ALARA WORKPLAN—SOUTH TANK FARM SITE DEVELOPMENT

APPENDIX A: ALARA WORKPLAN—
SOUTH TANK FARM SITE DEVELOPMENT

Scope

- The purpose of this plan is to address the radiological concerns with the work in the South Tank Farm Site Development as described in Engineering documents of Work Order 40141.

- This ALARA Plan is part of the general safety requirements of the Activity Hazards Analysis (AHA) completed for this work order. Following the general safety requirements of the AHA are vital to the successful practice of ALARA.

- Radiological Work Permits shall be issued to implement Radiological Protection Program requirements and this plan.

- Consideration has been given to the applicable sections from Environmental Safety & Health Procedure 3A-4.110, Work Preparation, and the Radiological Control Manual concerning ALARA Work Plans and Radiological Work Permit Requirements.

- The following activities will be conducted in and near radiological areas, that includes Radiation Areas, Contamination Areas, High Radiation Areas, High Contamination Areas. Due to the extreme radiological conditions in the tanks and piping, there is a high risk that Air borne Radioactivity Areas may be created. Fission products, Uranium, and Tansuranics have all been reported in the characterization documents.

- Unless otherwise directed herein, MK-F HP Procedures shall be considered as the best method of implementing ALARA and are the foundation for the success of this ALARA Plan. Practices and requirements in the procedures are not necessarily repeated in this ALARA Plan.

Summary of Work Activities

Pre-job & Mobilization

As areas are turned over to construction, MK-F HPs will conduct Pre-job surveys of the intended work area. Verify postings and boundaries are correct, and establish the needed entrance and exit facilities.

Some heavy equipment, (back hole, crane, etc.) will be located near or within the posted radiological areas.

Tank Riser Installation

Eleven risers will be installed on top of six Gunite tanks. Two each on tanks W5, W6, W7, W8, and W9. One riser will be installed on tank W10. Preferred order of work would be from low dose rate tanks to the higher dose rate tanks to build work crew experience before attempting the higher dose rate tanks.

Each riser will require excavation through back fill over the tanks of approximately six feet. As the excavation progresses, dose rates are expected to rise, and may surpass 100 mrem/h. The contents of the tank are concentrated radioactive wastes that are estimated to yield 1 mrem/h per gram at one foot.

The top of the tank will be prepared for the installation of the riser. A 31" hole will be drilled into the top of the tank. The risers will be positioned, and grout will be placed around the riser to secure the riser. The top of the riser will be blanked awaiting next stage of the Gunite Tank Program, which is not with in the scope of this work order and ALARA plan.

Modify Tank HEPA System

Modifications to the tanks' off gas system will be made to accommodate new platform and support equipment. Most of the area is a Radiation Area and it is expected that the internals of the existing system to be highly contaminated.

Site Utility Improvements

Electrical and water utilities will be provided for the platform. Some excavations will be required, and there is a reasonable probability of encountering elevated radiation and/or contamination.

Grounding rods for lightening protection will be installed. There will be several ground rods driven into the ground and connected to the platforms.

Platform Installation

The site will be graded, and gravel fill will be used to create a radiologically clean surface for the installation of the permanent platform. The footings for the platform are not expected to penetrate the gravel base. A crane will be used to place the steel structural pieces. Risers may be roped off and posted Radiation Area and/or Internal Contamination.

ALARA Concerns

Dose

Highest dose rates are expected at the surface of the tanks. As excavation progresses toward the tanks, radiation monitoring shall be performed, and controls adjusted to meet the current conditions as required by procedure.

Excavations around the tanks have a potential of uncovering contaminated soil with measurable dose rates. Doses in the attached estimates are based on expected conditions. Surveys will continue to monitor for changing conditions.

Total dose for this job is estimated to be 1800 mrem. The ALARA goal for the total exposure is 1300 mrem, or 72% of the estimate. The details of this estimate are provided in Attachment A. This estimate is based on survey data available at the time of preparing this plan, and estimated durations of individual tasks and craft assignments.

Contamination

Areas of high contamination are expected in the ground and inside pipes, tanks, and ventilation systems. Initial penetrations of pipes, tanks, and ventilation shall be done under caution. RWPs for such activities will address PPE and respirator use. Excavations shall be monitored and controlled as radiological conditions may require.

Airborne Radioactive Material

Although airborne radioactivity is not normally observed in this area, construction activities will create dust, which may contain radioactive material. Air monitoring shall be done to monitor occupied areas that are susceptible to airborne material from construction activities. Placement and duration of the sampling shall be determined by the lead HP on the job in accordance with procedure to assure range and magnitude of any airborne radioactive materials is identified and controlled, including the use of respirators, enclosures, and HEPA air handlers.

Due to the presence of transuranics in the systems and soil and therefore the potential for airborne transuranics, internal doses may exceed 100 mrem CEDE.

ALARA Actions

Time

- Minimize time in the radiation and high radiation areas.
- Practice work to be done in the radiation areas. Utilize training and mock ups to become familiar with the work to be done.
- Entries into High Radiation Areas shall be timed or controlled by alarming dosimeters.

Distance

- Utilize low dose waiting areas when not actively involved in work evolution.
- Complete as much work as reasonable in low dose areas.
- Use longer tag lines with lifts.
- Use remote controls of drilling equipment or additional shielding for operator.
- Radworkers should understand sources of radiation, and position themselves to minimize dose.

Shielding

- Utilize existing shielding, such as soil, walls, and structures, as much as is reasonable.
- Install temporary shielding where reasonable, considering the dose received for shielding installation and dose saved.

Misc.

- Housekeeping in general and be attentive to mobile sources of radiation and handle appropriately to minimize dose and the potential for the spread of contamination.

- Monitor for changing conditions, when in doubt, perform a survey.

- Each radworker is limited to 250 mrem under this ALARA plan. The MK-F Site HP Supervisor may grant extension up to 600-mrem total annual dose. Extension above 600-mrem total annual dose will require approval by the ORNL ALARA Steering Committee.

- Local HEPA ventilation shall be used during the penetrations of enclosed systems, manual welding and as radiological conditions may require.

- Catch all water drained from penetrations. Dispose of water as directed by LMER.

- HP, SSHO, and construction supervision shall conduct daily pre-job briefings.

- Doffing of protective clothing must always be done with care, minimizing the potential for personnel contamination or inhalation. In areas of alpha contamination, there is little tolerance with poor doffing practices because of the potential of large internal doses from extremely small amounts of alpha contamination.

- Due to the uncertainty of the number of pipes to be cut and capped, and their associated radiological conditions adjustments to this plan may be required. Should the radiological conditions exceed those described herein, work shall stop and the ALARA Plan revised/amended to address the new conditions. Such conditions are:

  — Dose rates 5 times greater than estimated in Attachment A, and the total dose of the task can not be met through on-the-spot ALARA actions, such as additional shielding or better work practices. Such on-the-spot actions should be documented in the daily activity log.

  — Total dose for the job exceeds the 1800 mrem estimate in Attachment A.

  — Projected dose for any task exceeds twice the estimated task dose in Attachment A.

  — Loss of contamination control evidenced by personnel contaminations or intakes.

Attachment A: ALARA dose estimates STF site development																			
		61	16	16	1	0	10	18	No. of workers at			250 mrem		4	2	1	0	1	3
									ALARA plan totals			1,798 mrem		820	348	4	0	72	554
			No. of craft workers										Collective dose by craft (man mrem)						
Task no.	Task description	Task location	Laborer	Pipefitter	Operator	Rigger	Electrician	HP	Dose rate (mrem/h)	Task duration (h)	Man-hours	Individual dose (mrem)	Task totals	Laborer	Pipefitter	Operator	Rigger	Electrician	HP
1	Pre-job survey											Task totals	2	0	0	0	0	0	2
		RA/CA						2	0.5	2	4	2		0	0	0	0	0	2
2	Mobilization											Task totals	12	8	0	0	0	0	4
		RA/CA	2						0.5	8	16	8		8	0	0	0	0	0
		RA/CA						1	0.5	8	8	4		0	0	0	0	0	4
3	Excavate at eleven riser locations											Task totals	1014	676	0	0	0	0	338
		RA/CA	2						1	88	176	176		176	0	0	0	0	0
		RA/CA						1	1	88	88	88		0	0	0	0	0	88
		HRA/CA	2						50	5	10	500		500	0	0	0	0	0
		HRA/CA						1	50	5	5	250		0	0	0	0	0	250
4	Core drill at eleven riser locations											Task totals	282	0	188	0	0	0	94
		RA/CA		2					1	44	88	88		0	88	0	0	0	0
		RA/CA						1	1	44	44	44		0	0	0	0	0	44
		HRA/CA		2					50	1	2	100		0	100	0	0	0	0
		HRA/CA						1	50	1	1	50		0	0	0	0	0	50
5	Install eleven new tank risers											Task totals	220	88	88	0	0	0	44
		RA/CA	2	2					1	44	176	176		88	88	0	0	0	0
		RA/CA						1	1	44	44	44		0	0	0	0	0	44
6	Cut and cap existing system lines											Task totals	24	0	16	0	0	0	8
		RA/CA		2					1	8	16	16		0	16	0	0	0	0
		RA/CA						1	1	8	8	8		0	0	0	0	0	8

Attachment A: ALARA dose estimates STF site development																			
		61	16	16	1	0	10	18	No. of workers at			250 mrem		4	2	1	0	1	3
									ALARA plan totals			1,798 mrem		820	348	4	0	72	554
			No. of craft workers										Collective dose by craft (man mrem)						
Task no.	Task description	Task location	Laborer	Pipefitter	Operator	Rigger	Electrician	HP	Dose rate (mrem/h)	Task duration (h)	Man-hours	Individual dose (mrem)	Task totals	Laborer	Pipefitter	Operator	Rigger	Electrician	HP
7	Modify tank HEPA system											Task totals	40	0	16	0	0	16	8
		RA/CA		2			2		1	8	32	32		0	16	0	0	16	0
		RA/CA						1	1	8	8	8		0	0	0	0	0	8
8	Install pit drywell extensions											Task totals	28	8	8	0	0	8	4
		RA/CA	2	2			2		1	4	24	24		8	8	0	0	8	0
		RA/CA						1	1	4	4	4		0	0	0	0	0	4
9	Grade site area/install aggregate base											Task totals	16	8	0	4	0	0	4
		RA/CA	2		1				1	4	12	12		8	0	4	0	0	0
		RA/CA						1	1	4	4	4		0	0	0	0	0	4
10	Platform removal and modifications											Task totals	24	16	0	0	0	0	8
		RA/CA	2						1	8	16	16		16	0	0	0	0	0
		RA/CA						1	1	8	8	8		0	0	0	0	0	8
11	Process water tie-ins											Task totals	24	0	16	0	0	0	8
		RA/CA		2					1	8	16	16		0	16	0	0	0	0
		RA/CA						1	1	8	8	8		0	0	0	0	0	8
12	Steam and air piping re-route											Task totals	24	0	16	0	0	0	8
		RA/CA		2					1	8	16	16		0	16	0	0	0	0
		RA/CA						1	1	8	8	8		0	0	0	0	0	8
13	Install platform lightening ground rods/cable											Task totals	40	16	0	0	0	16	8
		RA/CA	2				2		1	8	32	32		16	0	0	0	16	0
		RA/CA						1	1	8	8	8		0	0	0	0	0	8

Attachment A: ALARA dose estimates STF site development																			
		61	16	16	1	0	10	18	No. of workers at			250 mrem		4	2	1	0	1	3
									ALARA plan totals			1,798 mrem		820	348	4	0	72	554
			No. of craft workers										Collective dose by craft (man mrem)						
Task no.	Task description	Task location	Laborer	Pipefitter	Operator	Rigger	Electrician	HP	Dose rate (mrem/h)	Task duration (h)	Man-hours	Individual dose (mrem)	Task totals	Laborer	Pipefitter	Operator	Rigger	Electrician	HP
14	Install platform lightening ground rods/cable											Task totals	24	0	0	0	0	16	8
		RA/CA					2		1	8	16	16		0	0	0	0	16	0
		RA/CA						1	1	8	8	8		0	0	0	0	0	8
15	Install cable protection system											Task totals	24	0	0	0	0	16	8
		RA/CA					2		1	8	16	16		0	0	0	0	16	0
		RA/CA						1	1	8	8	8		0	0	0	0	0	8

APPENDIX B

SELECTION OF THE DRY BLEND ADDITIVES

APPENDIX B: SELECTION OF THE DRY BLEND ADDITIVES

The historical inorganic additives used for stabilization/solidification are Portland cement, fly ash, lime, and clay, but also include blast furnace slag, cement kiln dust, high alumina cements, natural pozzolans, masonry cements, special cements, and cement admixtures [Conner 1990; International Atomic Energy Agency (IAEA) 1993]. Conner cites the following reasons for the widespread use of these materials in treating wastes (Conner 1990):

- Relatively low cost
- Good long-term stability, both physically and chemically
- Documented use on a variety of industrial wastes over a period of at least ten years
- Widespread availability of the chemical ingredients
- Nontoxicity of the chemical ingredients
- Ease of use in processing (processing normally operated at ambient temperature and pressure and without unique or very special equipment)
- Wide range of volume increase
- Inertness to ultraviolet radiation
- High resistance to biodegradation
- Low water solubility
- Relatively low water permeability
- Good mechanical and structural characteristics

The International Atomic Energy Agency lists the following advantages and disadvantages of cement for the solidification of radioactive wastes (IAEA 1993):

Advantages

- Material and technology well known;
- Compatible with many types of waste;
- Most aqueous wastes chemically bound to matrix;
- Low cost of cement;
- Good self-shielding;
- No vapour problems;
- Long shelf life of cement powder;
- Good impact and compressive strengths;
- Low leachability for some radionuclides;
- No free water if properly formulated;
- Rapid, controllable setting, without settling or segregation during curing.

Disadvantages

- Some wastes affect setting or otherwise produce poor waste forms.
- pH adjustment of waste may be necessary.
- Swelling and cracking occur with some products when they are exposed to water.
- Volume increase and high density may develop.
- Excessive heat may develop during setting with certain combinations of cement and waste.
- Dust problems may occur with some systems.
- Equipment for powder feeding is difficult to maintain.

- Potential maintenance problems may result from premature cement setting, especially in the case of in-line mixers.

Portland cement, fly ash, Indian Red Pottery Clay (IRPC), ground granulated blast furnace slag, and bentonite were selected for use in this study. A brief history and reason for selection are presented in the following subsections for each material.

B.1 PORTLAND CEMENT

Portland cement, its composition, and its chemistry are discussed in great detail in several references and will not be discussed in detail in this report (Conner 1990; IAEA 1993; Lea 1970; Soroka 1979; Bye 1983; Ghosh 1983; Taylor 1990). The main points of interest for cement stabilization/solidification are the (1) normal high pH of cement matrices, (2) production of calcium hydroxide in normal cement hydration, and (3) strong binding matrix, resistant to advective water flow and leaching that interacts with and encapsulates the waste. Wastes are generally physically encapsulated heterogeneously in the calcium-silicate-hydrate (CSH) matrix, with the level of dispersion and homogeneity generally dependent on the energy and effort put into physically mixing waste and cement. Despite the inherent composite nature of cement waste forms, the wastes strongly interact with the cement, stabilizing contaminants as desired and sometimes interfering with cement hydration which is not desired. Although there is evidence that some contaminants are incorporated into the CSH matrix, the main stabilizing mechanism of cement waste forms are the high pH matrix, similar to the lime precipitation of metals in waste water treatment.

This high pH precipitation captures the majority of the RCRA metals and radionuclides. For example, the low solubility at high pH of copper, nickel, iron, cadmium, zinc, silver, and lead are illustrated in the published solubility curves with pH [Conner 1990; U. S. Environmental Protection Agency (EPA) 1987]. In general, these solubility curves pass through a minimum as the pH increases, meaning these metals actually start becoming more soluble with pH past a certain point, with the generation of complex hydroxide ions. The minimum solubility for these metals occurs in a pH range from about 9 to slightly more than 11. The normal production of calcium hydroxide during cement hydration and the presence of alkalis in the cement can produce a pore solution pH in the range of 12-13, well above the minimum solubility for most of these metals (Conner 1990). This combination (high matrix pH and increasing metal solubility at this pH level) can actually increase the leachability of some wastes after treatment. This is one reason neat cement pastes (i.e., pastes consisting only of mixtures of cement and water) are a poor choice for stabilizing wastes and why cement-fly ash combinations are almost always used. Fly ash consumes the calcium hydroxide produced during cement hydration, (1) moderating the matrix pH and (2) eliminating the large soluble portlandite crystals (these crystals dissolve upon immersion, leaving large accessible pores in the matrix, increasing porosity and leachability) found in neat cement pastes. Cementitious waste forms (typically, cement-fly ash) reportedly have a pH of about 11, much better suited for minimizing metal solubility (Armstrong and Klingler 1986). The solubility behavior of the RCRA metals in cement waste forms mimics these solubility curves to a certain degree, but differ enough to illustrate that "... factors other than hydroxide precipitation are in operation...." (Conner 1990; Cote 1986)

Cements are produced and sold in many forms, any of which may be suitable for stabilizing wastes. Portland cements are the most commonly available cements, typically locally available and cheap. The ASTM standards specify five standard Portland cements with optional properties available within each type (ASTM C 150-89) [American Society for Testing and Materials (ASTM) 1991a; Conner 1990]:

ASTM Type Portland Cement	Description
I	General-purpose Portland cement and usually the least expensive
II	Moderate sulfate resistance and moderate heat of hydration, Type II-fly ash is typical substitute when job size can't justify Type IV production
III	High early strength and cold weather use
IV	Low heat of hydration, used in massive structures (e.g., dams) where temperature rise can approach adiabatic, generally not available, mass produced for specific jobs
V	Sulfate resistant

ASTM Type I Portland cement is most commonly used for waste stabilization because of its wider availability and lower cost and can work in most cases with proper tailoring. The way the ASTM specifications are written, ASTM Type II Portland cement can be considered a subset of ASTM Type I Portland cement and quite often cement is marketed as Type I-II Portland cement. If Type II Portland cement is locally available, it may be better to specify Type II because of its better sulfate resistance and lower heat of hydration (many wastes contain sulfate and the heat of hydration can be a concern for some waste form applications). In addition, specifying the options of low alkali (LA) and low alumina (if available) may be desirable to make the final waste form more resistant to later destructive expansion from minerals, such as, alkali silicates, ettringite, or calcium chloroaluminate.

In summary, the best a priori cement selection may be ASTM Type II Portland cement-LA-low alumina-moderate heat of hydration. However, any of the cement types may be satisfactory for a given application and such selections should be made on a case by case basis, depending on waste composition, cement availability, technical performance, and costs. In the present study, the main function of the cement selected was to ensure activation of the ground granulated blast furnace slag; hence, it was not necessary to specify the cement listed above since it would not provide the basic waste form matrix. Type I, Type II, or Type I-II would be equally appropriate for this task, although Type II or I-II would still be preferred, if readily available, because of better sulfate resistance.

B.2 FLY ASH

Fly ash is an active pozzolan source that reacts with the caustic alkalis and alkalines, consuming hydroxide and producing alkali silicates and more CSH. Fly ash is only one of several possible pozzolans that can be used with cement or lime to produce cementitious waste forms. Other pozzolan candidates include volcanic glasses, volcanic tuffs, calcined clays and shales, diatomites, rice husk ash, volatilized silica (silica fume), blast furnace slag, and other slags (IAEA 1993). The key to the reactivity of the fly ash (and many of the other pozzolans) is its glassy structure. Only the amorphous glassy form provides a soluble silica source for reacting with the lime (and other caustics). The crystalline forms, like mullite, are too insoluble, stable, and inert. Fly ash was used in construction concrete decades prior to its use in waste disposal (Conner 1990; IAEA 1993; Laguna 1970; Berry and Malhotra 1980; Lane and Best 1982; Davis et al. 1937).

Using fly ash in concrete has many advantages in certain usages, the most important being cost, as it replaces 25-35 wt % of the Portland cement normally used (Conner 1990). Incorporating fly ash into cement lowers the heat of hydration, reducing curing temperature, an advantage in producing massive monoliths (Taylor 1990; Moore 1976; Atkinson et al. 1986; ASTM 1990c). Fly ash acts as both a pozzolan and a bulking agent, helping prevent settling in relatively low solids wastes and saving costs by substituting for cement (Conner 1990). However, such bulking does result in larger volume and weight increase than for Portland cement alone, "... usually only justified where low handling, transportation, and disposal costs are encountered." (Conner 1990) However, the relatively higher volume from fly ash is acceptable in its use as a pozzolan. Hydrating cement produces lime as a byproduct that form large soluble crystals in the cured neat cement paste matrix. These crystals dissolve upon immersion, leading to increased accessible porosity and leachability. Pozzolans react with this lime to produce more CSH to fill the available porosity, decreasing accessible porosity and leachability. In other words, fly ash "... helps to bind additional water, decrease the pore pH, and act as an adsorbent for metal ions." (Conner 1990)

Since strontium behaves similarly to calcium, cement-pozzolans will also tend to tie up 90Sr better than cement alone. Cement-fly ash has traditionally been the stabilizer of choice for 90Sr, although cement alone does stabilize 90Sr quite well (Laguna 1970; McDaniel et al. 1982; Moore et al. 1975; Moore 1976; Atkinson et al. 1986).

The ASTM standards specify two fly ashes and one natural or calcined pozzolan for use in Portland cement concrete (ASTM C 618 - 91) (ASTM 1990c; Conner 1990):

ASTM Mineral Admixture Class	Description
N	Raw or calcined natural pozzolans
F	Fly ash normally produced from anthracite or bituminous coal, has pozzolanic properties
C	Fly ash normally produced from lignite or subbituminous coal, has pozzolanic and cementitious properties, may contain lime >10 %

In general, a commercial industry has evolved to supply fly ash cheaply and with adequate QA/QC to routinely meet ASTM standards, making a valuable byproduct out of the large amounts of waste produced daily in the coal-fired power plants across the country. Although both can be and have been used, ASTM Class F fly ash is generally preferred for waste treatment, because of the possibility of "flash set" in the equipment with ASTM Class C fly ash. This difference in reactivity is indirectly related to the higher minimum specified content of silica, alumina, and iron oxide for Class F (^{3}70 wt %) compared to Class C (^{3}50 wt %). Although the lime content is not specified in the standard, a large fraction of the remaining composition is "free lime," which can lead to hydraulic cementitious reactions within the fly ash. Typically, the low lime content of Class F fly ash is quickly consumed, leaving the bulk of the fly ash relatively inert until caustically activated, e.g., by mixing with cement and the subsequent production of lime from hydration. Class C fly ash can contain lime concentrations as high as 30 wt % or higher, a highly reactive mix that can set into a cementitious product in a matter of minutes upon mixing with water ("flash set"). Since the lime content is not specified by the standard, the fly ash lime content varies from source to source and can vary from batch to batch. For these reasons, ASTM Class F fly ash was selected for this study.

B.3 INDIAN RED POTTERY CLAY

Over the years, illite (Indian Red Pottery Clay), (OH)4Kx(Al4Fe4Mg4Mg6)(Si8-xAl)O20, has become a proven standard additive in grout formulation development at Oak Ridge National Laboratory for making cementitious waste forms more resistant to the leaching of 137Cs (Moore et al. 1975; Moore 1976; Gilliam and Loflin 1986; Gilliam 1986; R. D. Spence, personal communication with T. L. Sams 1987). Illite has been known as an effective selective sorbent for 137Cs for decades (Tamura 1961; Tamura 1963; Tamura and Jacobs 1960). The gap between illite layers is apparently ideal to allow cesium ions to diffuse between the clay layers and essentially irreversibly trap these ions. Although there are other illitic sources (e.g., conasauga shale), Indian Red Pottery Clay (IRPC) is the most readily available commercial source. The standard recipe evolved into 8 wt % of IRPC in the dry blend of cementitious materials used to stabilize/solidify the waste liquids, solids, or sludges. The 8 wt % in the dry blend was far in excess of the stoichiometric amount needed to load the typical 137Cs contamination found in the wastes into the clay, because even a waste with high gamma activity from 137Cs has a quite low concentration of 137Cs on a molar basis. The main reason for 8 wt % IRPC in the dry blend was to distribute enough IRPC throughout the waste form so that all of the 137Cs had access to the IRPC and mass transport distances were minimized. This strategy has served well for many years as witnessed by the high ANSI/ANS-16.1 leachability indexes reported for 137Cs over the years for grouts containing IRPC.

B.4 GROUND GRANULATED BLAST FURNACE SLAG

Blast furnace slag is a normal byproduct of the iron and steel industry. In general, the slag is cooled in two ways (1) air cooling and (2) water quenching (granulation). Air cooling produces inert crystalline slag useful as an inert fill material, but useless as a cement substitute. The essential components of slag are the same oxides as are present in Portland cement, but "... for use as a cement, rapid cooling is necessary to quench the material to form a reactive glass and to prevent the crystallization of unreacted chemical compounds." (IAEA 1993) Granulated slag hydrates slowly on contact with water, but is activated by caustics (e.g., calcium hydroxide or sodium hydroxide), calcium sulfate, sodium carbonate, and sodium sulfate (IAEA 1993) . The granulated slag is finely ground and marketed as a substitute for cement. The ground granulated blast furnace slags (slags) "... have physical properties similar to those of ordinary Portland cements. The distribution of particle size and the surface area of blast-furnace slags depend on the method of manufacture, but in general their fineness is similar to that of Portland cements." (IAEA 1993; Nurse 1984)

Slags have been substituted for cement for decades (Daube and Bakker 1986). Slags hydrate slowly to form CSH, the same product formed by cements, but slag alters the morphology and properties of the final product, sometimes in subtle ways, but beneficially in general (IAEA 1993; Daube and Bakker 1986; Frigione 1986; Dubovoy et al. 1986; Mills 1986; Neville 1970; Palmer and Smith 1986; Brown et al. 1985; Glasser and McCulloch 1986):

- early strength development is slower,
- heats of hydration are lower,
- sulfate resistance is improved,
- lower permeability despite increased total porosity,
- improved frost resistance,
- lower ionic diffusion rates,
- increased salt stability,
- reduced setting rate,
- extended working time,

- pore water contains sulfur species in addition to hydroxide anions,
- high pH and low oxygen potential,
- reduced solubility of most contaminants,
- reduced rate of corrosion of steel containers, and
- other physical and mechanical properties similar to portland cements, e.g., density and compressive strength.

A slag:cement combination of 75:25 virtually eliminates calcium hydroxide as a hydration product, i.e., the presence of excess slag prevents build up of this cement hydration product (IAEA 1993). This implies that the proper proportion of slag-cement can replace cement-fly ash to stabilize 90Sr. In addition, a combination of 85:15 or higher slag produces a strong reducing environment within the matrix, suitable for reducing pertechnetates or chromates (Angus and Glasser 1986; Spence et al. 1989). Thus, slags have been used in grouts developed for radioactive and mixed wastes for a long time (Angus and Glasser 1986; Spence et al. 1989; Gilliam et al. 1990; Spence et al. 1995; Clark and Wilhite 1991; Langton et al. 1983; Langton 1989; Langton and Wong 1991; Pepper 1986; Wolf 1984).

The ASTM standards specifies three strength grades of ground granulated blast furnace slag for use in concrete and mortars based on the slag activity index (ASTM 1991d):

ASTM Slag Grade	Minimum Average Slag Activity Index, %	
	7 day	28 day
80	. . .	75
100	75	95
120	95	115

These slag grades are important for construction purposes, but not necessarily for waste treatment, where strength requirements are usually minimal. The chemical properties normally present in commercially available slag are their most important property for waste treatment and are generally not specified in the ASTM standard. Perhaps the most important property (Re: waste treatment) measured in the standard is the air permeability or Blaine fineness, although no limits are specified (ASTM 1991b). Finer slag usually means a lower permeability, not only in the dry slag, but also in the resulting cementitious matrix. A lower permeability implies "... improved resistance to frost, lower diffusion rates of ions through the hardened cement and improved stability in the presence of salts, such as chloride and sulphate." (IAEA 1993; Brown et al. 1985) Typically, Portland cement has a Blaine fineness of 3000-4000 cm2/g and slag, of 4000-5000 cm2/g, but slag >5000 cm2/g, or even >6000 cm2/g, can sometimes be acquired. In general, the finer, the better, although it is unlikely that special requests for finer grinding is worth the additional costs. Any commercially available slag suitable as a cement substitute generally improves the matrix properties and imparts the desired properties to the final waste form. Ground granulated blast furnace slag with a Blaine fineness of >4000 cm2/g was selected for this study.

B.5 WATER SORPTIVE-SUSPENSION AGENTS

When a grout is poured and allowed to remain static, the binding and pozzolanic agents (cement, fly ash, slag) tend to settle, leaving a drainable liquid on the grout surface (phase separation, bleed water, free-standing liquid, or free water) (R. D. Spence, personal communication with T. L. Sams 1987;

Gilliam et al. 1987; R. D. Spence, personal communication with E. W. McDaniel 1984). Traditionally, two methods have been used to control this free water generation: (1) increasing the solids-to-liquid mix ratio (or inversely decreasing the liquid, or water, to solids ratio W/S) and (2) adding gel clays. Gel clays disperse in water and form a thick, stable colloidal gel when mixing stops. This prevents suspended particles, such as, fly ash, cement, or slag, from settling while minimizing the dry blend added for treatment and the subsequent volume increase. The gel clays from oil field drilling fluids (muds) were adapted for this purpose in waste treatment grouts.

Water sorptive clays have been used in geotechnical applications, e.g., construction (slurry walls and clay caps) and drilling (drilling muds and cement mixes), for decades to resist solids segregation (suspension aid), prevent bleed water, and act as an engineered hydraulic barrier to water penetration (into a construction zone, waste disposal site, etc.). The most commonly used clay for these purposes is bentonite, sodium montmorillonite, "... a colloidal clay mined in Wyoming and South Dakota. It imparts viscosity and thixotropic properties to fresh water by swelling to about 10 times its original volume. Bentonite (or gel) was one of the earliest additives in oilwell cements to decrease slurry weight and to increase slurry volume." (Smith 1990; Smith 1951) The individual clay particles of bentonite are plate-shaped. The particle faces are positively charged while the edges are negatively charged. When mixed with water the platelets separate and disperse throughout the fluid. When mixing ceases, the clay particles form a multilayered colloidal gel structure due to the attraction of opposite charges. However, the electrostatic double-layer forces are lessened with increasing ionic strength (R. D. Spence, personal communication with E. W. McDaniel 1984; Grim 1962). Consequently, high-salt solutions (notably chloride, sulfate, and phosphate salts as well as acids and bases) collapse these gels, lessening their dispersive effectiveness and releasing the large volume of water collected around the clay particles (i.e., free water can form if salt solutions are grouted) (R. D. Spence, personal communication with E. W. McDaniel 1984; American Callard Co. 1954).

This susceptibility compromised the use of bentonite in off-shore oil drilling in salty waters. For this reason, attapulgite was adapted as the gel clay used in such salty applications. Attapulgite clay particles carry no charge and are not affected by high salt content (R. D. Spence, personal communication with E. W. McDaniel 1984). The individual attapulgite particles resemble needles, rather than platelets. When mixed with water, these needles are dispersed throughout the fluid and become aligned along shear planes. When mixing ceases, a gel structure is formed by the random entanglement of these particles, referred to as a "brush-heap effect". Attapulgite is commercially available only from northern Florida and southern Georgia (R. D. Spence, personal communication with E. W. McDaniel 1984). Thus, attapulgite has been adopted as the gel clay of choice for salty wastes. Note that although several forms of attapulgite have been tested for DOE salty wastes, only attapulgite 150 (Attagel 150) proved effective (R. D. Spence, personal communication with E. W. McDaniel 1984; de Laguna et al. 1968).

The American Petroleum Institute (API) has issued specifications for both bentonite and attapulgite [American Petroleum Institute (API) 1983; API 1984].

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Multi-Point Injection (MPI™) Technology Disclosure Statement

The information presented in this report discloses the basic elements of the multi-point injection (MPI™) process, as applied to in situ treatment of sludge in underground storage tanks. The MPI™ technology was invented by Dr. Joseph L. Kauschinger and is protected by U.S. Patent 5,645,377, with several other patents pending. The cold tank demonstration presented in this report was performed under a limited, no fee license to Lockheed Martin, which expired on January 30, 1998. The work presented in this report is considered limited rights data, as defined in the contract issued to Ground Environmental Services, Inc. (GES), who is the current assignee of all U.S. Patents.

GES secured private funding for reducing the MPI™ technology to practice. The essential features of MPI™ as a general purpose delivery system were successfully proven during commercial work conducted in March 1995. No government funding was ever used to reduce the MPI™ process to practice. The submission of this report shall not be construed to transfer the technology to the government nor provide an MPI™ license to the government, Lockheed Martin, or their employees or agents. This notice must accompany any use or publication of this report.