

# Pacific Northwest National Laboratory

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## Bench-Scale Feasibility Testing of Pulsed-Air Technology for In-Tank Mixing of Dry Cementitious Solids with Tank Liquids and Settled Solids

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Prepared for the U.S. Department of Energy  
under Contract DE-AC06-76RLO 1830

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## Summary

This report documents the results of testing performed to determine the feasibility of using a pulsed-air mixing technology (equipment developed by Pulsair Systems, Inc., Bellevue, WA) to mix cementitious dry solids with supernatant and settled solids within a horizontal tank. The mixing technology is being considered to provide in situ stabilization of the "V" tanks at the Idaho National Engineering and Environmental Laboratory (INEEL). The testing was performed in a vessel roughly 1/6 the scale of the INEEL tanks. The tests used a fine soil to simulate settled solids and water to simulate tank supernatants. The cementitious dry materials consisted of Portland cement and Aquaset-2H (a product of Fluid Tech Inc. consisting of clay and Portland cement). Two scoping tests were conducted to allow suitable mixing parameters to be selected. The scoping tests used only visual observations during grout disassembly to assess mixing performance. After the scoping tests indicated the approach may be feasible, an additional two mixing tests were conducted. In addition to visual observations during disassembly of the solidified grout, these tests included addition of chemical tracers and chemical analysis of samples to determine the degree of mixing uniformity achieved.

The final two mixing tests demonstrated that the pulsed-air mixing technique is capable of producing slurries containing substantially more cementitious dry solids than indicated by the formulations suggested by INEEL staff. Including additional cement in the formulation may have benefits in terms of increasing mobilization of solids, reducing water separation during curing, and increasing the strength of the solidified product. During addition to the tank, the cementitious solids had a tendency to form clumps which broke down with continued mixing. The vast majority of the settled soil was incorporated into the grout. In the second scoping test, 3.4 wt% of the soil was recovered as deposits. In the final two tests, the soil deposits were qualitatively smaller than those in the scoping test. The bulk of the solidified grout was very uniform. Except for the soil deposits (and in one case, a clump of cement which had not broken down), variations in composition were smaller than the analytical errors. In summary, the testing indicates that use of pulsed-air mixing for this application is feasible.

Parameters to be investigated using larger scale tests are identified and it is recommended that some tank-specific testing be performed prior to actual application. Mixing performance and cement clump formation and breakup should be investigated in a larger scale test. Such a test should include tank-specific features such as a sump or hemispherical ends. Also, any tank-specific data such as saline content of the liquid, tank level, and nature of settled solids should be considered for inclusion in larger scale testing.

## Nomenclature

$D_{hole}$	diameter of the hole in the upper mixing plate through which the gas flows. This is approximately equal to the outside diameter of the gas pipe, cm.
$D_{pipe}$	inside diameter of pipe supplying air to accumulator plate, cm.
$D_{plate}$	diameter of accumulator plate, cm
$h_{min}$	minimum standoff distance between upper plate and lower plate or upper plate and tank floor, cm
INEEL	Idaho National Engineering and Environmental Laboratory
$\Delta P$	compressed air pressure minus static head pressure, kPa
PNNL	Pacific Northwest National Laboratory
$R_{pulse}$	bubble pulse radius, cm
XRF	x-ray fluorescence

## Contents

Summary .....	iii
Nomenclature .....	v
1.0 Introduction .....	1.1
2.0 Background .....	2.1
3.0 Theory .....	3.1
4.0 Selection of Test Parameters .....	4.1
4.1 Selection of Tracer Compounds .....	4.2
5.0 Test Results .....	5.1
5.1 Characterization of Raw Materials .....	5.1
5.1.1 X-Ray Fluorescence Analysis of Soil, Aquaset-2H and Cement .....	5.1
5.1.2 Soil Moisture Content .....	5.3
5.1.3 Soil Sieve Analysis .....	5.3
5.2 Test 1 Narrative .....	5.5
5.3 Test 1B Narrative .....	5.12
5.4 Test 2 Narrative .....	5.19
5.4.1 Test 2 XRF Analysis .....	5.27
5.5 Test 3 Narrative .....	5.30
5.5.1 Test 3 XRF Analysis .....	5.37
6.0 Conclusions and Recommendations .....	6.1
6.1 Conclusions .....	6.1
6.2 Observations .....	6.2
6.3 Recommendations .....	6.2
6.4 Parameters for Further Investigation .....	6.3
7.0 References .....	7.1
Appendix A: Penetrometer Readings .....	A.1
Appendix B: Raw X-Ray Fluorescence (XRF) Compositional Data .....	B.1

## Figures

Figure 2.1. Installed Pulsed-Air Mixer in INEEL V-Tank .....	2.2
Figure 5.1. Schematic of Test 1 Air Delivery System .....	5.5
Figure 5.2. Test 1 Accumulator Plate Positioning. ....	5.6
Figure 5.3. Test 1 Configuration .....	5.6
Figure 5.4. Position of Valves and Pulsair Controller in Test 1 .....	5.7
Figure 5.5. Test 1 Grout Surface .....	5.9
Figure 5.6. End View of Drum in Test 1 .....	5.10
Figure 5.7. Profile Along Drum Bottom in Test 1. ....	5.10
Figure 5.8. Test 1, Profile of Cemented Material at an Accumulator Plate Position ....	5.11
Figure 5.9. Test 1, Profile of Cemented Material at Accumulator Plate Position .....	5.11
Figure 5.10. Revised Air Delivery System for Test 1B .....	5.12
Figure 5.11. Positioning of Accumulator Plates Prior to Test 1B .....	5.14
Figure 5.12. Setup for Tests 1B, 2, and 3 .....	5.14
Figure 5.13. End View of Grout Block From Test 1B .....	5.16
Figure 5.14. Test 1B Grout Block. Cross section with about 6 in. removed from end ..	5.17
Figure 5.15. Test 1B Grout Block. Grout appears uniform. ....	5.17
Figure 5.16. Test 1B, Small Patches of Unmixed Soil Near the Addition Point. ....	5.18
Figure 5.17. Test 1B, Deposit of Sand (Dark Area) Located at End of Drum Near Addition Point .....	5.18
Figure 5.18. End of Grout Block in Test 2 .....	5.22
Figure 5.19. Clump of Tracer Material Located Just Below the Surface at the Top Center of the End of the Grout Block .....	5.22
Figure 5.20. Grout Removed to ~6 in. from Drum End in Test 2 .....	5.23
Figure 5.21. Grout Removed to ~12 in. from Drum End in Test 2 .....	5.23
Figure 5.22. Very Small (1/2 in. diameter) Sand Deposit Located Along Drum Wall in Test 2 .....	5.24

Figure 5.23. Test 2, Approximately 1 ft of Grout Remaining .....	5.24
Figure 5.24. Test 2, Approximately 6 in. Grout Remaining in Drum .....	5.25
Figure 5.25. Test 2, Sand Deposit Found Near the Wall of Drum Nearer the Addition Point .....	5.25
Figure 5.26. Tracer Concentrations of Samples Taken from Test 2. ....	5.27
Figure 5.27. Comparison of Weight Loss on Drying and Cs Content for Test 2 Samples .....	5.29
Figure 5.28. Comparison of Relative Ca and Zr Contents for Test 2 Samples Not Noted as Representing Inhomogeneous Locations .....	5.29
Figure 5.29. Test 2 Ca and Zr Analyses for Samples Directed at Inhomogeneities .....	5.30
Figure 5.30. Soil Deposit Along Bottom of Drum at End Farthest From Addition Point	5.33
Figure 5.31. Test 3, Cross Section of Sand Layer ~ 4 in. From Drum End .....	5.33
Figure 5.32. Test 3, Grout Removed to Between 11 in. and 12 in. From End .....	5.34
Figure 5.33. Test 3, Cross Section at ~ 10 in. From Addition End of Drum .....	5.34
Figure 5.34. Test 3, Grout Piece Removed from Location Illustrated in Figure 5.33 ...	5.35
Figure 5.35. Test 3, Cross Section With ~ 4 in. of Grout Remaining in the Drum .....	5.35
Figure 5.36. Test 3, Sand Deposit at End of Drum Following Removal of Last 4 in. ...	5.36
Figure 5.37. Test 3 Tracer Concentrations .....	5.39
Figure 5.38. Test 3 Ca and Zr Concentrations of Samples Not Targeted at Inhomogeneities .....	5.39

## Tables

Table 3.1. Observed vs. Predicted $R_{\text{pulse}}$ Values .....	3.3
Table 5.1. Analysis of Raw Materials for Tracer Elements (ppm) .....	5.2
Table 5.2. Elemental Analysis by XRF (ppm) of Ca and Zr in Raw Material Samples ..	5.3
Table 5.3. Sieve Analysis of First Soil Batch Used in Tests 1, 1B and 2 .....	5.4
Table 5.4. Sieve Analysis of Second Soil Batch Used in Test 3 .....	5.4
Table 5.5. Sieve Analysis of Recovered Soil From Test 1B .....	5.19
Table 5.6. Percent Weight Loss on Drying for Various Samples from Test 2 .....	5.26
Table 5.7. Percent Weight Loss on Drying for Various Samples from Test 3 .....	5.37

## 1.0 Introduction

This report describes tests conducted in a bench-scale mockup of an underground horizontal tank similar to the "V" tanks at the Idaho National Engineering and Environmental Laboratory (INEEL). Staff from Pacific Northwest National Laboratory<sup>(1)</sup> conducted the tests on a concrete pad outside the 336 Building in the 300 Area of the Hanford site. The tests were performed to verify the ability of pulsed-air mixing technology (equipment developed by Pulsair Systems, Inc., Bellevue, WA) to mix grout-forming dry solids with supernatant within a horizontal tank. The objective was to determine if pulsed-air mixing technology will adequately mix dry solids added to the surface of the supernatant into a slurry and whether the mixing is adequate until the desired amount of dry blend has been added. A second objective was to determine if the mixing system could entrain and incorporate settled solids into the grout slurry and the extent of uniformity within the cementitious slurry. The tests used Aquaset-2H (a product of Fluid Tech Inc. consisting of clay and Portland cement) with and without additional type I/II Portland cement as the dry blend. Water was used to simulate supernatant and a fine, dusty soil was used to simulate the settled solids. The tests were conducted in a horizontal 55-gallon drum to simulate the horizontal tank. The drum was filled approximately half-full with equal mass portions of water and soil, the pulsed-air mixing system was activated, and the dry cementitious solids were added to the drum. After the mixing was completed, the grout was allowed to cure, checked for separated water, and then physically broken apart to check for inhomogeneity.

A total of four mixing tests were conducted. The first two tests were intended to investigate mixing feasibility, to adjust mixing parameters, and to investigate the degree to which additional Portland cement could be incorporated into the mix. The second two tests included tracer addition and chemical analysis to evaluate mixing uniformity.

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<sup>(1)</sup>Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.

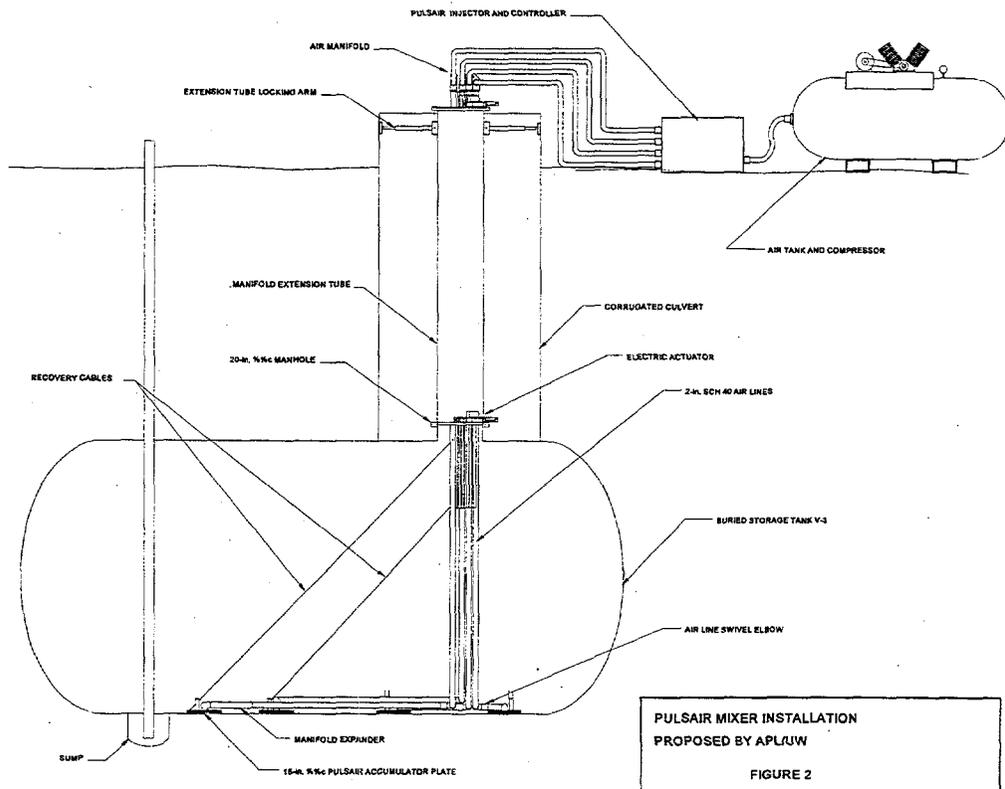
## 2.0 Background

The pulsed-air mixing technique uses brief pulses of air or inert gas to produce large bubbles near the tank floor. The bubbles rise toward the surface of the liquid and induce mixing. An array of horizontal, circular plates is positioned about 8 to 25 mm (0.25 in. to 1.0 in.) from the tank floor. Pipes connected to each plate supply the pulses of gas to the underside of each plate. The pulsed-air control equipment is used to control the pulse frequency, duration, gas pressure, and plate sequencing to create a well-mixed condition within the tank. The pulsed-air mixing technique has been successfully applied to a number of difficult mixing applications in various chemical process industries.

The pulsed-air mixing system is being considered for mixing grout dry blends consisting of Aquaset-2H and Portland cement with wastes within the "V" tanks at INEEL. Information on Tank V-3 was used in the experimental design. Tank V-3 is a horizontal, cylindrical, underground tank with a diameter of 10 ft. The length of the cylindrical portion of the tank is 16 ft and hemispherical ends extend the length up to an additional 3 ft on each end (at the centerline). The drum in which testing was performed measured 22.375 in. in diameter and was 32.75 in. long. Ignoring the hemispherical ends on tank V-3, the drum was between 1/5 and 1/6 the scale of Tank V-3.

In-tank mixing of grout at INEEL has been tested using conventional mixers in a vertical tank (Hyde and Farnsworth 1997), but it is not thought practical to deploy a conventional mixer in a horizontal tank such as Tank V-3 because the access to the tank is limited. Because it is believed feasible to deploy a pulsed-air mixing system in the tank, the pulsed-air mixing technology may offer substantial improvements in cost and/or performance over conventional mixers. A schematic of the deployment of a pulsed-air mixer in Tank V-3 is shown in Figure 2.1. Additional information is provided by Powell and Hymas (1996). Tank V-3 contains a sump at one end and a manway at the other. The deployment approach involves entering through

the manway and unfolding accumulator plates on extensions to provide agitation across the whole tank. After deployment, the accumulator plates are roughly evenly spaced with the manway between two plates at one end of the tank. The otherwise even spacing of accumulator plates is slightly disrupted by the presence of the sump.



**Figure 2.1.** Installed Pulsed-Air Mixer in INEEL V-Tank (reproduced from Powell and Hymas 1996).

### 3.0 Theory

The primary objective of this work was to determine if a pulsed-air mixing system can entrain cementitious dry solids into a grout slurry at the desired mix ratio. A secondary objective was to determine if settled solids could be suspended and incorporated into the slurry and the degree to which the grout slurry is uniformly mixed. While testing confirmed expectations that the cementitious solids would mix into the liquid and the slurry would be well mixed, correlations have not been developed to address these phenomena. However, an empirical correlation for the pulse radius has been developed by Powell (1997). The pulse radius is defined as the radius of the maximum horizontal expansion of the pulsed-air bubble across the tank floor. The correlation is based on visual observations and hot-film anemometry data for air pulses in water in a flat-bottomed tank (Powell and Hymas 1996). Data to confirm the visual observations were obtained using high-speed photography. The measurements of liquid velocity determined using a hot film anemometer indicated that the maximum velocity falls off rapidly beyond the pulse radius. In addition, observations made on the ability to resuspend kaolin clay slurries were consistent with the visually observed pulse radius data. The correlation developed by Powell and Hymas (1996) for scaling of  $R_{pulse}$  is:

$$R_{pulse} = 0.8 D_{plate}^{0.31} \Delta P^{0.39} D_{pipe}^{0.51} \quad (3.1)$$

where:

- $R_{pulse}$  = predicted pulse radius, cm
- $D_{plate}$  = diameter of accumulator plate, cm
- $\Delta P$  = compressed air pressure minus static head pressure, kPa
- $D_{pipe}$  = inside diameter of pipe supplying air to accumulator plate, cm.

This equation may not apply if the gas flow is choked where it turns the corner in the accumulator plate. This condition can be avoided by assuring the following condition is met:

$$h_{min} = \frac{D_{pipe}^2}{4 D_{hole}} \quad (3.2)$$

where:  $h_{min}$  = minimum standoff distance between upper plate and lower plate or upper plate and tank floor, cm

$D_{pipe}$  = inside diameter of the gas pipe, cm

$D_{hole}$  = diameter of the hole in the upper mixing plate through which the gas flows. This is approximately equal to the outside diameter of the gas pipe, cm.

The correlation was used in this test to roughly determine the number of plates required and the pressure needed to mobilize solids from the bottom of the drum. Scaling calculations indicated that for a standoff distance of  $>0.136$  cm, a pressure of 30 psi should cause four circles with radius =  $R_{pulse}$  to just touch along the bottom of the drum. The prediction of  $R_{pulse}$  is uncertain because the data supporting the correlation was collected in water or dilute kaolin slurries within a flat-bottomed tank. The effects of the fluid properties of the cement slurry and the curvature of the tank bottom are unknown. As a first approximation, a pressure of 50 psi was selected as a reasonable guess.

Observations from Test 1, operated at 50 psi, indicated that the soil was mobilized only in about a 5-in.-diam. circle ( $R_{pulse} = 6.4$  cm) around the plate. This is only about half of the 13.5 cm predicted by the correlation. Part of this disagreement was due to choked flow in the tubes supplying air to the plates. However, the data supporting the correlation for small plate sizes such as used in the testing were reviewed. The data for the smallest plate used in developing the correlation (6.1 cm diam.) was compared to correlation predictions (Table 3.1).

**Table 3.1.** Observed vs. Predicted  $R_{\text{pulse}}$  Values

Pressure (psig)	$R_{\text{pulse}}$ Visually Observed for 6.1-cm Plate (cm)	$R_{\text{pulse}}$ Predicted by Correlation <sup>1</sup> for 6.1-cm Plate (cm)	$R_{\text{pulse}}$ Predicted by Correlation <sup>1</sup> for 6.35-cm Plate (cm)
20	7	9.3	9.5
40	8	12.2	12.4
50	NA	13.4	13.5
60	9	14.3	14.5
80	11	16.0	16.2
100	12	17.5	17.7

<sup>1</sup> Data from Powell and Hymas (1996), correlation from Powell (1997).

The comparison in Table 3.1 shows that the correlation tends to overestimate the  $R_{\text{pulse}}$  for the 6.1-cm plates used to develop the correlation. The difference between the predicted  $R_{\text{pulse}}$  values for the 6.1-cm plate and the 6.35-cm plate used in this testing is minor. The observed radius over which soil mixing occurred in Test 1 was much closer to the visual  $R_{\text{pulse}}$  observations for the 6.1-cm-radius plate than to the correlation predictions. In subsequent tests, the air supply system was modified to prevent choked flow and attempts were made to test at 90 psi in order to obtain the 11-cm  $R_{\text{pulse}}$  based on visual observations for small plates. In Test 1B, the air supply to the system would support a pressure of only 67 psi, although in Tests 2 and 3 a modification to the system allowed a pressure of 90 psi to be obtained.

## 4.0 Selection of Test Parameters

The mixing system was intended to roughly approximate a concept for deploying a pulsed-air mixing system in Tank V-3 at INEEL through the single 20-in.-diam. manway. As discussed in Section 2.0, the 55-gallon drum is geometrically approximately 1/5 to 1/6 the scale of the V-tanks and does not model several tank details such as hemispherical ends and a sump located towards one end of the tank. The selection of four plates along the length of the drum corresponds to the selection of four plates in the deployment concept for the tank. The 2.5-in.-diam. accumulator plates are geometrically scaled (1/6 scale) from the 15-in.-diam. plates in the V-3 deployment concept. The pulse pressure was initially set at a value of 50 psi to achieve overlapping pulse radii along the bottom of the drum. However, the pulse pressure and frequency were adjusted to obtain the desired mixing during the initial tests (see Section 3.0).

Guidance from INEEL included two suggested formulations for the grout:

- |    |                  |    |                      |
|----|------------------|----|----------------------|
| A) | 100 g solids     | B) | 100 g solids         |
|    | 100 g water      |    | 100 g water          |
|    | 50 g Aquaset 2-H |    | 35 g Aquaset 2H      |
|    |                  |    | 15 g Portland cement |

The objective was to determine if slurries with higher cement ratios than the suggested formulations could be mixed. The solids were described as fine, dusty material possibly obtained as a result of sweeping concrete floors. A tank level of roughly half-full was suggested for testing. Based on this information, a dusty soil consisting largely of wind-blown dust was selected. The material was screened through a #10 screen (2.0-mm opening) prior to use. In addition, the relative weights for water and soil shown above were adjusted to account for about 1.7-wt% moisture in the soil, as determined by weight loss on drying at 105°C. This resulted in a slight increase in soil weight added and a slight decrease in the water added. The formulations

were translated to test quantities as follows:

A)	75.7 kg soil	B)	75.7 kg soil
	73.1 kg water		73.1 kg water
	37.2 kg Aquaset-2H		26.0 kg Aquaset-2H
			11.2 kg Portland cement (or more)

The Aquaset-2H was received from INEEL and the Portland cement was standard Type I/II Portland cement purchased locally<sup>(1)</sup>.

#### 4.1 Selection of Tracer Compounds

In the final two tests, one soluble tracer and two insoluble tracers were added to assess mixing uniformity. The soluble tracer was dissolved in the water before the cementitious solids were added. The insoluble tracers were mixed in after adding the cementitious solids to determine the degree of mixing uniformity. Other constraints applied to the tracer selection were that

- the tracer compound should not pose any special health hazard
- the tracer element should not be present as a major component of the soil cement or Aquaset-2H to avoid an analytical "baseline" problem
- the detection limit for the tracer element using x-ray fluorescence (XRF) should be low and if possible should be able to share an excitation target with other tracers to reduce cost
- the tracer compound should not cause the final grout to be hazardous from a waste disposal standpoint, and

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<sup>(1)</sup>Portland cement bags were printed with the following certification: "Complies to Federal Specification SS-C 1960/s and ASTM specification C-150 for Type I and II Portland cement."

- the tracer compound should not have a significant effect on the grout curing reactions.

The tracers selected were CsCl as the soluble tracer and  $Y_2O_3$  and  $Ga_2O_3$  as insoluble<sup>(1)</sup> tracers. These chemicals pose no special health threat and do not result in a hazardous final product in the amounts being added (100 g CsCl, 30 g  $Y_2O_3$ , 30 g  $Ga_2O_3$ ). These amounts correspond to about 700 ppm for Cs and 200 ppm for Y and Ga in the final product (dry basis). The soil, cement, and Aquaset-2H were analyzed separately by XRF to confirm that baseline concentrations for these elements are acceptable (see Section 5.0 for analysis results). As a result of this analysis,  $ZrO_2$  was rejected in favor of  $Ga_2O_3$  due to elevated levels of zirconium in the soil selected for the test. The addition of  $Y_2O_3$  and  $Ga_2O_3$  is not expected to have significantly influenced the cementitious reactions. Yttrium oxide ( $Y_2O_3$ ) should be essentially insoluble while  $Ga_2O_3$  may participate in the cement reactions in a similar manner as  $Al_2O_3$ . However, Portland cement generally contains between 3 wt% and 8 wt% of  $Al_2O_3$  (Neville 1981). X-ray fluorescence analysis indicates a value at the low end of this range for the Portland cement used in testing (see Appendix B). The large amount of  $Al_2O_3$  relative to  $Ga_2O_3$  is expected to make the addition of 200-ppm Ga as  $Ga_2O_3$  negligible from a cement chemistry standpoint. The CsCl may have a slight accelerating effect on the set of the grout. Calcium chloride ( $CaCl_2$ ) is a common set accelerator added in concentrations of approximately 1% to 2% of the cement weight in concrete applications. The accelerating effect is more pronounced at lower water:cement ratios (Neville 1981). The effects of NaCl (which is expected to be similar to CsCl) are less pronounced and less predictable. Lea (1971) indicates that NaCl has a slight and variable accelerating effect. Sodium chloride (NaCl) is used as an accelerant in oil well cementing where it may be applied in concentrations of 1.5 wt% to 5 wt% of the cement weight (Smith 1976). High gel salt cements, used in oil well cementing applications, are made from a

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<sup>(1)</sup> The solubility of gallium increases significantly at high pH (pH 11.2,  $10^{-6}M$ ; pH 12.2,  $10^{-4}M$ ; pH 13, 0.01 M) in a similar manner as aluminum. The pH of pore water will increase due to dissolution of CaO in the Portland cement and Aquaset. Saturated CaO solutions produce a pH of 12.3 at 30°C and pH of 12.45 at 25°C (CaO solubility decreases with increasing temperature). Thus, it is estimated that between 2% ( $10^{-4}M$ ) and 20% ( $10^{-3}M$ ) of the gallium may be soluble in the elevated pH of the pore water after the material is uniformly mixed. This partial solubility was deemed acceptable for the purposes of this test.

dry blend of Portland cement with 3 wt% to 7 wt% NaCl, and 12 wt% to 16 wt% bentonite. In this application, the NaCl can act as both a set accelerator and a dispersant<sup>(1)</sup> to reduce viscosity of the bentonite clay (Smith 1976).

However, a significant effect on set time is not expected because the mass of CsCl was only 0.41% or 0.54% of the Portland cement mass which, by analogy to NaCl, is lower than typically used for set acceleration. In addition (and perhaps more importantly), the mix ratio with water was about 3 (i.e. 3 g water per gram of Portland cement) compared to a typical ratio for Portland cement in structural applications of about 0.46. This implies the solution concentration in the test will be about a factor of 6 lower than if the salt was added to the Portland cement in a structural application. Therefore, the impacts of the CsCl were deemed acceptable. The Cs was not added as a carbonate because the alkali carbonates are known to produce a very strong acceleration of set, while bicarbonates have a retarding effect (Lea 1971). The oxide and hydroxide were discarded due to the hazardous nature of the chemical but would also be expected to have an accelerating effect.

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<sup>(1)</sup> The description of dispersant is oversimplified. Sodium montmorillonite (which is the major component of bentonite) consists of plate-like particles which have opposite face and edge charges. In the absence of any salt, the clay agglomerates edge-to-face to form a structure with a substantial yield stress. Addition of a small amount of salt reduces the electrostatic attraction and lowers the yield stress. As additional salt is added, the yield stress increases again as van der Waals forces augment the reduced edge-to-face electrostatic attraction. However, at high salt concentrations, the face-to-face repulsion is overcome and some face-to-face agglomeration occurs which results in reduced structure in the clay and a lower yield stress (van Olphen 1977). This type of agglomeration is likely the source of the "dispersant" effect referred to by Smith (1976). The salt effects noted for bentonite are unusual. Other clays show much less pronounced sensitivity to salt concentrations. The clays included in the Aquaset-2H are sepeolite and attapulgite, which have a needle-like rather than plate-like structure. As a result, the salt sensitivity of the clay is not believed to be an issue for the current testing.

## 5.0 Test Results

A total of four mixing tests, designated 1, 1B, 2, and 3, were performed. Tests 1 and 1B were scoping tests to determine if the mixing approach was feasible and to select appropriate mixing parameters for Tests 2 and 3. Tests 1 and 1B determined that the overall approach was feasible and that cement in excess of the amount in the suggested formulation was easily incorporated. Tests 2 and 3 made use of the results from Tests 1 and 1B to select mixing parameters and included the chemical tracers and XRF analysis of the cured grout to assess the degree of mixing uniformity. Test 2 used an Aquaset-2H plus Portland cement formulation with twice the amount of Portland cement suggested by INEEL, while Test 3 used a formulation consisting only of Aquaset-2H. Tests 2 and 3 demonstrated that the mixing approach is feasible. The cementitious solids were easily incorporated into the slurry, the majority of the settled soil was incorporated into the grout, and the bulk of the grout product was uniformly mixed. A small amount of the soil existed as small deposits on the vessel wall in both Tests 2 and 3.

This section provides the characterization data for raw materials followed by the detailed results obtained during each mixing test. Conclusions and recommendations based on the test results are provided in Section 6.

### 5.1 Characterization of Raw Materials

This section presents the characterization data for the soil, cement, and Aquaset-2H used in testing.

#### 5.1.1 X-Ray Fluorescence Analysis of Soil, Aquaset-2H, and Cement

Prior to testing, the dry materials (soil, Aquaset-2H, and Portland cement) were analyzed by XRF to determine if the elements to be used as tracers may already be present in one or more

of the bulk materials. Based on the results, the tracers were selected to be Ga, Y, and Cs (see Section 4.1). The levels detected based on a single sample of each material are summarized below. These are compared to the planned nominal spike level in the last column.

**Table 5.1.** Analysis of Raw Materials for Tracer Elements (ppm)

Tracer Element	Portland Cement	Aquaset-2H	Soil (batch 1)	Nominal Spike Target
Cs	<6.6	5.8	12.8	200
Ga	9.5	14.0	30.4	200
Y	<40	<48	<43	700

In addition to analysis for tracers, the analytical results were examined to determine if the uniformity of mixing between the soil and the cementitious solids could be evaluated based on the chemical composition. The soil shows elevated levels of Ti and Zr relative to dry blend materials, while the Portland cement and Aquaset-2H have elevated levels of Ca, S, and Cr relative to soil. After reviewing the quality of data for these compounds, Ca and Zr were selected as the best compounds for tracking the soil relative to the Aquaset-2H and Portland cement<sup>(1)</sup>. As shown in Table 5.2, both Aquaset-2H and Portland cement are high in Ca while the soil is high in Zr. Thus, if it is assumed that the Ca uniformly follows the cement fraction and Zr follows the soil fraction, the uniformity of the mixture can be examined based on the ratio of Ca to Zr. This allows the composition of a sample of cured grout to be examined to determine if it is higher or lower in cement or soil relative to other locations.

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(1) Analysis of the Aquaset-2H Ca content was complicated by the significance of absorption for Ca and the lack of a suitable standard. Results varied when analyzed against a cement standard compared to a soil standard. However, the qualitative result that the calcium content is high relative to soil is not in doubt. Calcium results for the soil, cement and hydrated grouts do not have the same uncertainty due to the availability of suitable standards.

**Table 5.2** Elemental Analysis by XRF (ppm) of Ca and Zr in Raw Material Samples

Element	Portland Cement	Aquaset-2H	Soil
Ca	480000	293000	35300
Zr	61.1	83.5	272

### 5.1.2 Soil Moisture Content

Soil was obtained in two batches, the first batch used for Tests 1, 1B, and 2 and the second used for Test 3. The soil was collected from the same general location. Only batch 1 was analyzed by XRF. From the first batch, samples were taken from the top, middle, and bottom of the container of soil and dried at 200°C for a minimum of 1 hour. The results indicated moisture contents of 1.77 wt%, 1.67 wt%, and 1.72 wt% for the top, middle, and bottom samples, respectively, for an average of 1.72 wt% moisture. Samples were taken from the second batch from the middle of the pile prior to removing material for the test, two samples taken from a bucket that was turned end-over-end prior to removing each sample, and one sample taken from the bin after removing the soil for the test. The moisture content was determined by drying at 105°C over 22 hr for the first sample and several days for the remainder. The moisture contents were 1.73 wt%, 1.66 wt%, 1.28 wt%, and 1.49 wt%, respectively, for an average moisture content of 1.54 wt%.

### 5.1.3 Soil Sieve Analysis

The soil was sieved through a number 10 screen prior to use. The remainder was sampled and sieved to obtain the wt% breakdowns shown in Tables 5.3 and 5.4 for soil batches 1 and 2, respectively. As can be seen, the second batch of soil has less material retained on and above the number 50 sieve and more material passing the number 200 sieve. Qualitatively, the second batch of soil felt, looked, and handled essentially the same as the first batch of soil.

**Table 5.3.** Sieve Analysis of First Soil Batch Used in Tests 1, 1B, and 2.

USA Sieve Size	Screen Opening (µm)	Sample 1, wt% passing	Sample 2, wt% passing	Sample 3, wt% passing	Average, wt% passing	Average wt% retained on screen
10	2000	100 <sup>1</sup>	100 <sup>1</sup>	100 <sup>1</sup>	100 <sup>1</sup>	0
20	841	88.5	89	88.9	88.8	11.2
30	600	83.6	84.5	84.2	84.1	4.7
50	300	75.7	76.6	76.5	76.2	7.9
70	212	73.1	73.8	73.8	73.6	2.7
100	150	68.6	69.2	69.2	69.0	4.5
200	75	49.4	49.0	49.9	49.4	19.6
pan	0	0	0	0	0	49.4

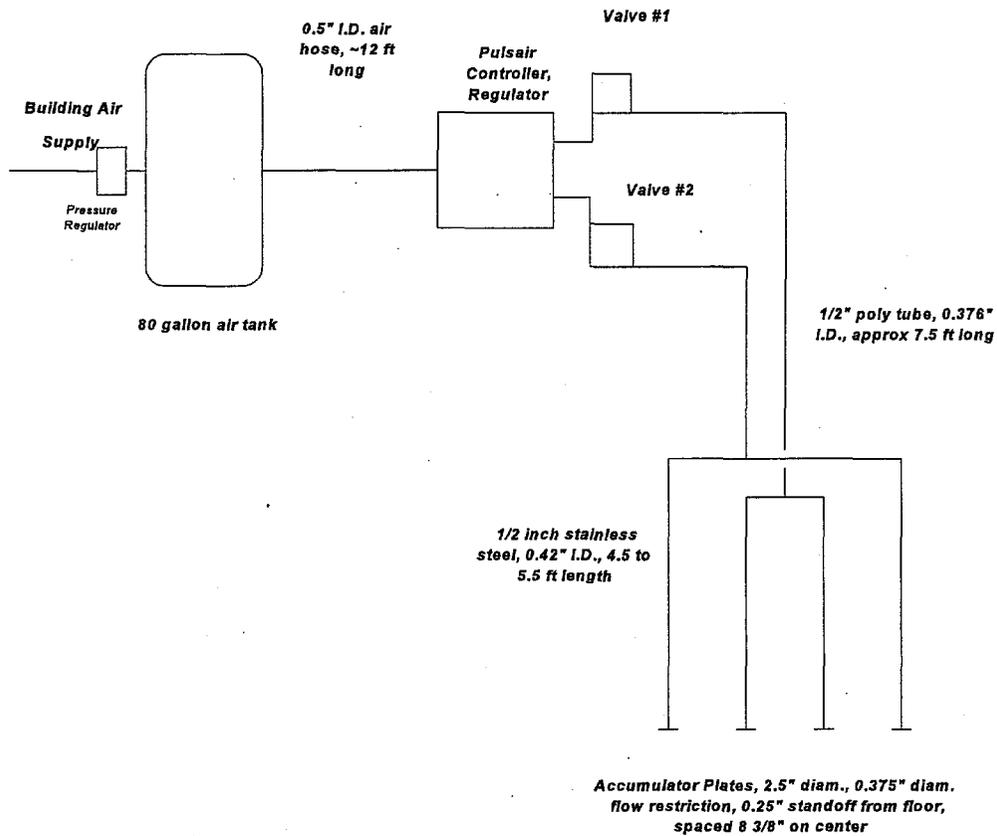
<sup>1</sup> Prior to sampling for sieve analysis, the soil was passed through a number 10 screen. Thus, it was assumed that all material would pass the number 10 screen. A number 10 screen was actually used in the second batch and did catch a few particles, as indicated in Table 5.4.

**Table 5.4.** Sieve Analysis of Second Soil Batch Used in Test 3.

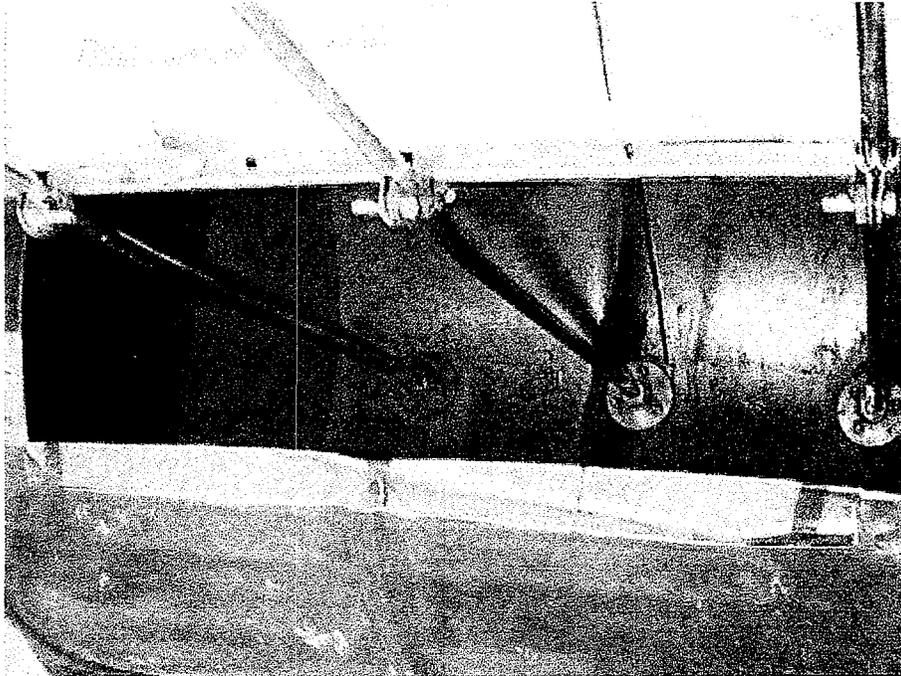
USA Sieve Size	Screen Opening (µm)	Sample 1, wt% passing	Sample 2, wt% passing	Sample 3, wt% passing	Sample 4, wt% passing	Average wt% passing	Avg wt% retained on screen
10	2000	99.6	99.6	99.3	99.4	99.46	0.54
20	841	94.1	92.2	91.6	92.1	92.52	6.94
30	600	91.5	89.0	88.1	88.8	89.36	3.15
50	300	86.3	83.7	82.1	83.3	83.83	5.53
70	212	84.2	81.7	79.8	81.1	81.68	2.15
100	150	80.1	77.6	75.4	76.9	77.49	4.19
200	75	62.0	59.3	56.3	57.9	58.88	18.60
pan	0	0	0	0	0	0	58.88

## 5.2 Test 1 Narrative

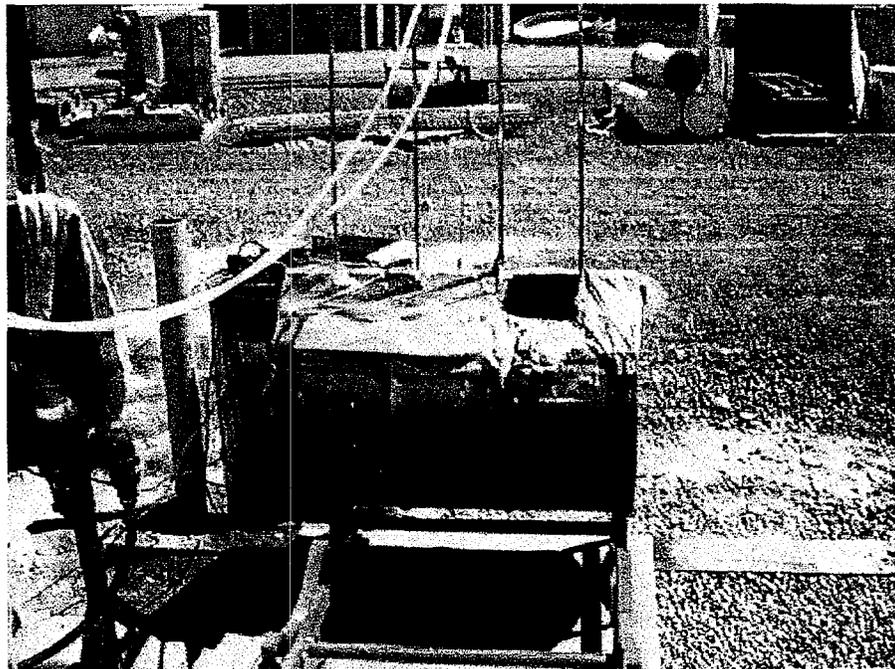
A schematic configuration of the pulsed-air control equipment is shown in Figure 5.1. Photographs showing the accumulator plates within the drum and the air supply test setup are provided in Figures 5.2 through 5.4. Prior to actual testing, water was placed in the drum and the air pulsing system tested. Operating in water, it appeared that the system had minimal effect on coarse sand particles on the bottom of the drum and it appeared unlikely that the soil would be suspended by the system. The system as configured could supply a much higher pulsing frequency than was used in this test.



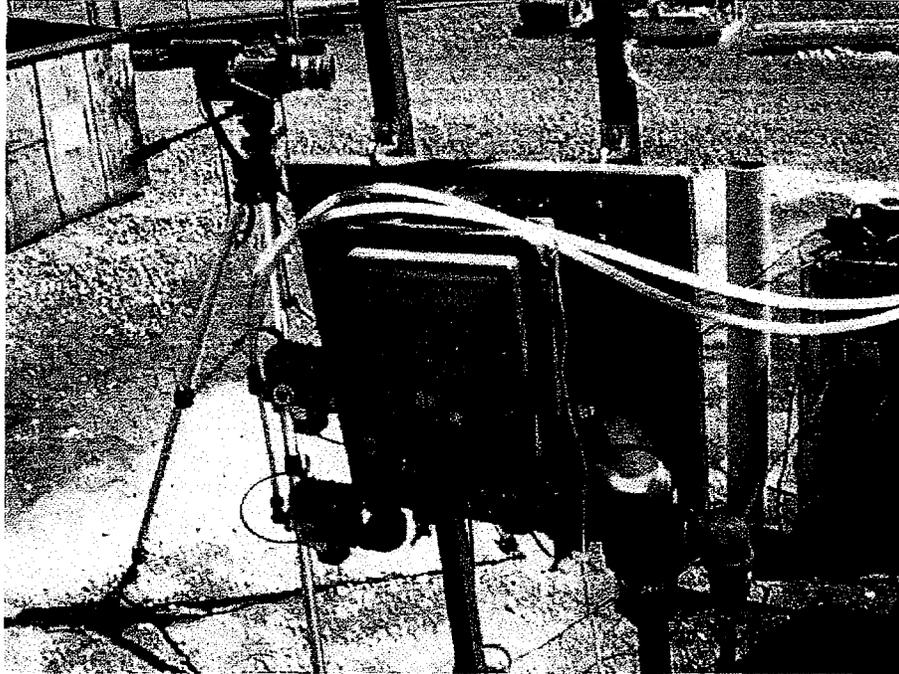
**Figure 5.1.** Schematic of Test 1 Air Delivery System



**Figure 5.2.** Test 1 Accumulator Plate Positioning. Dark area on drum floor is epoxy used to fill in the drum ribs. The thermocouple is also visible.



**Figure 5.3.** Test 1 Configuration. The polyethylene tubing that supplied air to each pair of accumulator plates was believed to be choking flow in this test.



**Figure 5.4.** Position of Valves and Pulsair Controller in Test 1. Each polyethylene tube leads to a pair of accumulator plates. An air hose supplies the system at bottom right of photo.

The drum was emptied and dried and then 73.1 kg of water was added to the drum, followed by 75.7 kg of soil dumped as evenly as possible along the length of the drum. The pulse air system was started at 50 psi, with the frequency set at 6.5 pulses per minute on each set of two plates (13 pulses/minute total). Feeling below the surface while operating with soil and water it was clear that the soil was not suspended in the water. The soil quickly resettled and buried the accumulator plates between pulses. It was unclear whether or not the material near the wall was moving with each pulse.

The soil-water system was allowed to mix for approximately 20 minutes before any solids were added. All dry materials were added at the point between accumulator plates at one end of the drum.

Aquaset-2H was added over a 30-minute interval (10:10 to 10:40). Initially, the material sank almost immediately beneath the surface and a scoop was added every couple pulses. At 10:27, it was noted that a ball had formed just beneath the surface and addition was stopped. At 10:30, the ball could not be located by touch and relatively solid banks of solids that were not mixing in were noted running parallel to the row of plates. Aquaset-2H addition was resumed at 10:30 and complete by 10:40.

The first container of Portland cement containing 11.2 kg was added from 10:44 to 10:48. The material mixed in relatively quickly. The liquid layer at the surface was quite fluid. At 10:52, addition of the second container of Portland cement was started. At 10:57 an island formed on top of the slurry so addition was stopped for a few minutes to allow the cement to be mixed in. Addition was slowed by repeated formation of floating islands of dry materials. After 11:30, the cement was added in half-scoop amounts. Reducing the amount added appeared to reduce clump formation. Addition of the second container was complete at 11:55 (30.9 kg in the second container, for a total of 42.1 kg). Feeling by hand, the top layer of slurry was very fluid and beneath that layer was a hard layer which was not mixing. The presence of the hard layer was not apparent without feeling beneath the surface.

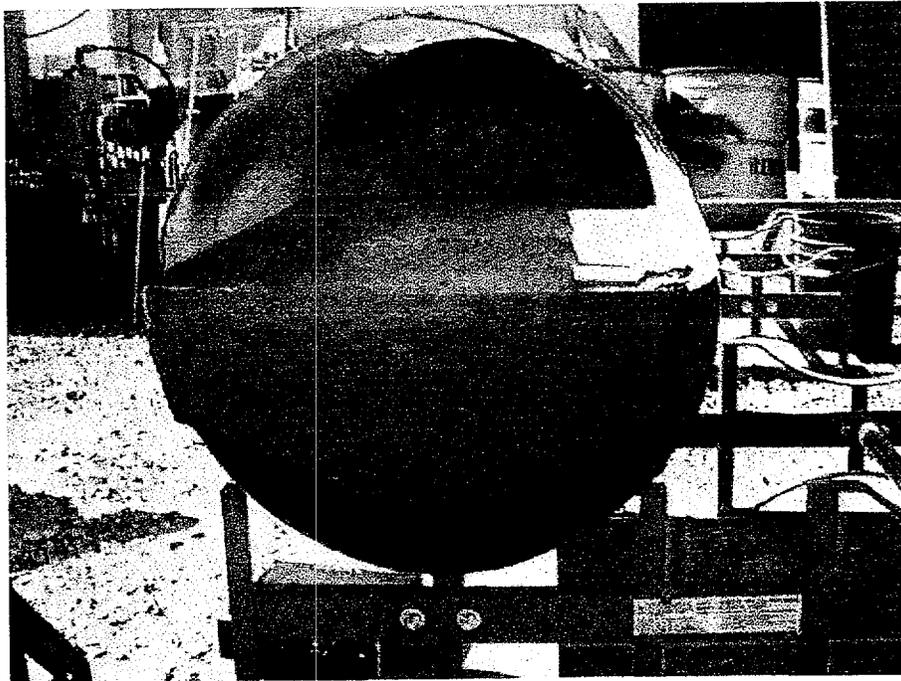
The temperature of the water in the drum was initially 27°C when Aquaset addition was started and was 29°C near the end of the Aquaset-2H addition. The temperature increased to 33°C by 11:55 when the cement addition was completed. By 17:40, the temperature had increased to 51°C. By 9:15 the next morning, the temperature had cooled to 40°C and after an additional 24 hours, to 28°C.

Approximately 45 hours after mixing was completed, the drum was disassembled to examine the grout product. No separated liquid was present on top of the grout. About a dozen small mounds were evident above the otherwise perfectly flat surface (Figure 5.5). Three mounds were clustered around the thermocouple. It is suspected that these mounds may have been created by clumps of incompletely mixed cement floating just beneath the surface of the

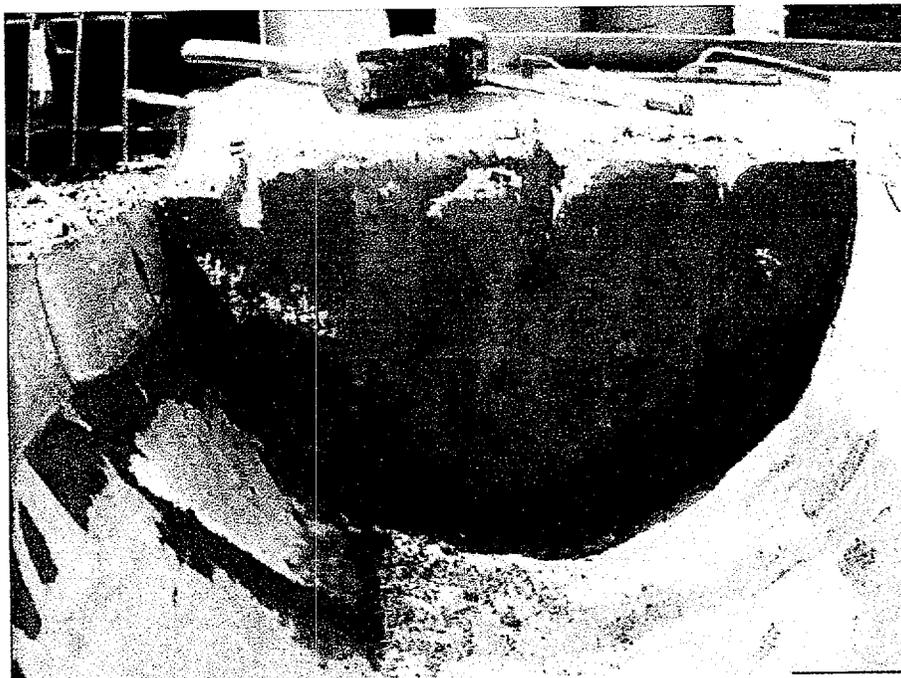


**Figure 5.5.** Test 1 Grout Surface. Small mounds were noted on an otherwise perfectly flat surface. Mounds are believed to be cement clumps which did not break up.

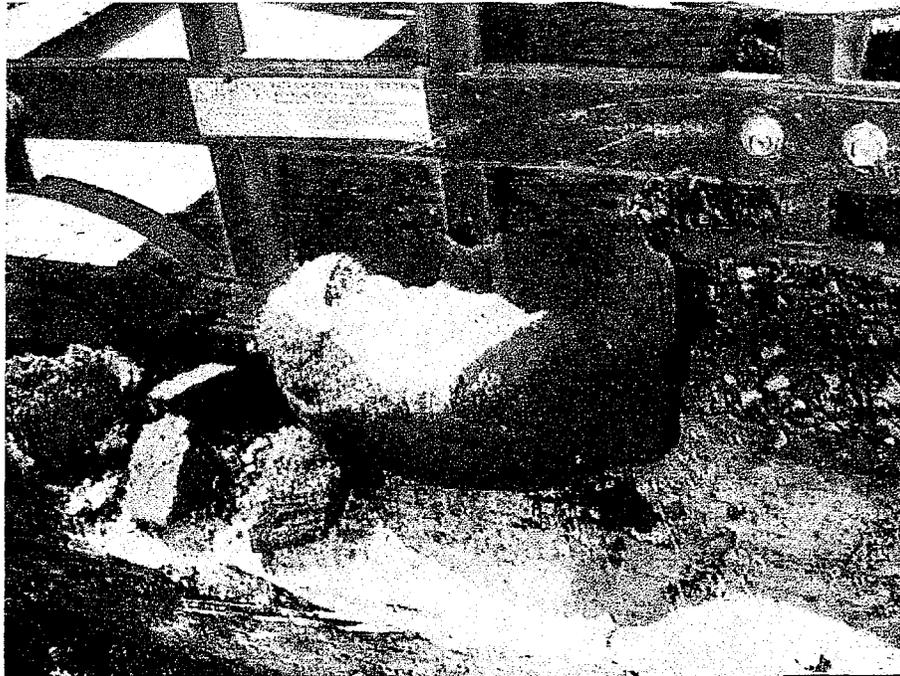
slurry. One end of the drum and the drum wall above the grout level was cut away. It was clear upon removal of the end of the drum that most of the soil did not mix into the grout product (Figures 5.6 and 5.7). Non-cemented soil was mounded between accumulator plates and piled along the sides of the drum. Mixing of cement to the floor of the drum occurred only within about a 5-in.-diam. circle surrounding each accumulator plate (Figures 5.8 and 5.9).



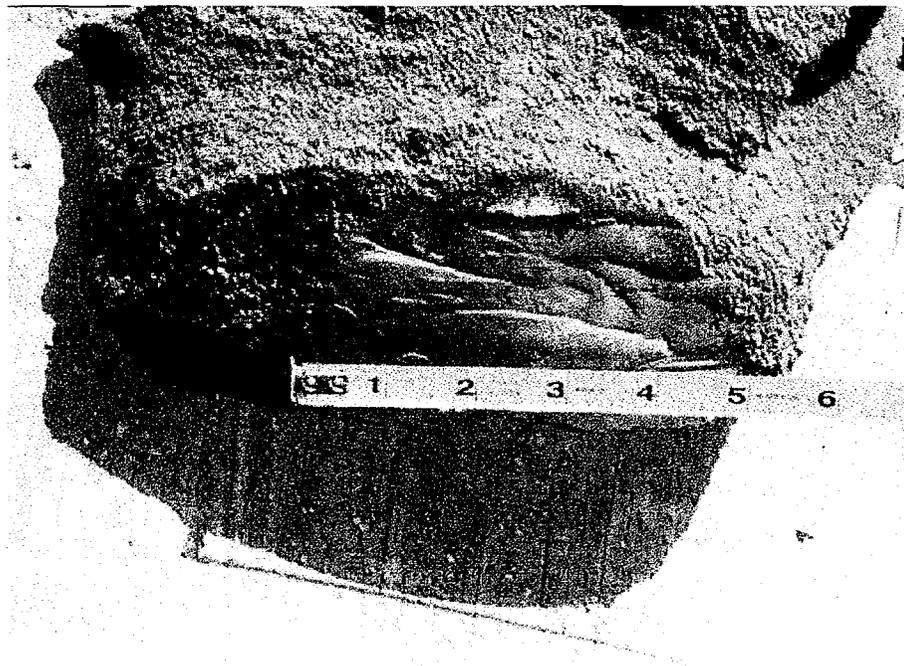
**Figure 5.6.** End View of Drum in Test 1. Dark area shows soil that is poorly mixed.



**Figure 5.7.** Profile along Drum Bottom in Test 1. Dark area shows soil that is poorly mixed.



**Figure 5.8.** Test 1, Profile of Cemented Material at an Accumulator Plate Position.



**Figure 5.9.** Test 1, Profile of Cemented Material at Accumulator Plate Position.

### 5.3 Test 1B Narrative

Because the soil failed to mix into the slurry, the air delivery system was reviewed. The cross sectional area available for flow in the tubes running between the pulsed-air valves and the tees which, in turn, supplied air to each pair of accumulator plates was determined to be insufficient. This resulted in a “choked-flow” situation which limited flow of air to the accumulator plates during each pulse. It was decided to repeat Test 1 with some modifications. The pulsed-air valves were mounted directly above the drum on larger tees to avoid flow restrictions and the air hose between the air tank and the pulsed-air controller/valves was eliminated. It was decided to simultaneously pulse both plates at one end of the drum in order to increase the mixing action at the addition point and to use a higher pressure (see Chapter 3) and frequency for the pulsing. A schematic of the revised pulsing system is shown in Figure 5.10.

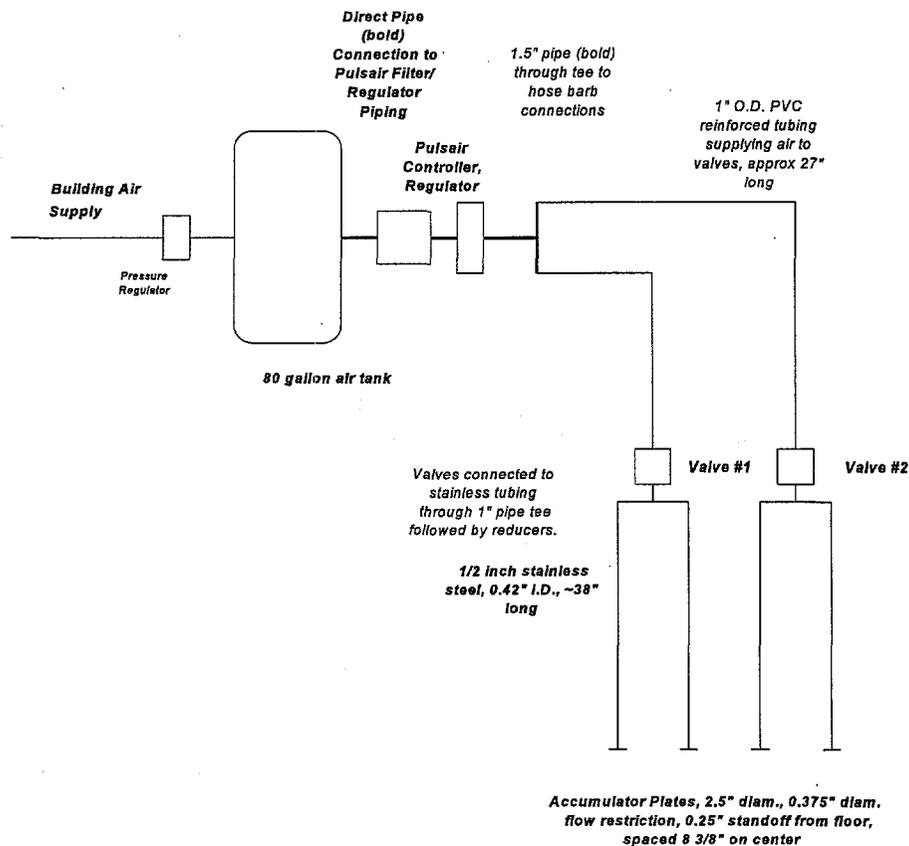
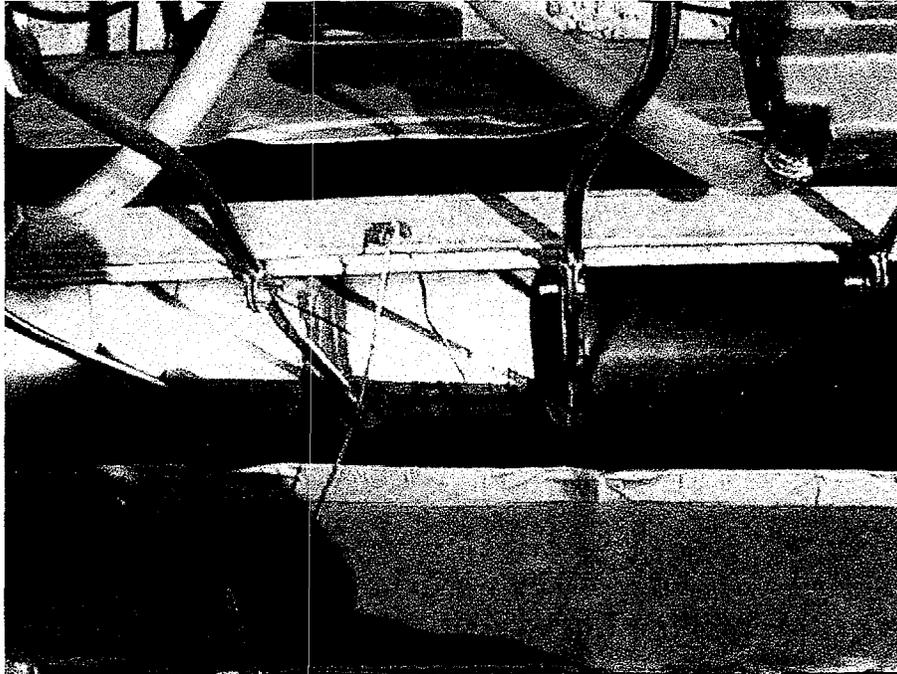


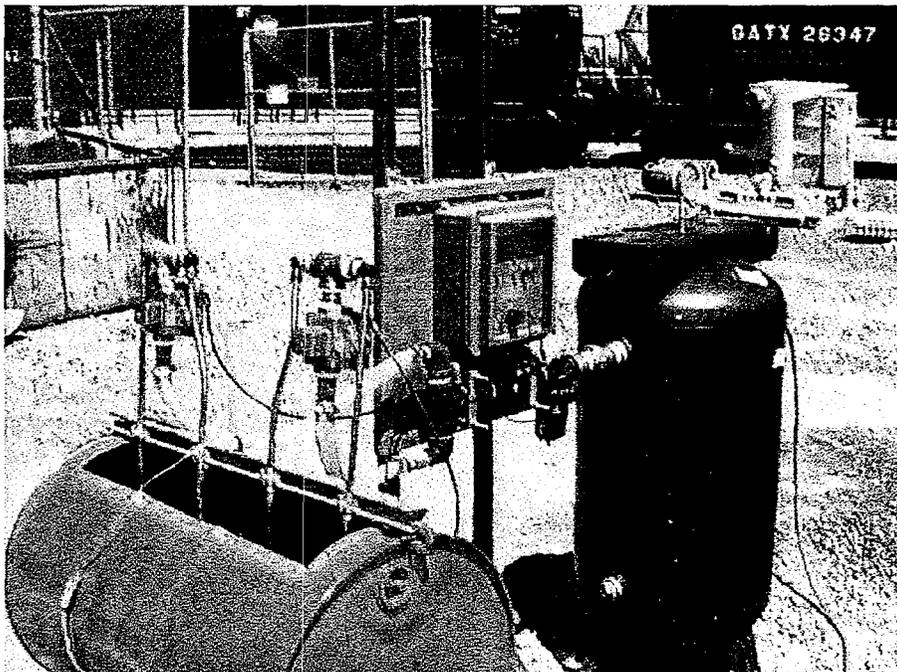
Figure 5.10. Revised Air Delivery System for Test 1B.

Photographs of the test setup prior to testing are provided in Figures 5.11 and 5.12. The pulse frequency was set at 21/minute for each valve (42 pulses/minute total). The pressure was approximately 65 to 67 psi, the highest pressure that could be maintained during operation. To allow sustained operation at higher pressures, a second air supply hose was added in Tests 2 and 3.

The mixing induced by the pulsing was noticeably more vigorous than during Test 1. It was noted that aerosols were visible exiting the drum through the addition flap. It is believed that these are water fog aerosols resulting from cool, expanded air passing through the warm slurry. The presence of the fog made it difficult to obtain video of the surface motion. Feeling under the surface while mixing with soil (75.7 kg) and water (73.1 kg), it was clear that soil settled to the bottom between pulses but for the most part was a mobile bed that was redisturbed with each pulse. A total of 26 kg of Aquaset-2H was added over a 20-minute period with a starting drum temperature of 34°C. The mixing was sufficiently vigorous that floating clumps of added dry solids were pulled beneath the surface or were broken up in one or two pulses. After Aquaset addition it was noted that there were some hard deposits on one side of the drum axis. These deposits felt harder than the deposits that existed before Aquaset-2H was added. The reason for the preferential deposition is not clear although it is possible that some shifting of the bracket holding the accumulator plates, or a shift in the drum within the stand, could have contributed to the deposition pattern. An additional 11.2 kg of Portland cement were added to the drum over the next 15 minutes without any difficulty. The top of the drum was then sealed with plastic to prevent evaporation during curing.



**Figure 5.11.** Positioning of Accumulator Plates Prior to Test 1B



**Figure 5.12.** Setup for Tests 1B, 2, and 3. (Tests 2 and 3 included an additional air hose to supply tank)

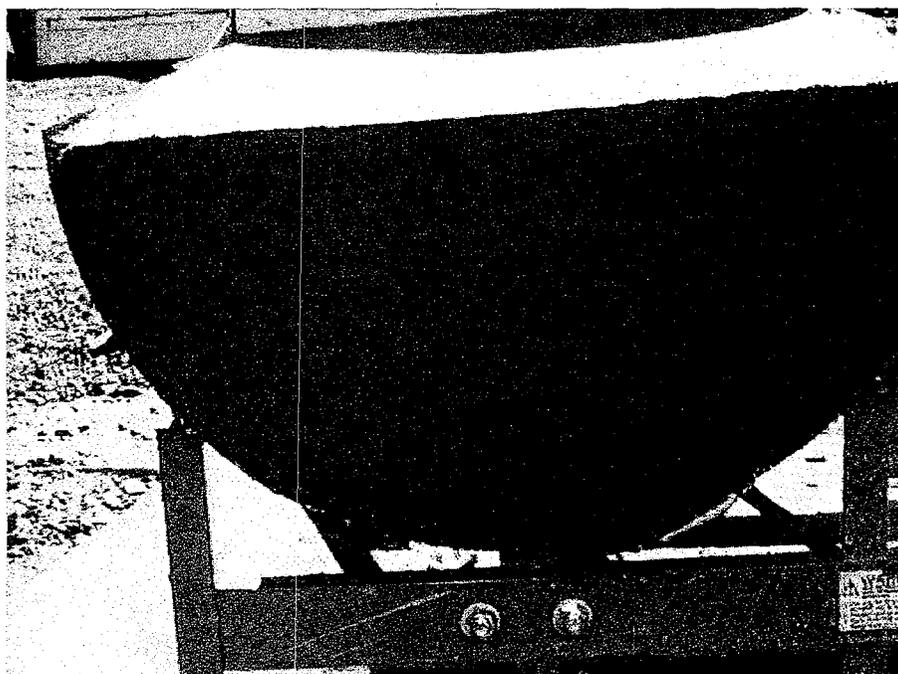
The temperature history data is summarized below:

<u>Date and Time</u>	<u>Temperature</u>	<u>Test Phase</u>
7/21/97 3:51 pm	34°C	During Aquaset-2H addition.
7/21/97 4:52 pm	31°C	Completion of mixing operation.
7/22/97 9:00 am	33°C	Curing
7/22/97 1:00 pm	34°C	Curing
7/22/97 2:00 pm	34°C	Curing
7/22/97 3:00 pm	35°C	Curing
7/22/97 4:00 pm	37°C	Curing
7/23/97 9:35 am	26°C	Curing

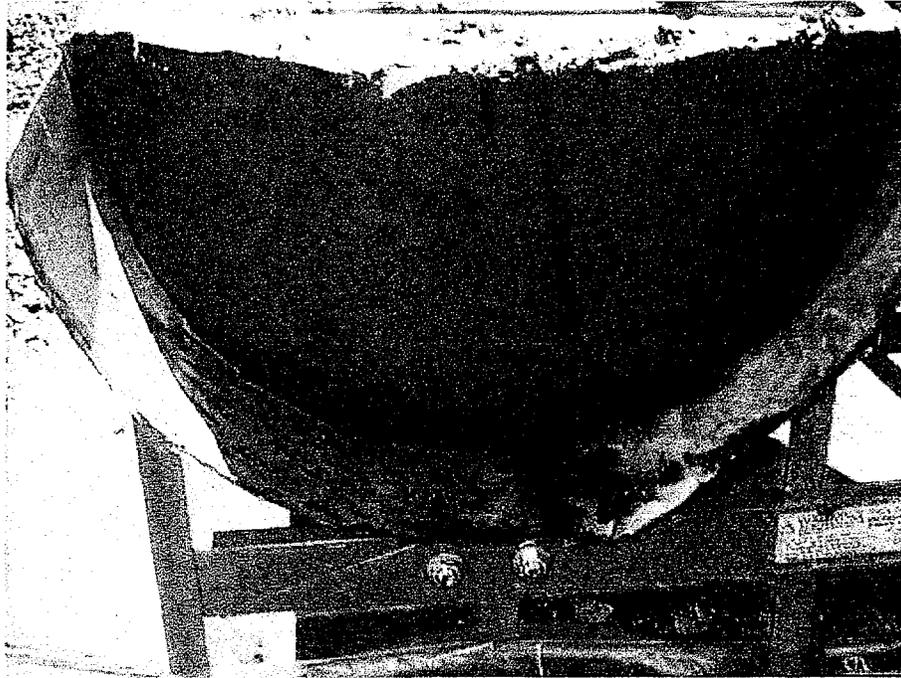
Forty-nine hours after mixing was complete, a total of 663 g of bleed liquid was collected from the top of the cured grout. Ignoring the mass of soluble components, this is equivalent to slightly less than 1% of the water initially added to the drum. A Soiltest CT-421 concrete penetrometer was used in four locations and all four locations indicated greater than 700 psi, the capacity of the instrument.

Disassembly of the grout was started approximately 65 hours after completing the mixing. As in Test 1, the top half of the horizontal drum and the end of the drum farthest from the addition point was removed first. The surface of the grout was smooth with no evidence of floating cement clumps that had been observed in Test 1. Next, the grout was chiseled away in about 6-in. increments down the length of the drum. Much less unmixed sand was observed in this test compared to Test 1. The deposits seemed to be biased towards the end farthest from the addition point and to one side of the line of accumulator plates. Small silvery specks were noted in several samples. Observation of bubbles within the cured grout indicate the specks may have a tendency to attach to air bubbles. It is postulated that the specks may be related to the stainless steel epoxy used to fill the ribs along the bottom of the drum. Photographs of the disassembly of the grout are shown in Figures 5.13 through 5.17.

Soil deposits were collected from Test 1B, dried, and weighed. To the extent possible it was attempted to make a clean separation between cement and separate soil phases, although some cement undoubtedly was included in the sample. The dry weight was 2521 g or approximately 3.4 wt% of the soil initially added to the drum. Thus, only a very small fraction of the sand failed to mix into the grout. The dried material was crushed using a plastic cylinder to break up clumps and then sieved to determine the change in size distribution. A comparison of the average size distributions is provided in Table 5.5. Clearly, the settled sand that did not mix in is overweighted in larger particles and underweighted in smaller particles, although the content of fine particles is not negligible.



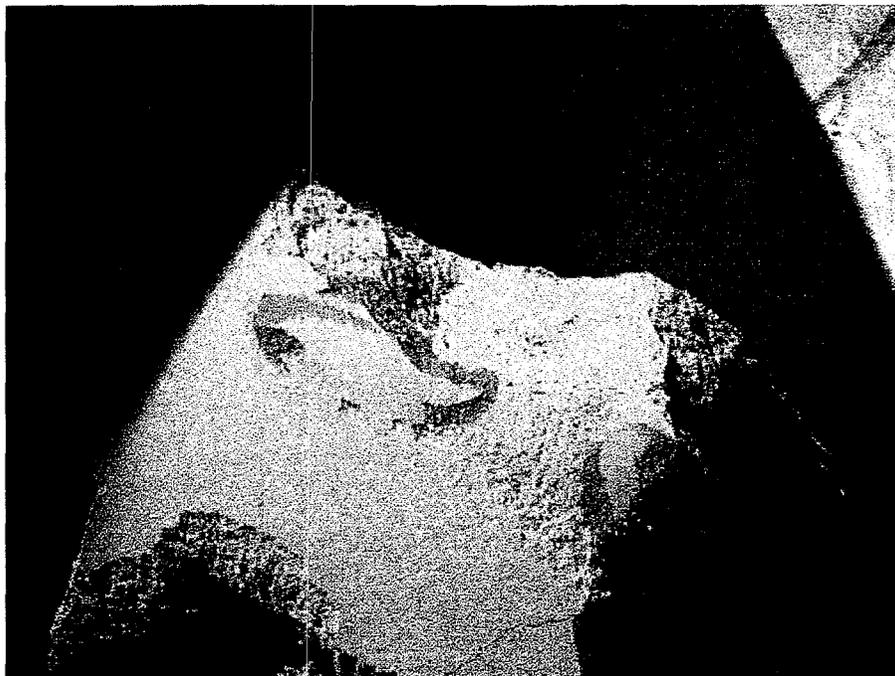
**Figure 5.13.** End View of Grout Block From Test 1B. The dark area is soil that is poorly mixed into the grout.



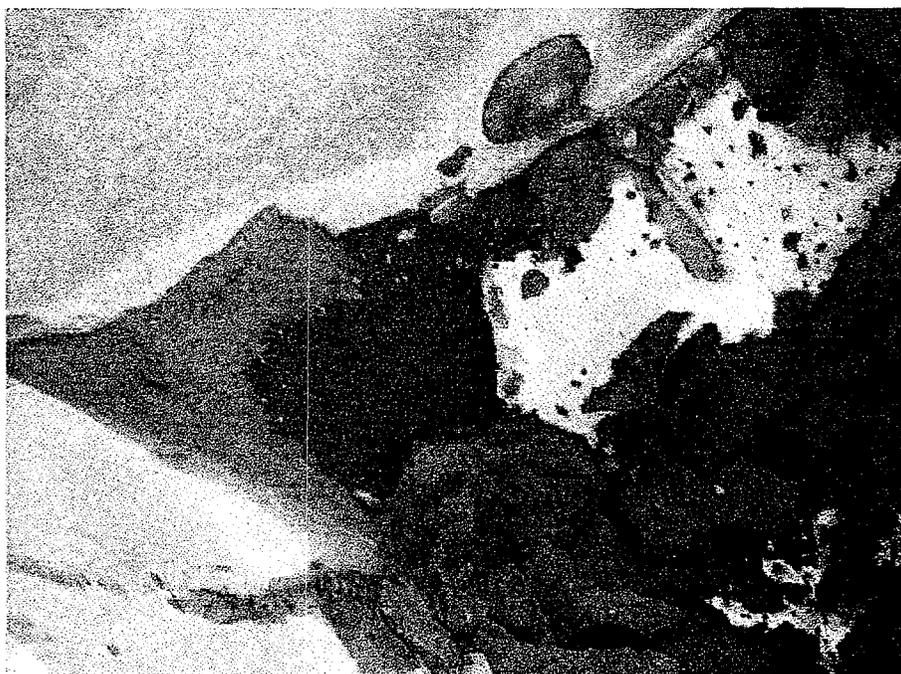
**Figure 5.14.** Test 1B Grout Block. Cross section with about 6 in. removed from end. Dark portion shows soil that is poorly mixed into the grout.



**Figure 5.15.** Test 1B Grout Block. Grout appears uniform. No soil deposits are visible.



**Figure 5.16.** Test 1B, Small Patches of Unmixed Soil Near the Addition Point.



**Figure 5.17.** Test 1B, Deposit of Sand (Dark Area) Located at End of Drum Near Addition Point.

**Table 5.5. Sieve Analysis of Recovered Soil from Test 1B.**

Particle Size, $\mu\text{m}$	Initial Soil, Wt%	Recovered Soil, Wt%
>841	11.2	29.1
600 to 841	4.7	12.1
300 to 600	7.9	16.8
212 to 300	2.7	4.1
150 to 212	4.5	5.0
75 to 150	19.6	12.0
<75	49.4	21.0

#### **5.4 Test 2 Narrative**

The setup for Test 2 was essentially the same as that for Test 1B, shown in Figures 5.11 and 5.12, with the exception that an additional air supply hose was added to the air tank in order to allow sustained operation at a higher pressure. The test was conducted with a pressure of 90 psi. The pulse frequency was set at 40/minute and over the course of the test drifted slightly to 44/minute. The test started with addition of 73.1 kg of water and 75.7 kg of soil. Feeling beneath the surface, very firm deposits were detected. When disturbed, the deposits would reform in a matter of minutes. The piles were not being moved by the pulsing as far as could be detected and were difficult to move by hand. While pulsing with water and soil only, it was noted that the drum had rotated slightly in its stand, leading to sand deposits forming preferentially on one side of the drum (the same side where deposits were seen previously). It is suspected that this is the reason for the preferential deposits that occurred in Test 1B. Times associated with additions and observations following the CsCl addition were as follows:

<u>Date and Time</u>	<u>Test Phase/Temperature</u>
7/29 10:50am	100 g CsCl was added to the drum after mixing water and soil
10:59	Begin addition of Aquaset-2H
11:06	Addition of Aquaset-2H complete, total added=26.0 kg
11:10	Begin addition of Portland cement container #1
11:14	Container #1 addition complete (11.2 kg of Portland cement)
11:17	Feeling below surface, the sand is no longer on the bottom and is being mixed. Numerous cement clumps can be felt below the surface.
11:22	Begin addition of container #2 of Portland cement
11:25	Addition of Portland cement container #2 complete (11.2 kg)
11:27	Feeling below the surface, only a few very small cement clumps remain, sand is mixed in.
11:45	30 g of $Y_2O_3$ added at addition point
12:05pm	30 g of $Ga_2O_3$ added at addition point
12:26	Pulsing discontinued, accumulator plates removed, tank covered with plastic to prevent evaporation
12:40	Temperature= $26^{\circ}C$
3:16	$27^{\circ}C$
7/30 10:08 am	$30^{\circ}C$
7:25 pm	$35^{\circ}C$
7/31 1:10 pm	$30^{\circ}C$

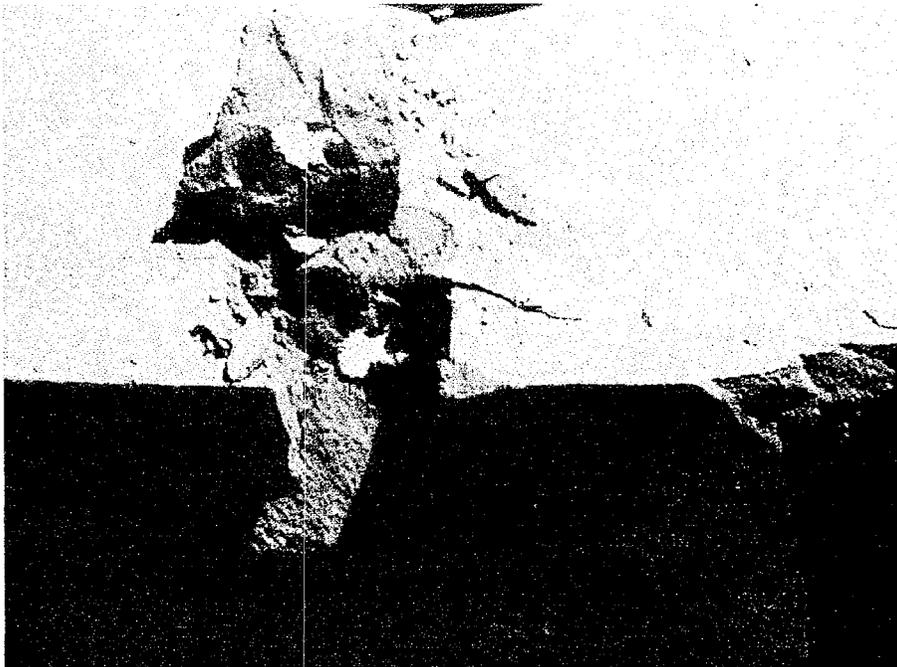
The grout was disassembled starting at 1:10 pm on 7/31/97. A total of 1678 g of liquid was collected from above the grout. It is believed that some or all of this moisture is the result of rain water getting into the drum through the thermocouple penetration of the plastic cover. Thus, no conclusions can be made about the degree of separated water that might be obtained with this mixture. The approach to drum disassembly was similar to previous tests. The top of the drum and the end farthest from the addition point were first cut away and then the solidified grout was chipped out of the drum. In this test, samples were obtained for XRF analysis to determine the

degree to which tracers were uniformly mixed.

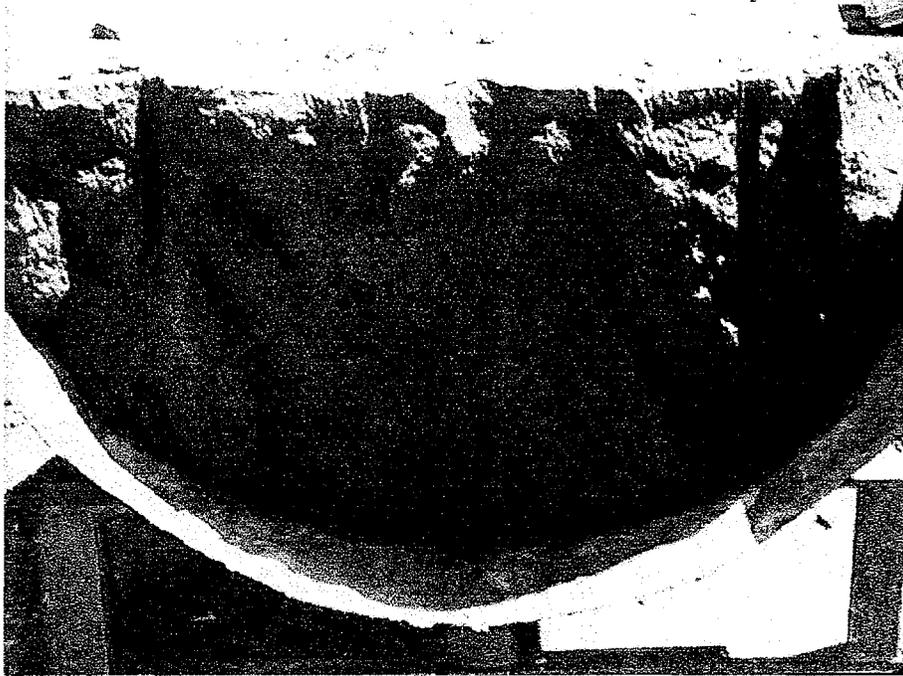
During disassembly, the end of the grout farthest from the addition point appeared uniformly mixed. Near the top center of the end of the grout, a few inches into the block and beneath the surface, was a white ball of tracer material as seen in Figure 5.19. XRF analysis determined that this “ball” was formed by the  $\text{Ga}_2\text{O}_3$  tracer. Additional views of the grout disassembly are shown in Figures 5.18 through 5.25.



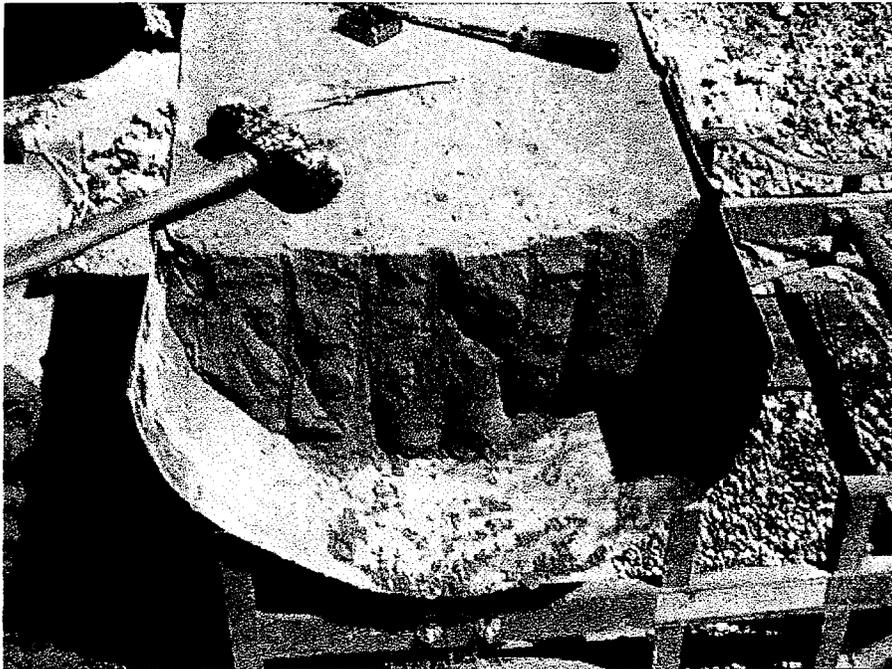
**Figure 5.18.** End of Grout Block in Test 2. Uniform appearance in grout. The different textures are a result of some of the grout being removed with the end of the drum.



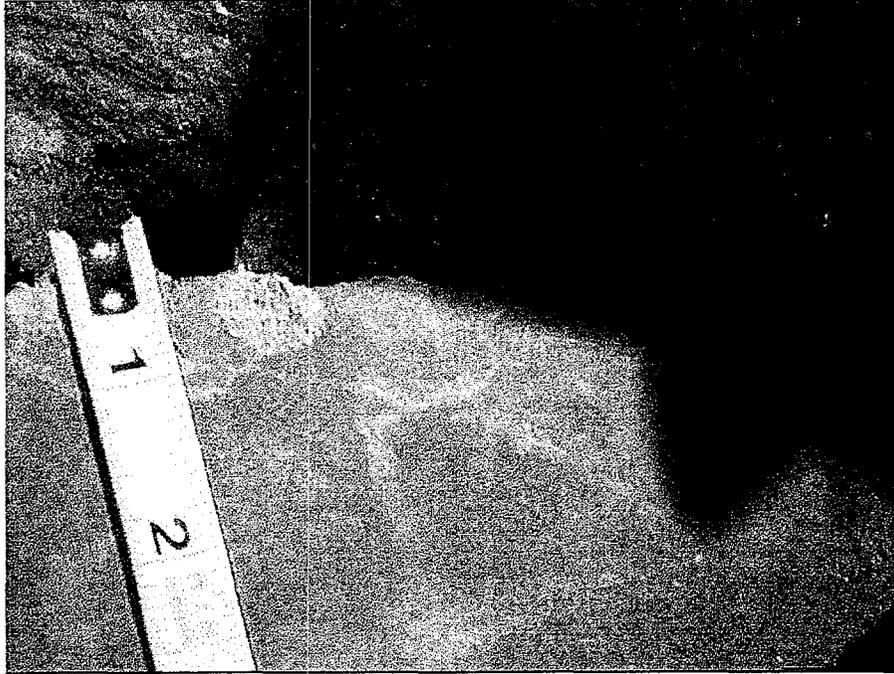
**Figure 5.19.** Clump of Tracer Material Located Just Below the Surface at the Top Center of the End of the Grout Block. XRF indicates this material is gallium tracer.



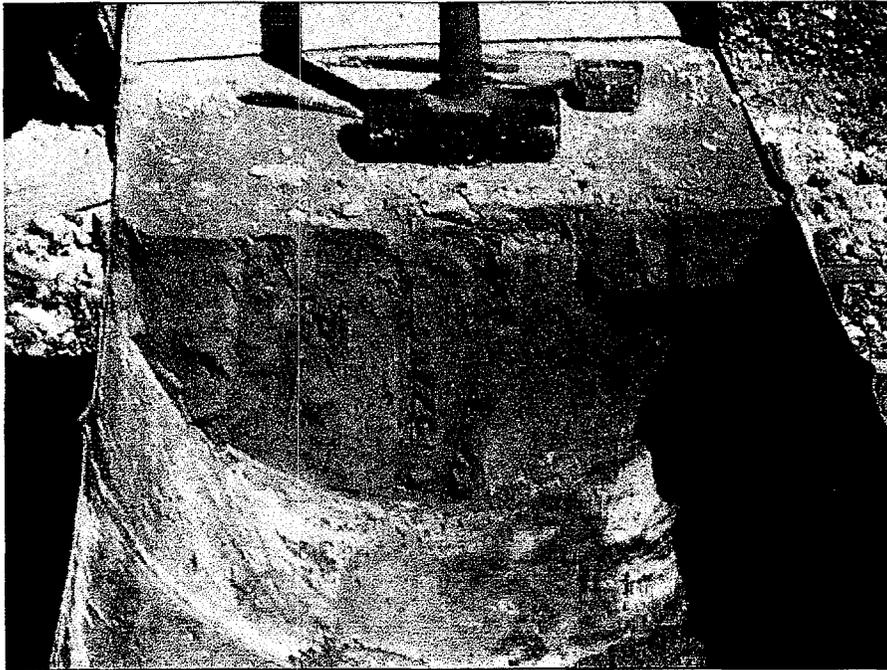
**Figure 5.20.** Grout Removed to ~ 6 in. from Drum End in Test 2. Grout appears uniform.



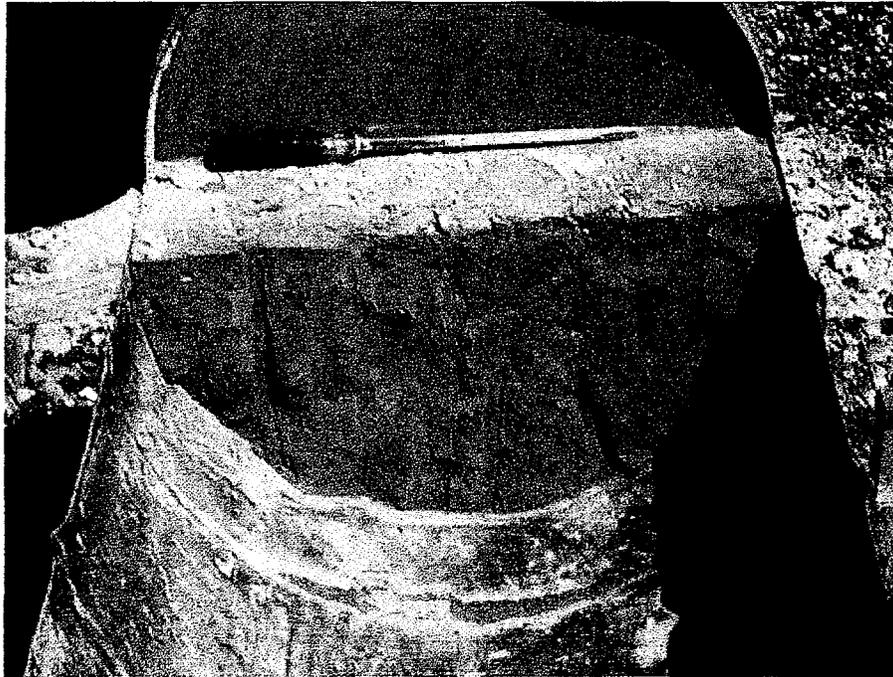
**Figure 5.21.** Grout Removed to ~12 in. from Drum End in Test 2. Grout appears uniform.



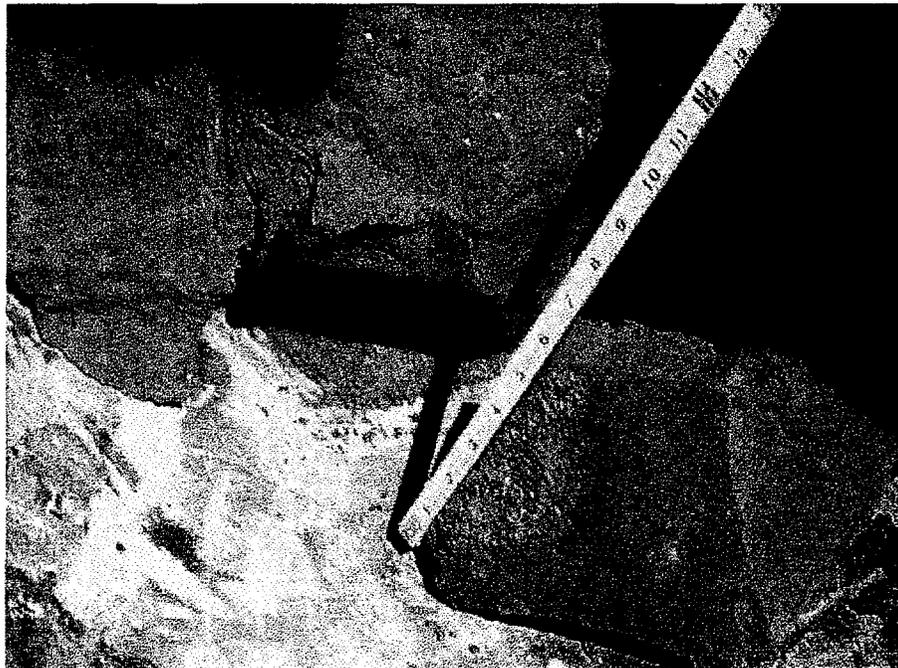
**Figure 5.22.** Very Small (1/2 in. diameter) Sand Deposit Located Along Drum Wall in Test 2.



**Figure 5.23.** Test 2, Approximately 1 ft of Grout Remaining. Grout appears uniform.



**Figure 5.24.** Test 2, Approximately 6 in. Grout Remaining in Drum. Appearance is uniform.



**Figure 5.25.** Test 2, Sand Deposit Found Near the Wall of Drum Nearer the Addition Point. This was the largest sand deposit found during disassembly of the material from this test.

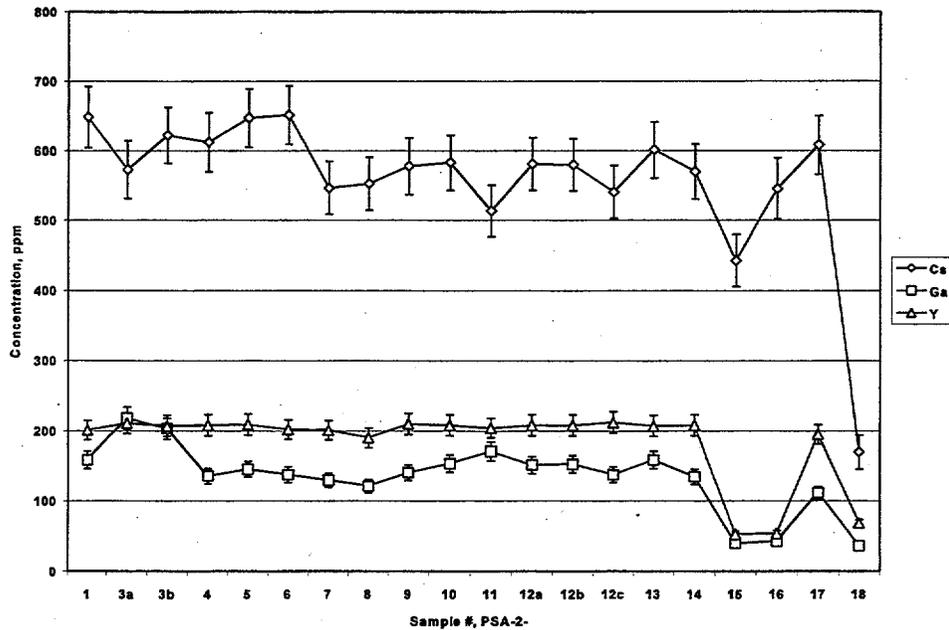
A number of samples were taken as the grout was disassembled. The samples were dried at 105°C to determine the weight loss on drying, and then crushed and made uniform in a mortar and pestle. A subsample was submitted for XRF analysis. Table 5.6 shows the wt% loss on drying along with a note on sample taken.

**Table 5.6. Percent Weight Loss on Drying for Various Samples From Test 2**

Sample #	%wt loss on drying	Notes
PSA-2-1	34.4	Top center of grout block end opposite addition point
PSA-2-2	37.2	Tracer deposit
PSA-2-3	33.1	4.5 in. back, 5 in. off center left, appearance is uniform
PSA-2-4	32.9	Bottom center, 8.5 to 10 in. back
PSA-2-5	34.2	Center of left quadrant, 8.5 to 10 in. back
PSA-2-6	33.9	Center of right quadrant, 8.5 to 10 in. back
PSA-2-7	32.8	1/16 in. sand layer with surrounding material
PSA-2-8	30.9	Sand deposit in drum rib with surrounding material
PSA-2-9	32.5	Sand deposit under second pulse plate with surrounding material
PSA-2-10	34.1	2 to 4 in. deep above inside plate next to addition point
PSA-2-11	33.7	12 in. from addition end wall, bottom center
PSA-2-12	33.7	12 in. from addition end wall, center of left quadrant
PSA-2-13	33.2	12 in. from addition end wall, left quadrant, center bottom
PSA-2-14	33.9	12 in. from addition end wall, top right corner against wall
PSA-2-15	11.4	Sand deposit scraped off of grout piece
PSA-2-16	32.5	Small deposit of lighter color, suspect cement clump
PSA-2-17	33.5	Sample from bubble and material directly below bubble
PSA-2-18	10.7	Larger sand deposit at addition end of drum

### 5.4.1 Test 2 XRF Analysis Results

Figure 5.26 shows the XRF analysis results for samples taken from the cured grout.



**Figure 5.26.** Tracer Concentrations of Samples Taken From Test 2.

Significant deviations in Ga content are seen for samples 2, 15, 16 and 18. Sample 2 is not shown in Figure 5.26 because it consisted primarily of a portion of the Ga tracer that had formed a solid clump and was not dispersed. XRF analysis sufficient to determine that the clump was the Ga tracer was performed but detailed results were not pursued for this sample. Sample preparation consisted of grinding in a mortar and pestle followed by a “cone and quarter” procedure to obtain the subsample for XRF analysis. Samples 3a and 3b were reanalyses of the same sample. It is believed that sample 3 was contaminated by being processed through the sample preparation steps following the Ga tracer clump. Thus, its elevated Ga reading may be due to contamination. Samples 15 and 18 are from sand deposits where the gallium may not have been mixed, and sample 16 is believed to be a clump of cement or Aquaset-2H that formed a ball and did not mix.

Results for Y are much more uniform than those for Ga. The relatively large scatter in the Ga tracer results compared to Y results may be due to the Ga ball breaking down as the slurry continued to mix. The Y results for samples 15, 16, and 18 show the same significant deviation from the uniform concentration as the Ga. As noted above, samples 15 and 18 are primarily sand deposits and 16 is believed to be a cement clump that failed to break up.

The Cs tracer results are much more scattered as a result of the poorer analytical capability for this analyte. The Cs content is low as is expected for samples containing significant sand (15, 18). For sample 16 (the deposit of lighter color, which is expected to be a clump of cement or Aquaset-2H), the Cs content is close to the average value. This tends to suggest that the Cs was in solution and was drawn into the region by capillary pressures. The Cs tracer content was compared to the weight loss on drying as seen in Figure 5.27. For samples 15 and 18, which contained a significant amount of sand, both the Cs and moisture contents were low. However, the variation in Cs content has little correlation to the weight loss on drying data for samples not noted to have contained sand.

The samples were also examined for their Zr and Ca contents. The data are shown in two plots. In Figure 5.28, the relative concentrations of Zr and Ca are shown for all samples that were not targeted at some sort of inhomogeneity such as a sand deposit. The relative value is determined by averaging all samples in the plot and dividing by the average. Thus, if there were no variation, all results would be equal to 1.0 in the plot. These samples best represent the degree of uniformity in the bulk grout. As can be seen in the figure, within the analytical uncertainty, the bulk of the grout is quite uniform.

Figure 5.29 shows the samples targeted at an inhomogeneous location in the cured grout. The data have been normalized by dividing by the average concentration of uniform samples as in Figure 5.28. The relative compositions of the raw materials are shown to the left of the plot for reference. Samples 7 and 8 were of very small sand deposits and included the immediately

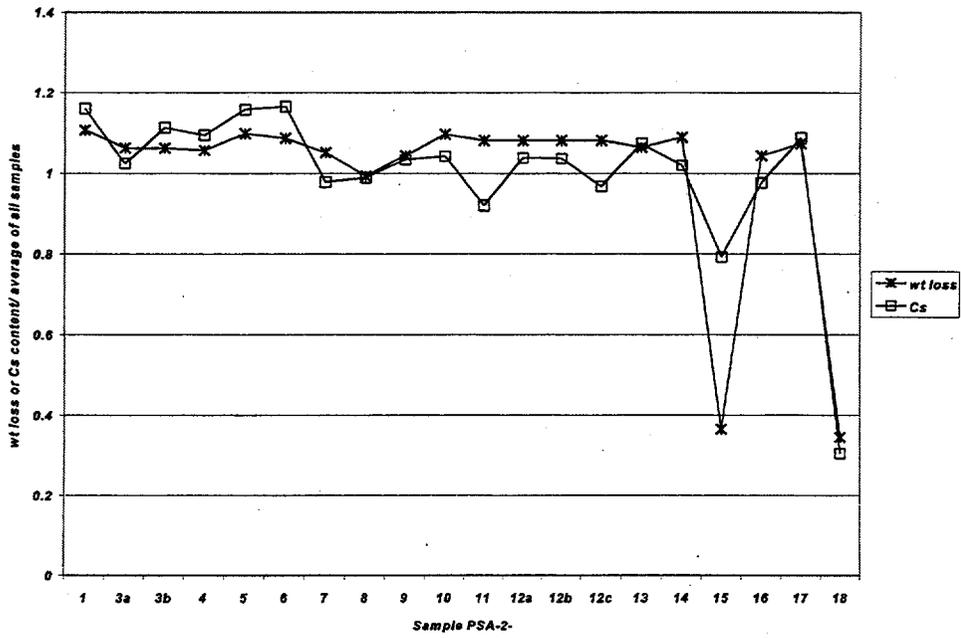


Figure 5.27. Comparison of Weight Loss on Drying and Cs Content for Test 2 Samples

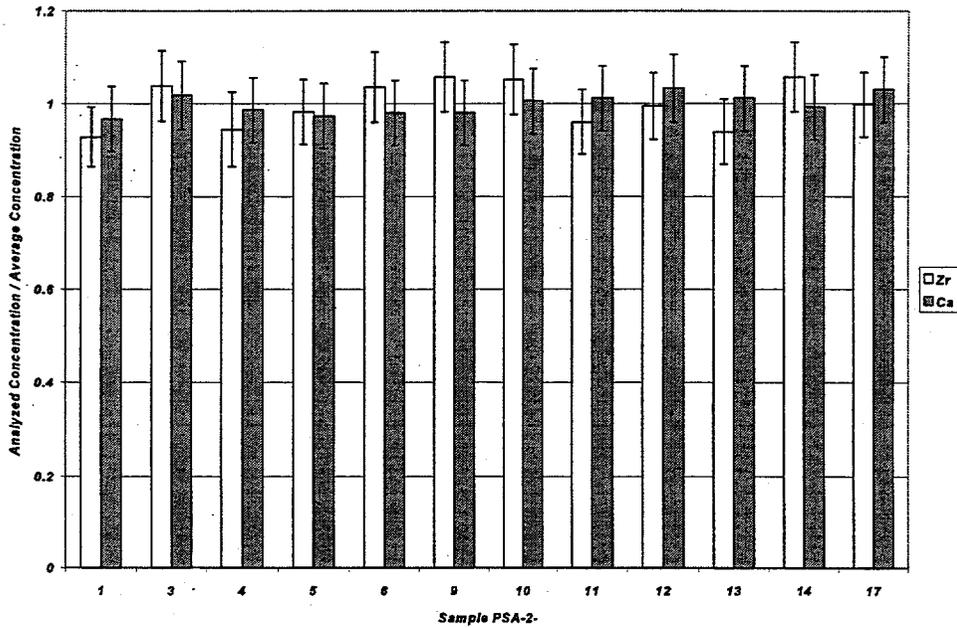
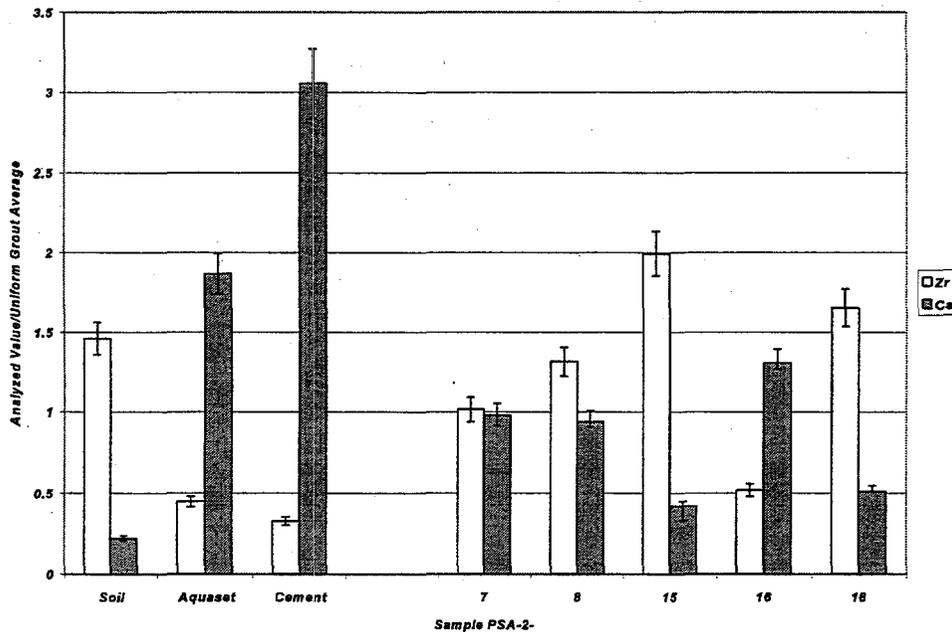


Figure 5.28. Comparison of Relative Ca and Zr Contents for Test 2 Samples Not Noted as Representing Inhomogeneous Locations



**Figure 5.29.** Test 2 Ca and Zr Analyses for Samples Directed at Inhomogeneities

adjacent material. Sample 7 is within analytical error of being the average composition while sample 8 shows a moderate excess of the sand. Samples 15 and 18 appear to be primarily sand deposits while sample 16 appears to be primarily cement or Aquaset-2H (Ca) with little soil (Zr).

### 5.5 Test 3 Narrative

The equipment setup for Test 3 was the same as for Test 2 and is accurately represented by Figures 5.10 through 5.12. Due to the extra scoping test performed (Test 1B), the soil initially collected was exhausted and additional soil was needed for Test 3. Because a second soil batch was collected, there are minor differences between the soil used in earlier tests and the soil for Test 3. The additional soil was collected from the same source and was analyzed for soil moisture and size distribution by sieving (see Section 5.1).

The chronology of Test 3 was as follows:

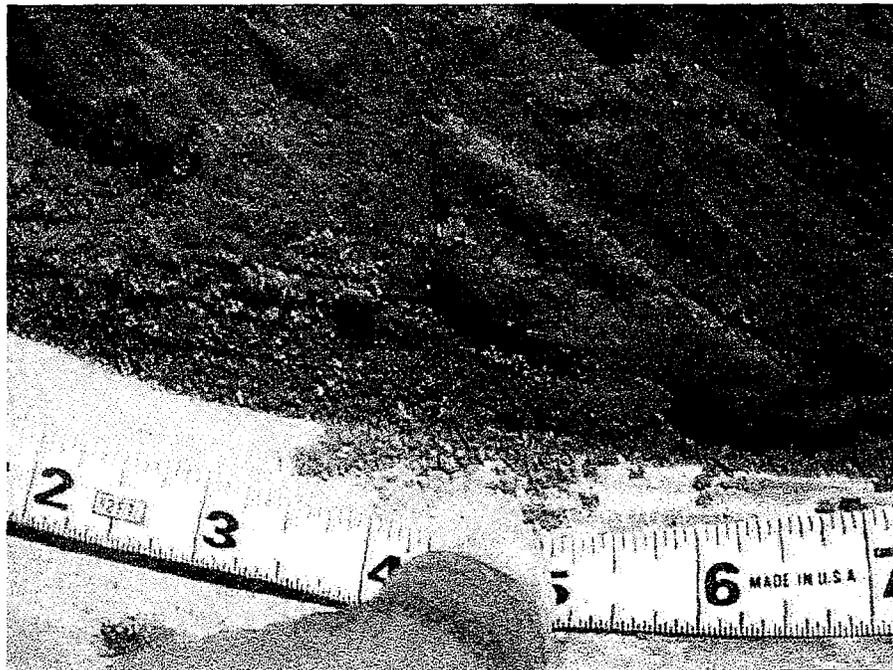
<u>Date and Time</u>	<u>Test Phase/Temperature</u>
8/5 4:00 pm	Placed 73.1 kg water in drum and poured 75.7 kg soil into the drum. Allowed to settle overnight.
8/6 10:17 am	Began mixing operation. Sustained pressure of 90 psi, 40 pulse/minute total between plates. Significant sand deposits felt on either side of plates.
10:19	CsCl tracer added as solution of 100.1 g CsCl and 100 ml water.
10:33	Began scoop addition of Aquaset-2H to drum.
10:40	Aquaset-2H addition completed (37.2 kg total)
10:44	Temp = 32°C
11:00	A few cement clumps were felt below the surface. Sand deposits are significantly reduced but could be felt along walls on either side of accumulation plates.
11:02	Y <sub>2</sub> O <sub>3</sub> tracer was added as a water slurry of 29.8 g Y <sub>2</sub> O <sub>3</sub> and 100 ml water.
11:05	Pulse frequency was measured at 41 pulses/minute.
11:20	Some sand deposits could be felt below the surface along the wall opposite the addition hatch. Fewer deposits were along the near wall. No cement clumps were felt.
11:22	Ga <sub>2</sub> O <sub>3</sub> tracer was added as a slurry of 29.1 g Ga <sub>2</sub> O <sub>3</sub> and 100 ml water.
11:27	T= 32°C
11:40	A few cement clumps were felt below the surface. No clumps were noted.
11:42	Shut down the mixer, removed plates, and covered tank with plastic.
2:22 pm	T= 43°C
3:58	T= 47°C
5:51	T= 43°C
8/7/97 9:34 am	T= 32°C
11:36	T= 33°C
2:54 pm	T= 41°C
8/8/97 12:48pm	T= 33°C, began breaking grout apart.

The thermocouple was several inches off center to the west and was therefore measuring temperature to the west of the centerline. There was no appreciable separated water on top of the grout after 48 hours of curing, although the surface felt moist. On the day of disassembly, it was discovered that the corner of the plastic, which was held down with duct tape to prevent evaporation, had been lifted. This may have allowed a small amount of evaporation to occur. The surface of the grout was covered with a thin flaky white material that may have resulted from evaporation of a thin layer of liquid containing soluble material. The grout was relatively softer than previous tests and could easily be dented with a finger. With pressure from a finger, moisture could be forced to the surface of the grout. Using the Soiltest CT-421 penetrometer, readings between 415 and 581 psi were obtained with an average of 542 psi (17 measurements). It is not clear whether the variations were due to the approximate nature of the measurement technique or actually the result of some variability in penetration resistance in the material itself (see Appendix A).

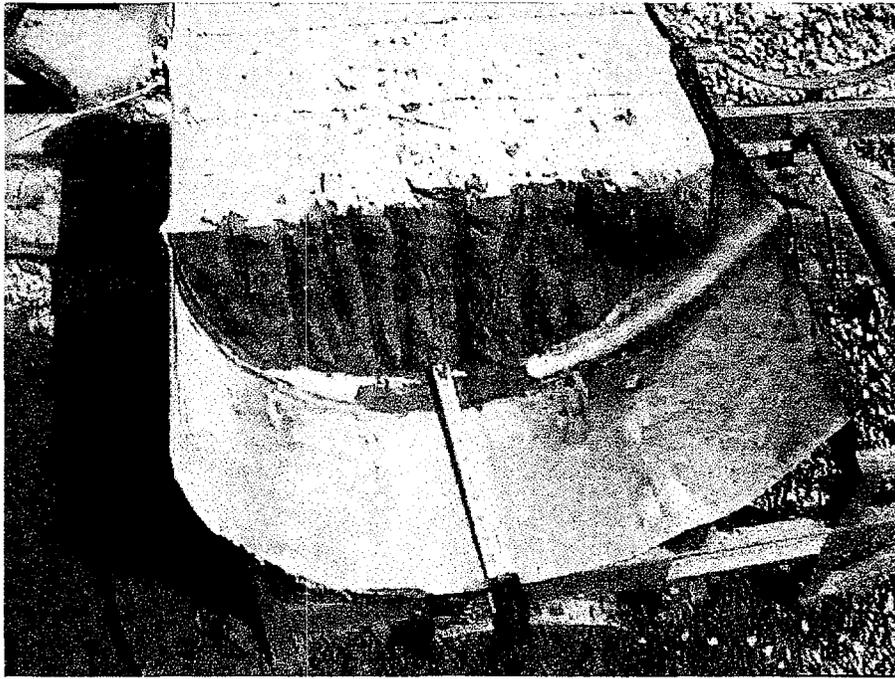
As was done previously, the grout was disassembled by cutting away the upper portion and the end of the drum farthest from the addition point. Samples were taken for analysis by XRF and pictures were taken. The pictures shown in figures 5.30 through 5.36 illustrate observations made during disassembly. Because the soil and Aquaset-2H have similar colors, the soil layers are more difficult to see for this test than was the case in Test 2.



**Figure 5.30.** Soil Deposit Along Bottom of Drum at End Farthest From Addition Point. Soil can be seen by slightly different color and texture.



**Figure 5.31.** Test 3, Cross Section of Sand Layer ~ 4 in. From Drum End. Deposit exists from drum end (see Figure 5.30) to about 6 in. into the block. Dimensions are up to about 5 in. wide and a maximum of 1 in. thick. Deposition is off center to the east of the bottom drum centerline.



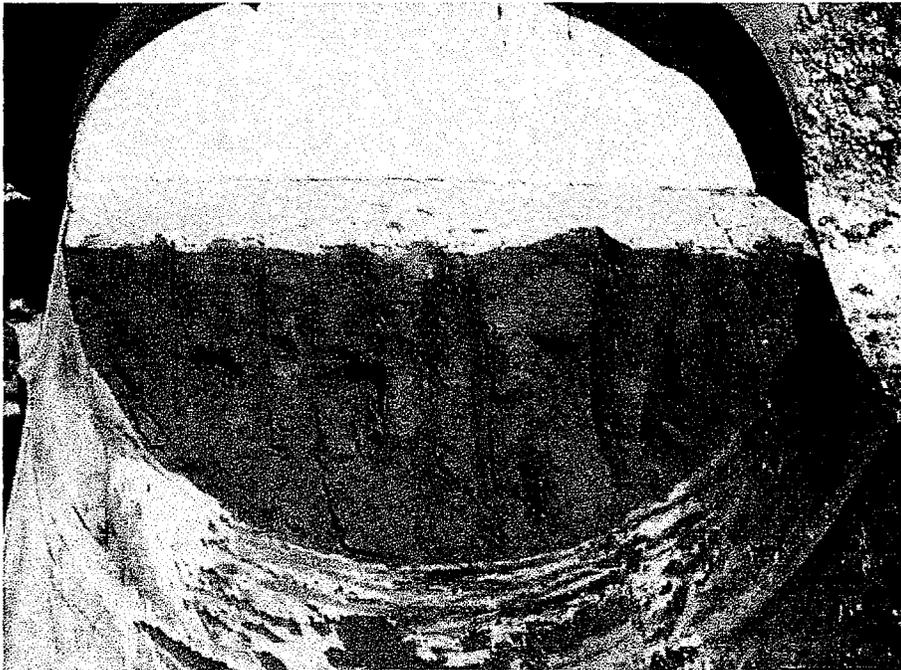
**Figure 5.32.** Test 3, Grout Removed to Between 11 in. and 12 in. From End. Approximate position of second accumulator plate from. No sand deposits apparent at this cross section.



**Figure 5.33.** Test 3, Cross Section at ~10 in. From Addition End of Drum. Sand deposit runs from ~8 in. to ~12 in. from addition end of drum and is up to 1/2 in. thick.



**Figure 5.34.** Test 3, Grout Piece Removed from Location Illustrated in Figure 5.33. The side facing down was facing the camera in Figure 5.33.



**Figure 5.35.** Test 3, Cross Section With ~ 4 in. of Grout Remaining in the Drum. Removing sample numbers PSA-3-14, 15 and 16 created divets in the wall.



**Figure 5.36.** Test 3, Sand Deposit at End of Drum Following Removal of Last 4 in.

A number of samples were taken as the grout was disassembled. The samples were dried at 105°C to determine the weight loss on drying, and then crushed and made uniform in a mortar and pestle and a subsample submitted for XRF analysis. Table 5.7 shows the percent weight loss on drying along with explanatory notes.

**Table 5.7. Percent Weight Loss on Drying for Various Samples from Test 3**

Sample #	%wt loss on drying	Notes
PSA-3-1	36.98	Top center of grout at end of drum farthest from addition point.
PSA-3-2	11.31	Soil deposit on bottom, off center to east (left), running 6 in. into the grout block
PSA-3-3	37.70	Taken between first two plate location (~8 in. from end) mid height, off center to right
PSA-3-4	36.50	Taken between first two plate location (~8 in. from end) bottom center
PSA-3-5	38.30	Taken between first two plate location (~8 in. from end) mid height, off center to left
PSA-3-6	36.51	Taken 8 to 12 in. from end, from rough texture material, difference may simply be a difference in what stuck to the wall when removed
PSA-3-7	36.71	Taken 8 to 12 in. from end, from smooth texture material, difference may simply be a difference in what stuck to the wall when removed
PSA-3-8	30.51	At second plate from cut-away end of drum, center, 4 in. below surface
PSA-3-9	38.71	12 in. from end nearest addition point, top center, 2 in. below surface
PSA-3-10	37.54	12 in. from end nearest addition point, bottom center 2 in. above floor
PSA-3-11	38.36	12 in. from end nearest addition point, 4 in. down, 4 in. from left wall
PSA-3-12	38.13	12 in. from end nearest addition point, 4 in. down, 4 in. from right wall
PSA-3-13	6.15	Sample of sand deposit running from 8 to 12" from intact drum end reaching up to 1/2 in. thick
PSA-3-14	38.61	3 to 4 in. from intact drum end, 5 in. deep, 3.5 in. from left wall
PSA-3-15	38.38	3 to 4 in. from intact drum end, 5 in. deep, 8 in. from left wall
PSA-3-16	38.26	3 to 4 in. from intact drum end, 5 in. deep, 14 in. from left wall
PSA-3-17	11.03	Sample of sand deposit off center to the left and running several inches out from the wall of the drum. Was not visible on cross section of grout made 4 in. from intact wall of the drum.

### 5.5.1 Test 3 XRF Analysis Results

The analyses of tracer compounds in the grout are shown in Figure 5.37. Samples 2, 13, and 17 represent sand deposits and are low in all tracers. With the exception of the sand deposits, the Y and Ga appear to have very uniform compositions. In Test 3, the tracers were slurried in water prior to their addition to prevent clumping of the dry powder. This may be the reason for the lower degree of variability in the Ga compared to Test 2. The Cs results are similar to those for Y and Ga but are more scattered due to the poorer analytical accuracy. As in Test 2, the high soil content samples have both low Cs and low weight loss values. However, there is little or no correlation between water content and Cs content for samples not noted to have contained excess soil.

Figure 5.38 shows the XRF results for Zr (a marker for soil) and Ca (a marker for Aquaset-2H) for samples that were not targeted at an inhomogeneity. The results show that within the analytical error the samples are uniform<sup>(1)</sup>. Figure 5.39 shows the Ca and Zr analyses for samples which were targeted at an apparent inhomogeneity. The XRF results for samples 2, 13, and 17 confirm the expectation that these deposits consist primarily of unmixed soil.

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<sup>(1)</sup>All samples except #12 encompass the value of 1.0 within the analytical error estimate. Sample 12 Zr value narrowly misses a value of 1.0. However, the Ca value is at the expected average and since this is a binary mixture of soil and Aquaset, the small Zr deviation is attributed to analytical error. For a 95% confidence interval one deviation per 20 samples would be expected, so a single deviation out of the 28 samples is not surprising.

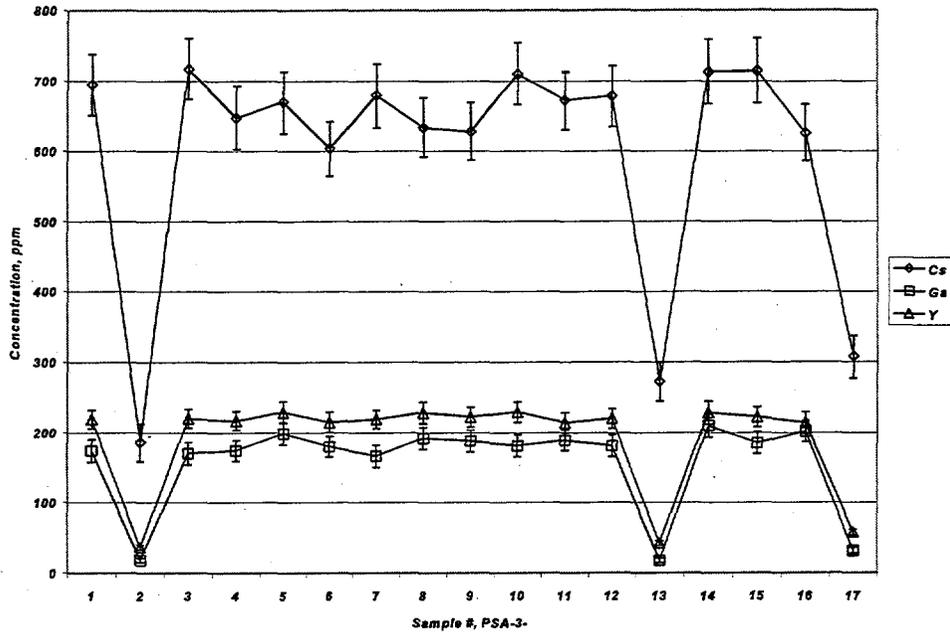


Figure 5.37. Test 3 Tracer Concentrations

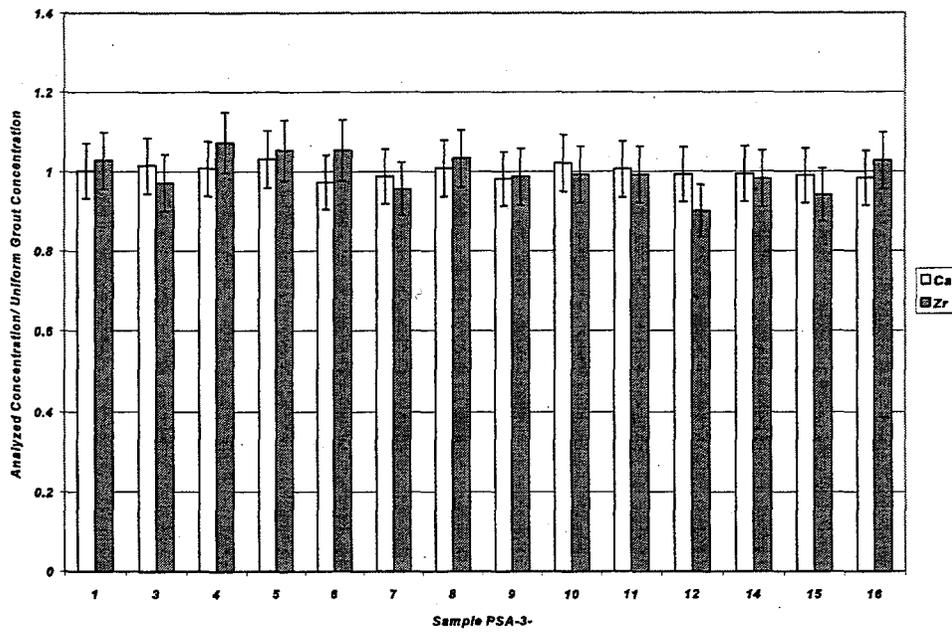
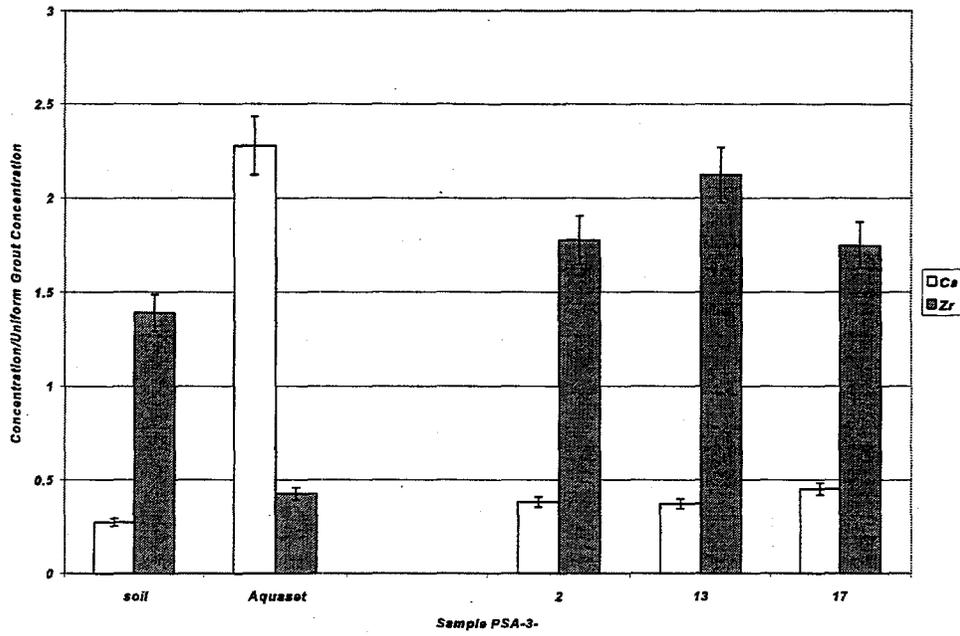


Figure 5.38. Test 3 Ca and Zr Concentrations of Samples Not Targeted at Inhomogeneities



**Figure 5.39.** Ca and Zr Analyses of Test 3 Samples. All samples clearly have an excess soil component with very little Ca (Aquaset-2H) present.

## 6.0 Conclusions and Recommendations

This section contains the key conclusions from the testing along with recommendations concerning full-scale testing and application.

### 6.1 Conclusions

Several key conclusions were reached as a result of this testing:

- 1) The testing indicates that the use of pulsed-air mixing technology to mix cementitious dry solids with water in a horizontal, cylindrical tank is feasible. The pulsed-air mixing did an excellent job of creating sufficient surface agitation to mix floating dry solids into the liquid. In the testing, the pulsed-air mixing technology was able to mix slurries of cementitious solids at concentrations much higher than the formulations initially suggested for use by INEEL. While some cement clumps were observed to form below or just at the surface of the liquid as the dry solids were added, they tended to break down over time and mix into the slurry.
- 2) The pulsed-air mixing technology did a relatively good job of mixing settled, non-cohesive solids into the cement slurry. Test 1B left only about 3.4 wt% of the sand in deposits, while Tests 2 and 3 had qualitatively less soil existing as deposits. However, in all cases there were some small deposits of sand or soil along the bottom of the drum.
- 3)  $R_{\text{pulse}}$  is very important to the soil suspension performance. Taking into account the choked flow in the air delivery system, the mobilization radius in Test 1 agreed reasonably well with the  $R_{\text{pulse}}$  values determined when previously testing a similar plate in water (Powell and Hymas 1996). Resolving the choked flow problem and increasing the pressure to expand the  $R_{\text{pulse}}$  dramatically increased the suspension performance in

Tests 1B, 2, and 3.

- 4) The concentration of cementitious solids is important in the suspension of the soil. Higher cementitious solids concentrations do a superior job of suspending the soil from the bottom of the drum. When the mixing system was operated with water and soil only, the sand was observed to be primarily on the bottom of the drum. The deposits felt hard and it was initially doubtful that they would mix in. However, with the addition of cementitious dry solids, the vast majority of the material was mixed in. It is expected that the qualitatively better solid suspension performance obtained in Test 2 compared to Test 3 was a result of the increased concentration of the cementitious solids.

## **6.2 Observations**

- 1) The product produced using the Aquaset-2H-only formulation was much softer than the mixture of Aquaset-2H and Portland cement. The product was moist to the touch and could be deformed by hand to produce water at the surface of the product. The product criteria will need to consider to what degree such properties are acceptable.
- 2) Suspension performance was qualitatively superior in Test 2 which used the Aquaset-2H and Portland cement blend with twice the suggested Portland cement. It is believed this may be due to the higher density and viscosity of the slurry which may enhance the ability to suspend the soil particles.

## **6.3 Recommendations**

- 1) Higher concentrations of cement in the slurry can easily be mixed into the slurry, appear to increase the suspension of solids, and result in a stronger final product while reducing the potential for bleed water. The only disincentives for higher concentrations of cement may be the cost of the additional cement, the availability of volume in the tank, and any

potential problems associated with excessive heat generation.

- 2) Testing experience indicates that the errors in the  $R_{\text{pulse}}$  correlation were significant for the smallest plate sizes. While the extent of error may not be as significant for larger plates, it is recommended that when selecting test parameters for the larger scale test, predictions of  $R_{\text{pulse}}$  should be made both by using the correlation by Powell (1997) and by examining the supporting data taken under conditions most similar to the test conditions.

#### **6.4 Parameters for Further Investigation**

**Solid addition and clump formation** - Larger scale testing should include a solid addition system representative of what may be used for addition to an actual tank. The formation of clumps which broke up over a period of mixing was noted in the scaled testing. The scaling of the clump formation and breakup processes is uncertain and may or may not scale favorably.

**Effect of saline supernatants and actual sludge** - There is a potential that the dissolved salts and the solids in the tank may participate in the cementitious reactions. This possibility should be investigated prior to application in an actual tank.

**Representativeness of simulant for solids on tank bottom** - The soil used in testing was selected with little knowledge of the actual size distribution of actual tank solids. Some investigation to determine if the size distribution is representative or at least conservative relative to the tank being considered is recommended. Additional scoping tests with a variety of different settled materials could be performed to determine the sensitivity of the suspension result on the solid size distribution.

**Confirm  $R_{\text{pulse}}$  behavior** - Because it is not possible to tell whether all settled solids are being mixed into the slurry in the actual application, the mixing performance of the system should be confirmed at larger scale prior to implementation in an actual tank.

**Higher cement concentrations and heat generation** - There is a potential for high temperatures to occur if cement-rich formulations are used. If larger scale testing is performed, insulating the vessel and improved temperature monitoring may be advisable.

**Effect of tank level on mixing** - The current testing has not addressed the degree to which tank level may influence mixing performance. If it is required to operate at a level significantly different than roughly 1/2 full, testing to check the significance of this factor should be performed.

**Aerosol generation** - Aerosol generation should be investigated to determine if this may be an issue for full-scale application. At the higher pressures, an aerosol fog was observed in the tank head space. It is suspected that this fog was primarily water vapor formed by passing the cool expanded gas through a warm water slurry. However, if these aerosols contain more than water vapor, measures to mitigate the aerosol generation may be needed.

**Collection of solids in sump, hemispherical ends or other special locations** - The test vessel in this testing did not include the sump or hemispherical ends on Tank V-3. It is possible that these areas may preferentially collect faster settling solids. Testing at larger scale in a vessel including these features could address these issues.

**Optimization of full-scale mixing parameters prior to application (pressure, frequency, pulse volume, pulse patterns)** - If additional large scale testing is to be performed prior to deployment, some optimization of pressure, frequency, and pulse volume may be helpful. The pattern used to pulse the plates in Tests 2 and 3 appear to work well but may not be optimum.

## 7.0 References

Hyde TA and RK Farnsworth. 1997. *Tank Mixing and Stabilization Activities at the INEEL Cold Test Pit*. INEL/EXT-97-00614, Idaho National Engineering and Environmental Laboratories, Idaho Falls, Idaho.

Lea FM. 1971. *The Chemistry of Cement and Concrete*. 3rd ed. Chemical Publishing Company, New York, New York.

Neville AM. 1981. *Properties of Concrete*. 3rd ed. Pitman Publishing Inc., Marshfield, Massachusetts.

Powell MR and CR Hymas. 1996. *Retrieval Process Development and Enhancements FY96 Pulsed-Air Mixer Testing and Deployment Study*. PNNL-11200, Pacific Northwest National Laboratory, Richland, Washington.

Powell MR. 1997. *Retrieval Process Development and Enhancements Pulsed-Air Mixing DOE Assessment*. PNNL-11584, Pacific Northwest National Laboratory, Richland, Washington.

Smith DK. 1976. *Cementing*. American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.

van Olphen H. 1977. *An Introduction to Clay Colloid Chemistry*. John Wiley and Sons, New York, New York.

**Appendix A**

**Penetrometer Readings**

## Appendix A

### Penetrometer Readings

A concrete penetrometer was used to test the cured grouts from Tests 1B and 3. All measurements in Test 1B exceeded the capacity of the penetrometer. A picture of the penetrometer is provided in Figure A.1. The penetrometer consists of a 0.25" diameter shaft, with a mark scribed 1" up the shaft. Pressing the shaft into the grout compresses a spring and a sliding ring records the maximum force required. The penetrometer was pushed into the cured grout until it penetrated into the grout at least 1" and the maximum reading taken. The test procedure used is very similar to ASTM C 403/C 403M-95 "*Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance*" using the spring-loaded device option described in section 6.3 of the test method<sup>1</sup>.

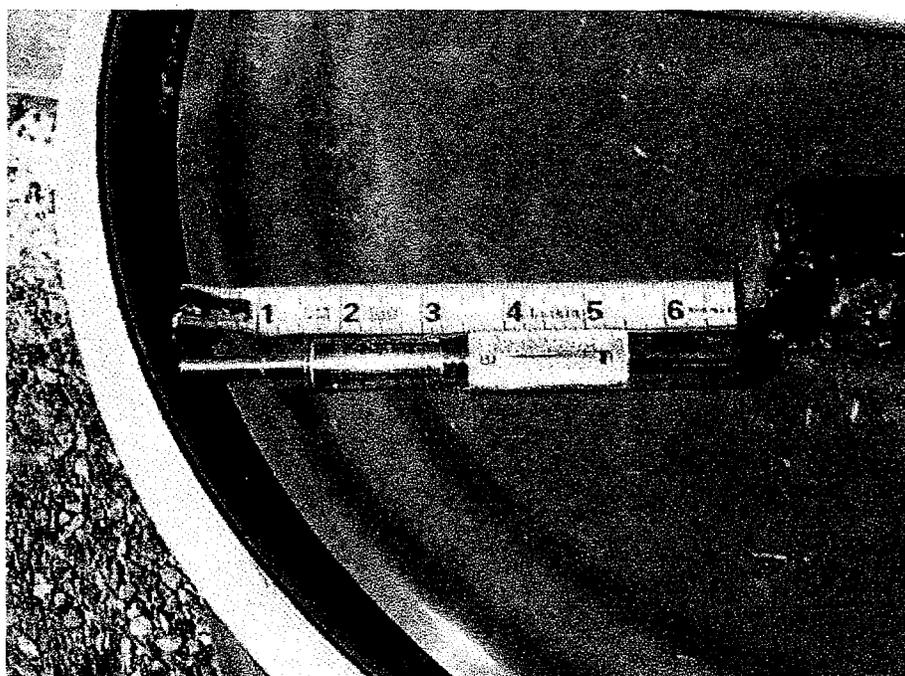


Figure A.1. Concrete Penetrometer Used to Obtain Penetration Resistance Measurements

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<sup>1</sup>Key deviations from the ASTM procedure include taking readings over about 5 seconds rather than  $10 \pm 2$  s, the accuracy of the spring loaded measurement device did not meet the accuracy specification. Also, the ASTM procedure describes a series of measurements over time to monitor setting while only a single confirmatory set of readings were made prior to disassembly of the grout block.

To check the accuracy of the penetrometer, it was placed in a TA-XT2 Texture Analyzer (Manufactured by Stable Micro Systems Ltd., Surrey, England) and the force required to achieve displacement was measured at 1 mm intervals over a total of 25 mm displacement moving in both the compressing and decompressing directions. A few additional data points were taken by pressing the device onto a platform scale by hand. Based on the force exerted, the pressure on the penetrometer shaft was calculated and compared to the instrument readings. The results of the calibration effort are shown in Figure A.2. The readings from the penetrometer appear to be consistently about 17% higher than the actual pressure applied by the texture analyzer. The platform scale data were generally consistent with this trend although much more scattered due to the requirement to apply a steady load and catch the scale reading at the maximum force. The

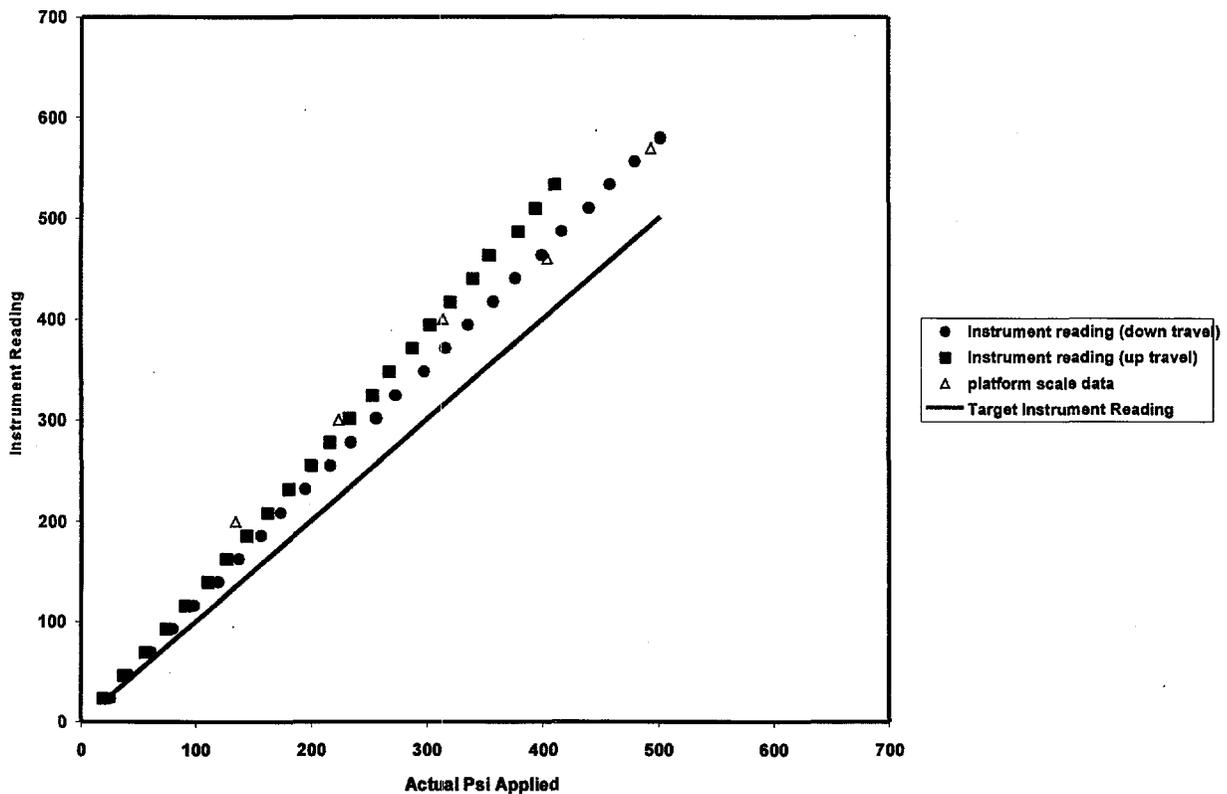


Figure A.2. Results of Penetrometer Calibration

data from the texture analyzer indicated that the applied force to obtain a given reading was lower while the instrument was being decompressed. Since the penetrometer readings are taken in the compression mode, only the compression data were used. Based on these calibration data, readings taken using the penetrometer were reduced by 17% to account for the discrepancy between actual psi and instrument indication.

Data were collected using the penetrometer for Test 1B which used the INEEL suggested recipe containing both Portland cement and Aquaset. In 4 locations the penetration resistance after 2 days of curing exceeded the upper range on the penetrometer (700 psi uncorrected). The penetrometer penetrated only about 1/4" at the maximum spring reading so it is suspected that the penetration resistance exceeds 700 psi by some margin. No measurements of penetration resistance were made in Test 2 because this test used the recipe from Test 1B with twice the Portland cement addition and was qualitatively harder than Test 1B. Test 3 used the INEEL suggested recipe containing Aquaset-2H without any additional Portland cement. This material was not as hard as the previous tests. Penetration resistance measurements and the corresponding locations of the measurements are indicated in Figure A.3.

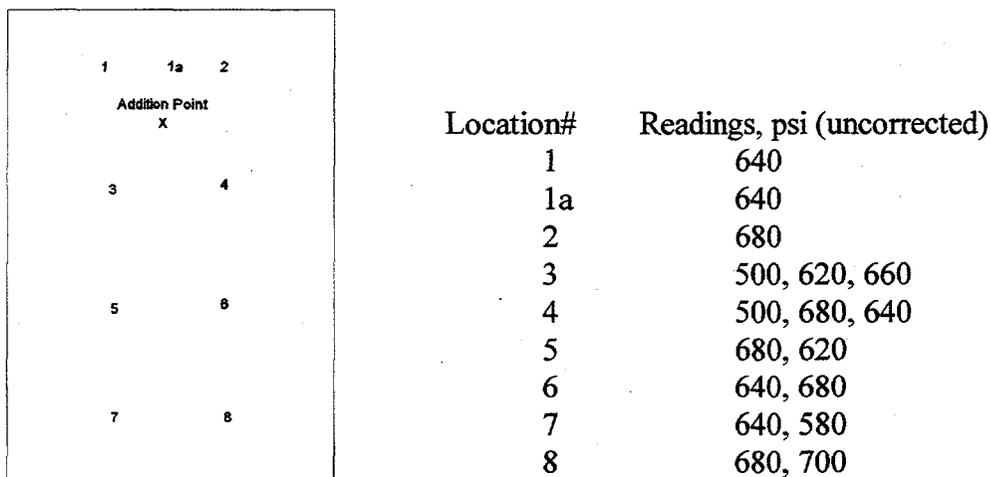


Figure A.3. Plan View of Drum Showing Penetrometer Measurement Locations and Readings

Taking an average of all 17 readings provides an average of 634 psi and correcting for the 17% calibration factor provides a penetration resistance of the grout of approximately 542 psi.

## **Appendix B**

### **Raw X-Ray Fluorescence (XRF) Compositional Data**

## Appendix B

### Raw X-Ray Fluorescence (XRF) Compositional Data

This Appendix provides the raw XRF data obtained in the process of evaluating the levels of tracer elements in the grout samples. The data is provided in the event that it is useful at some future date. However, only the data for tracer elements (Ga, Y, Cs), Zr and Ca were actually used in this report. The data for other elements should be used with caution since there may be errors in some elements due to interferences (corrected or uncorrected) or absorption corrections which are not accounted for in the error estimates provided. Values for vanadium are known to have a large correction for interference from titanium. Generally, the X-rays from lower atomic number elements tend to be weaker and more subject to errors in absorption corrections than elements with higher atomic number.

The data provided in Table B.1 excludes a number of elements which were routinely near or below detection limits. Also, the analysis results for standards are not shown. Analysis of samples with 1000 ppm spikes of Zn, Y, and Cs were performed (see sample PSA-2-12). The Zn was used in place of Ga because a standard for Ga was not available. Where performed, the duplicate analyses of samples are also provided in the Table B.1.

#### B.1 Details of Analysis

Analysis was performed by KLM Analytical of Richland Washington using energy dispersive X-ray fluorescence. The instrument is initially calibrated against thin film standards. Where available, calibration against an appropriate matrix standard was used which provides a better correction for absorption within the sample. In most cases the difference in calibration between the thin film and matrix standard is less than 10%. The corrections may be larger for some elements in cement due to a particle-size dependent absorption correction which is unique to Portland cement. The appropriate standard to use for the Aquaset was uncertain. Analysis

using both a soil standard and a cement standard is provided and the actual composition may be somewhere between the two results where the values differ. After hydration and regrinding the special particle size dependent behavior of cement is no longer a concern.

Samples were processed in accordance with PNL test procedure ALO 266. All analyses were obtained using a Ag/Fe excitation target except for Cs and Ba which used a Gd excitation target. Standards of United States Geological Survey (USGS) W-1 and AGV-1 were processed with the samples for control and test equipment check. Spike standards used were NBS3168 (Zn), NBS3167 (Y) and NBS3111 (Cs). Other standards used in analyzing the samples included International Atomic Energy Agency (IAEA) Soil 5, USGS Basalt Columbia River (BCR)-1, Standard Reference Material (SRM) 2704 sediment, and SRM 639 Cement.

Tracer Analyte	Portland Cement value	Soil from batch 1 value	Aqaset using Cement Sid		Aqaset using Soil Standard		Aqaset /soil sid rep 1		Aqaset /soil sid rep 2		Aqaset /soil sid rep 3		PSA-2-1		(b) PSA-2-3a		(b) PSA-2-3b		PSA-2-4		PSA-2-5		
			value	+-	value	+-	value	+-	value	+-	value	+-	value	+-	value	+-	value	+-	value	+-	value	+-	value
Cs, ppm	<40	<43	2.2	2.2	4.8	2.1	12.3	1.7	10.7	1.7	9.3	6.8	44	573	41	622	40	612	42	647	42	42	
Ga, ppm	9.5	1.3	30.4	2.4	14	1.5	11.7	1.2	10.7	1.7	9.3	159	12 218 (a)	16 203 (b)	15	208	15	136	11	146	11	15	
Y, ppm																							
Other Elements																							
Al, %	2.92	0.37	6.55	0.51	2.02	0.3	1.82	0.27	1.77	0.32	2.09	0.32	0.4	4.33	0.41	4.03	0.41	3.92	0.4	3.87	0.4	0.4	
Si, %	10.54	0.77	27.9	2	20.8	1.5	17.3	1.2	16.4	1.2	17	1.2	1.3	17.8	1.3	16.7	1.3	17.6	1.3	17.4	1.2	1.2	
S, %	1.077	0.079	0.058	0.016	0.538	0.042	0.879	0.07	0.816	0.066	0.825	0.067	0.045	0.542	0.047	0.531	0.048	0.499	0.045	0.513	0.046	0.046	
K, %	0.85	0.047	1.51	0.11	0.77	0.055	0.89	0.042	0.552	0.041	0.571	0.041	0.061	0.87	0.062	0.882	0.063	0.869	0.062	0.851	0.06	0.06	
Ca, %	48	3.4	3.53	0.25	29.3	2	23.5	1.6	21.7	1.5	22.5	1.6	1.1	15.5	1.1	16.5	1.2	15.5	1.1	15.3	1.1	1.1	
Ti, %	0.126	0.0096	0.739	0.052	0.1269	0.0094	0.1175	0.0087	0.101	0.007	0.101	0.008	0.027	0.406	0.029	0.437	0.031	0.402	0.028	0.394	0.028	0.028	
V, ppm	<39		175	20	56	15	47	12	31.4	9	40	9.5	16	144	16	122	16	143	16	150	16	16	
Cr, ppm	81	17	25.1	5.9	82	11	63.5	8.8	59	8.3	57.6	8.6	7.2	23.7	7.3	20.3	7.8	23.1	7.3	29.2	7.4	7.4	
Mn, ppm	236	38	829	65	310	35	310	35	218	37	176	38	49	561	55	597	59	543	54	540	54	54	
Fe, %	1.95	0.14	4.87	0.34	1.97	0.14	1.79	0.13	1.73	0.12	1.69	0.12	0.24	3.41	0.24	3.78	0.27	3.33	0.23	3.43	0.24	0.24	
Cu, ppm	90	11	40.1	5.4	55.8	7.5	46.5	6.2	38.7	6.7	30.1	6.6	6.5	32.6	6.7	50.2	7.6	30.2	6.6	35.1	6.7	6.7	
Zn, ppm	35.1	5.7	67.5	5.9	53.1	5.7	44.3	4.7	49	5.5	50	5.8	6.1	52.2	6.1	67.3	7.3	55	6.2	59.1	6.6	6.6	
Rb, ppm	19.9	1.8	56.6	4.3	36.6	2.9	30.5	2.4	31	2.9	33.8	3.1	40.6	3.3	42.6	3.4	42.5	3.4	44	3.5	43.4	3.4	
Sr, ppm	407	29	318	22	689	48	574	40	585	41	578	41	353	25	358	25	362	26	359	25	364	25	25
Zr, ppm	61.1	4.7	272	19	83.5	6.3	69.5	5.3	68.5	5.6	69.6	5.7	173	12	195	14	192	14	176	13	183	13	
Ba, ppm	536	39	668	45	391	38	391	38	291	46	337	44	46	552	44	510	44	557	44	561	44	44	

(a) Ga contamination is suspected from previous sample PSA-2-2 which consisted of a ball of the Ga2O3 tracer.  
(b) samples ending in a, b, c are actually the same sub-sample analyzed in duplicate or triplicate

Table B.1. Raw Data From XRF Analysis

Tracer Analyte	PSA-2-6		PSA-2-7		PSA-2-8		PSA-2-9		PSA-2-10		PSA-2-11		(b) PSA-2-12a		(b) PSA-2-12b		(b) PSA-2-12c		Spike 1000 ppm, Zn, Y, Cs		PSA-2-12-spilte-a		PSA-2-12-spilte-b		PSA-2-13			
	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-
Ca, ppm	651	42	547	38	553	38	576	38	583	40	514	39	581	37	590	37	541	38	1617	88	1597	85	601	85	601	85	801	40
Ga, ppm	138	11	130	10	121.5	9.9	141	9.9	154	11	171	12	162	12	153	12	138	11	144	11	134	11	159	12	159	12	159	12
Y, ppm	202	14	201	14	190	14	210	14	208	15	204	15	208	14	208	15	212	15	1198	84	1172	82	207	82	207	82	207	15
Other Elements																												
Al, %	3.73	0.39	4.13	0.41	4.33	0.42	4	0.42	3.96	0.4	4.21	0.42	3.66	0.39	3.6	0.4	4.24	0.41	3.45	0.38	3.25	0.38	3.68	0.38	3.68	0.39	3.68	0.39
Si, %	16.8	1.2	18.4	1.3	18.6	1.3	18.1	1.3	17.5	1.2	18.2	1.3	17.1	1.2	17.6	1.3	19.1	1.4	18.2	1.3	17.4	1.2	16.8	1.2	16.8	1.2	16.8	1.2
S, %	0.455	0.042	0.464	0.043	0.477	0.044	0.524	0.044	0.484	0.044	0.466	0.044	0.584	0.05	0.489	0.046	0.44	0.041	0.431	0.043	0.435	0.043	0.535	0.043	0.535	0.047	0.535	0.047
K, %	0.858	0.061	0.802	0.064	0.891	0.063	0.876	0.062	0.824	0.059	0.868	0.062	0.815	0.058	0.856	0.061	0.985	0.071	0.887	0.063	0.879	0.062	0.804	0.057	0.804	0.057	0.804	0.057
Cs, %	15.4	1.1	15.4	1.1	14.8	1	15.4	1.1	15.8	1.1	15.9	1.1	16.2	1.1	17	1.2	15.5	1.1	15.8	1.1	15.7	1.1	15.9	1.1	15.9	1.1	15.9	1.1
Ti, %	0.387	0.028	0.439	0.031	0.476	0.034	0.399	0.028	0.395	0.028	0.389	0.028	0.373	0.026	0.398	0.028	0.447	0.032	0.413	0.029	0.413	0.029	0.369	0.026	0.369	0.026	0.369	0.026
V, ppm	137	16	127	16	163	18	122	15	120	15	108	15	128	15	111	15	129	16	137	17	152	17	134	16	134	16	134	16
Cr, ppm	21.5	7.2	23.6	7.5	21.9	7.4	39.4	7.8	37.1	7.8	42.3	7.9	27.3	7.4	29.3	7.7	32.5	7.7	32.5	7.7	32.5	7.7	37.7	7.6	37.7	7.6	37.7	7.6
Mn, ppm	526	53	573	57	664	62	512	52	560	57	642	60	543	56	519	56	611	58	521	55	487	54	601	54	601	58	601	58
Fe, %	3.4	0.24	3.72	0.26	4.13	0.29	3.55	0.25	3.61	0.25	3.57	0.25	3.59	0.25	3.67	0.26	3.67	0.26	3.65	0.26	3.58	0.25	3.6	0.25	3.6	0.25	3.6	0.25
Cu, ppm	35.2	6.9	43.3	7.1	38	7.4	32.4	6.8	33.9	7.1	52.5	7.7	46.2	7.8	38.1	7.5	48.4	7.4	38.7	7.4	48.4	7.8	45	7.5	45	7.5	45	7.5
Zn, ppm	59.7	6.5	58.4	6.4	76.6	7.4	62	6.5	69.3	6.6	55.8	6.6	63	6.9	68.3	7.2	64.4	6.8	107.3	7.7	109.4	7.8	57.4	6.5	57.4	6.5	57.4	6.5
Rb, ppm	40.6	3.3	44.7	3.5	42.4	3.4	41.8	3.5	42	3.3	42.4	3.4	44	3.4	44	3.4	43.8	3.9	44.9	3.6	40.6	3.3	45.7	3.6	45.7	3.6	45.7	3.6
Sr, ppm	361	25	353	25	352	25	367	26	366	25	354	25	359	25	356	25	372	26	353	25	344	24	358	25	358	25	358	25
Zr, ppm	193	14	189	14	245	17	197	14	196	14	179	13	180	13	184	13	192	14	201	14	183	13	175	13	175	13	175	13
Ba, ppm	482	41	503	40	528	40	574	42	463	39	462	39	510	37	524	38	482	42	449	42	524	42	500	40	500	40	500	40

Table B.1 (continued). Raw Data From XRF Analysis

Tracer Analyte	PSA-2-14	PSA-2-15	PSA-2-16	PSA-2-17	PSA-2-18	PSA-3-1	PSA-3-2	PSA-3-3	PSA-3-4	PSA-3-5	PSA-3-6	PSA-3-7
	value	value	value	value	value	value	value	value	value	value	value	value
Cs, ppm	378	6.95	2.58	3.49	6.42	4.05	6.75	4.06	3.64	4.09	4.06	4.16
Ga, ppm	16.6	1.2	1.9	17.1	26.2	1.9	29.6	2.1	1.5	20.5	1.5	20.6
Y, ppm	0.505	0.045	0.028	0.523	0.189	0.027	0.052	0.02	0.041	0.423	0.04	0.387
Other Elements												
Al, %	0.8	0.057	0.1	0.548	0.061	0.039	0.072	0.11	0.069	0.86	0.068	0.074
Si, %	15.6	1.1	6.58	0.46	20.5	1.4	16.2	0.57	12.88	13.26	12.51	0.88
S, %	0.38	0.027	1.109	0.078	0.147	0.011	0.42	0.069	0.469	0.032	0.031	0.89
K, %	114	15	374	31	81	11	119	0.72	0.453	0.438	0.478	12.7
Ca, %	27.6	7.3	<16	8.1	25.7	24	261	0.448	0.032	127	0.034	0.448
Ti, %	549	55	1143	38	8	139	<14	137	143	16	16	140
V, ppm	3.64	0.28	0.46	517	8	21.3	7.3	30.2	7.4	38	7.5	19.7
Cr, ppm	43.9	7.3	6.82	3.48	6	597	7.8	57	569	55	600	591
Mn, ppm	62.3	6.7	8.3	58.4	42.3	3.71	6.08	0.43	3.85	3.77	3.81	3.89
Fe, %	43.9	3.5	48.2	3.3	46.3	40.3	24.6	6.4	33.8	37.6	37.2	44.3
Cu, ppm	365	28	329	349	25	69.4	7	60	77.1	73	66.6	69
Zn, ppm	197	14	371	186	308	47.3	54.6	47.6	51.1	41	48.8	47.7
Rb, ppm	558	43	628	47	656	201	347	22	408	29	376	383
Sr, ppm						14	25	180	210	15	206	15
Zr, ppm						551	612	47	545	42	488	457
Ba, ppm						45	38	503	39	488	43	457

Table B.1 (continued). Raw Data From XRF Analysis

Tracer Analyte	PSA-3-8		PSA-3-9		PSA-3-10		PSA-3-11		PSA-3-12		PSA-3-13		PSA-3-14		PSA-3-15		PSA-3-16		PSA-3-17	
	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-	value	+/-
Cs, ppm	634	42	628	44	710	44	672	44	678	43	272	28	713	46	714	46	626	40	307	30
Ga, ppm	182	15	188	14	181	14	189	14	181	14	178	3.4	210	16	185	14	202	15	31.9	4.1
Y, ppm	228	16	222	16	229	16	214	15	220	16	42.6	3.4	228	16	222	18	214	15	58	4.4
Other Elements																				
Al, %	3.89	0.39	4	0.4	3.83	0.39	4.38	0.41	3.84	0.39	7.1	0.57	3.86	0.39	3.53	0.38	4.3	0.42	6.54	0.54
Si, %	20.6	1.5	21	1.5	20	1.4	20.4	1.4	19.7	1.4	28	2	19.8	1.4	20	1.4	20.5	1.5	28.2	2
S, %	0.431	0.04	0.382	0.038	0.404	0.039	0.361	0.037	0.403	0.038	-0.04	0.43	0.43	0.04	0.395	0.039	0.36	0.037	0.122	0.022
K, %	0.965	0.068	0.975	0.069	0.988	0.07	1.015	0.072	0.986	0.068	1.48	0.11	0.979	0.069	0.999	0.068	1.018	0.072	1.49	0.11
Ca, %	12.95	0.91	12.62	0.88	13.13	0.92	12.93	0.91	12.76	0.89	4.8	0.34	12.78	0.9	12.72	0.89	12.64	0.89	5.81	0.41
Ti, %	0.431	0.031	0.479	0.034	0.456	0.032	0.464	0.033	0.495	0.035	1.71	0.082	1.454	0.032	0.459	0.032	0.526	0.037	0.921	0.065
V, ppm	127	16	138	16	153	17	154	17	157	17	329	29	153	17	125	15	152	17	205	21
Cr, ppm	30	7.3	32.9	7.4	19.4	7.3	22.9	7.2	24.2	7.2	36.1	8.2	29.4	7.1	25.5	7	23	7.2	22.7	7.1
Mn, ppm	630	59	651	61	584	57	610	58	634	59	1162	94	586	55	587	57	651	62	950	80
Fe, %	3.78	0.27	3.99	0.28	3.72	0.26	3.8	0.27	3.87	0.27	7.09	0.5	3.74	0.26	3.7	0.26	4	0.28	5.95	0.42
Cu, ppm	44.9	7.2	47.2	7.4	36.1	6.8	36.1	6.9	43.3	7	31.6	6.8	45.1	6.8	36.1	6.4	40.6	6.9	32.8	6.8
Zn, ppm	64.2	6.9	73	7.3	67.9	6.8	64.4	6.8	63.7	6.7	88.3	8.4	68.5	6.9	63.1	6.7	76.4	7.5	88.8	8.3
Rb, ppm	48.4	3.8	48.5	3.8	50.6	3.9	50.2	3.9	48.5	3.8	48.7	3.8	51.5	4	51	3.9	50.2	3.9	51.8	4
Sr, ppm	394	28	393	28	390	28	381	27	389	27	320	23	420	30	394	28	388	27	343	24
Zr, ppm	202	14	193	14	194	14	194	14	176	13	415	29	182	14	184	13	201	14	342	24
Ba, ppm	473	38	491	40	555	41	513	39	521	39	647	44	618	43	439	40	478	38	563	44

Table B.1 (continued). Raw Data From XRF Analysis

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