FINAL REPORT
PERFORMANCE VERIFICATION
STUDY ON THE
SOLIDIFICATION/STABILIZATION
WASTE FORM
FOR
PCB-CONTAMINATED SOILS AT
THE RAIL YARD
IN PAOLI, PENNSYLVANIA

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1.0 INTRODUCTION

In May of 1991 and under the direction of Groundwater Technology, Inc. (GTI), a treatability study was performed by VFL Technology Corporation, which developed a solidification/stabilization formula to sequester PCBs found in the soils of the Paoli rail yard. This initial treatability study was performed on behalf of the Southern Pennsylvania Transportation Authority (SEPTA), the National Railroad Corporation (AMTRAK), and the Consolidated Rail Corporation (CONRAIL) (the Rail Companies). The study successfully demonstrated the durability of the cement/pozzolan waste form and its ability to resist leaching. However, further investigation regarding long-term durability and the interactions between a solidification/stabilization waste form matrix and PCBs were desired by GTI and the Rail Companies. Therefore, the purpose of this study was to measure qualities of the waste form that indicate the longevity of its solid matrix and its ability to immobilize PCBs within its matrix.

In order to establish the scientific basis of this solidification/stabilization remedy, GTI hired QualTEC, Inc. (QT) is a subsidiary of Ogden Environmental and Energy Services and provided a grant in aid to the Materials Research Laboratory (MRL) at the Pennsylvania State University to further characterize and verify the performance of the proposed waste form. QT applies solidification/stabilization technologies to immobilize heavy metals and PCBs at Superfund sites and is experienced in developing and testing waste forms. MRL is a fully equipped and staffed materials science laboratory with experience in evaluating waste forms for several national programs for the Department of Energy (DOE). While Dr. Dole was a senior scientist at the Oak Ridge National Laboratory for the DOE, he developed waste forms and participated in waste form evaluation programs with the MRL and Drs. Grutzeck and Licastro. MRL and QT bring a great deal of relevant experience and expertise to this project.

2.0 APPROACH

The following tasks were developed by QT and MRL to demonstrate the long-term durability of the waste form and the interactions of PCBs with the constituent phases of the binding matrices in the proposed waste form for the Paoli Rail Yard. The tasks assigned to QT were:

[1] On-site preparation of all test specimens

[2] Autogenic curing and distribution of specimens

[3] Unconfined compressive strengths (after 28 days)

[4] Permeability (after 28 days)

[5] Wet/dry resistance (after 28 days, 12 cycles)

[6] Freeze/thaw resistance (after 28 days, 12 cycles)

The tasks researched by the Materials Research Laboratory at Penn State were:

[7] Effects of immersion in deionized and simulated acid rain on unconfined compressive strength and permeability to 120 days

[8] Mercury porosimetry

[9] Scanning electron microscope and elemental dispersive X-ray analyses after different curing periods

[10] Pass pressurized deionized water through waste form cured for 56 and 90 days and analyze leachate

[11] Long-term static leaching at 56 and 90 days

[12] X-ray diffraction phase analyses

[13] Thermodynamic phase stability diagrams

These tasks include the traditional immersion, wet/dry and freeze/thaw durability tests. In addition, the tasks examine the physical and chemical effects of these durability tests on the strength, porosity, and permeability of the waste form's pozzolanic matrix. The

results of these exposures and the detailed examination of the waste form's material fabric afterward give evidence to establish its potential long-term durability.

In all cases, the strength of the waste form increased and the permeability decreased as the pozzolanic reactions continued throughout the durability exposure tests. The density and physical durability of this waste form improved continually with age. The waste form's ability to sequester PCBs was not lowered by exposures to these durability tests.

3.0   QUALTEC RESULTS

QT prepared all of the test specimens on site according to the formula from the previous treatability study. The testing protocols performed in QT's Knoxville Laboratory were the standard ASTM physical tests for unconfined compressive strength (UCS) and permeability. Also, QT used these standard engineering exposure tests to measure the waste form's durability in terms of its wet/dry and freeze/thaw resistances. The results of these tests describe the performance of the waste form on a gross physical scale as a civil engineering material.

The Materials Research Laboratory used more experimental diagnostic tests to examine the nature of the waste form's microstructure and its relationship to its leaching and durability performances. Also, MRL studied the impact of various exposures, such as immersion, percolation, freezing, and drying on the development of the waste form's microstructure.

Task 1:   On-site Preparation of Test Specimens

On-site test specimen preparation was carried out on February 12, 1992 at Paoli Rail Yard. First, the soil samples provided by GTI were analyzed for moisture content, which was 17% (see Table 1 below). The moisture content of this sample was higher than that used in the previous study (13%) by VFL (see Table 1 of Appendix C in the Paoli Feasibility Study Report in the Paoli Rail Yard RI/FS). PCB analyses of the soil were performed by GTEC. (See Appendix A, Table 1A.) The untreated soil sample with 780

ppm was taken at the start of specimen preparation. The soil sample with second 5,300 ppm was taken halfway through specimen preparation. Chemical analyses of the untreated soil were performed by MRL. See Appendix A, Table 1B.

Table 1: General properties of Paoli Rail Yard soils used in these tests.	
Property	Value
Moisture, % by weight	17.4
Total Petroleum hydrocarbon, % by weight of solids	3.7
pH	8.3
Bulk Density, pounds/cubic foot	96
PCBs, ppm	780-5,300

QT adjusted the formula (as shown in Table 2) to correct for the additional moisture and to maintain the original soil/solids-to-binder ratio that was used by VFL.

Table 2: Description of the formula used in this study	
Property	Value
Binder/soil-solids ratio	0.12
Soil solids, % by weight	70.3
Portland I Cement, % by weight	8.9
Total Water, % by weight	20.8
Density, pounds/cubic foot	106

Measured quantities of soil and Portland 1 cement were placed in a Hobart mixer. Water was added and the contents were mixed until a uniform consistency (3-5 minutes). A mix similar to moist sand was produced The resulting soil-grout was packed in cylindrical molds of three different dimensions: 1.6" x 3.2", 2" x 4" and 2.9" x 4". Because

of the limited size of the field mixer, the test specimens were molded from 28 batches of this formula. The test specimens from these batches were labeled P1 through P28.

Task 2:   Autogenic Curing and Distribution of Specimens

All treated test specimens were transported to QT's laboratory, Knoxville, TN. Of these, 27 test specimens (2" x 4" molds) were sent to Dr. Grutzeck at the MRL on the 17th of February. The remaining samples (28 molds measuring 1.6" x 3.2" and 11 molds measuring 2.9" x 4") were stored until their completion curing prior to QT's permeability, UCS, wet/dry and freeze/thaw cycle studies. After curing for 28 days, dry/wet and freeze/thaw tests started on the 16th of March, 1992.

Task 3:   Unconfined Compressive Strength (UCS) Testing

ASTM Method D4219-83 was used to determine the UCS. The UCS results are presented in Table 3. The average UCS (in psi) after 28 days of curing is 727 $\pm$35. After being subjected to wetting and drying tests, the UCS increased to 833 $\pm$119. After the freeze/thaw test, the specimens had a UCS of 847 $\pm$159. These UCS results show significant strength improvement in the waste form considering the extreme exposure conditions of these tests. The increases in strength over the additional exposure periods are evidence of the continued curing of the slowly reacting pozzolanic phases in the Paoli soils. The matrix continues to react and become more dense and strong.

Table 3:	UCS Results (psi)	
At 28 Days	After Wet/Dry Test	After 28 Freeze/Thaw Test
727	833	847

Task 4:   Permeability Testing

ASTM Method D5084-90 was used to determine the permeability of the samples. This is a triaxial method that seals a flexible membrane onto the longitudinal cylinder walls using a hydraulically-pressurized annulus. On rough samples, this eliminates water flow

along the surface of the test specimens. Then a constant water pressure is impressed on one end and across the longitudinal axis of the right circular cylinder of the waste form. The permeability is calculated from the longitudinal pressure drop and the quantity of water that is expressed from the low pressure end of the grout cylinder with time. Samples cured and tested after 28 days gave an average of 2.3×10^{-7} cm sec^{-1} $\pm$ 1.3×10^{-7} cm sec^{-1} (Table 4). After the wetting and drying tests, a permeability of 2.4×10^{-6} cm sec^{-1} $\pm$ 2.0×10^{-6} was measured. After the freeze/thaw tests, the samples showed a 1.2×10^{-5} cm/sec^{-1} $\pm$ 1.9×10^{-5} cm sec^{-1} permeability. All samples survived as cohesive solid monoliths.

There is a much greater scatter in the data for the exposed samples. It is postulated that the sample cell did not seal completely in some instances due to increased sample surface roughness that resulted from handling during these tests. If one outlying datum is eliminated from each post-exposure set, the data then become more consistent with the 28 day results. The wet/dry data becomes 1.3×10^{-6} $\pm$ 9.6×10^{-7} cm sec^{-1}, and the freeze/thaw data becomes 8.1×10^{-7} $\pm$ 7.0×10^{-7} cm sec^{-1}. These results are within overlapping variances of one another and the 28-day data.

The strength data presented earlier confirm that the wet/dry and freeze/thaw samples were stronger than before exposure at the end of the 28-day cure. Therefore, the higher premeasureability measured are probably a result from damage to the surface of the specimens. Pits, irregularities, and scratches were present after the exposures to the wet/dry and freeze/thaw testing cycles. Once the outlying data points are eliminated, the permeability results are all within acceptable limits for safely using this waste form at the Paoli site.

Table 4:	Constant head permeability (cm sec^{-1})	
At 28 Days	After Wet/Dry Test	After Freeze/Thaw Test
$2.3\times10^{-7} \pm 1.3\times10^{-7}$	$2.4\times10^{-6} \pm 2.0\times10^{-6}$	$1.2\times10^{-5} \pm 1.9\times10^{-5}$
	$1.3\times10^{-6} \pm 9.6\times10^{-7}$*	$8.1\times10^{-7} \pm 7.0\times10^{-7}$*

* One out lying value (one of three) eliminated from average and standard deviation calculations

Task 5: Wet/Dry Resistance

Wetting and drying tests of the solid wastes were performed according to ASTM Method D4843-88. From the batches (P16, P18 and P19) with diameters 1.53 and 2.88 inches, specimens gave average cumulative corrected relative mass losses of between 0.16 and 0.19% (Table 5). Under the civil engineering specifications from Method D4843-88, less than a 30% relative mass loss is considered a success. The results on this waste form were 150 to 180 times better than the maximum allowable value for an engineering material in wet/dry testing.

Task 6: Freeze/Thaw Resistance

ASTM Method D4842-90 was used to determine the resistance of solid wastes to freezing and thawing. An average of 1.49% cumulative relative mass loss for specimens from batches P2 and P6 of samples with diameters of 1.53 inches was obtained (Table 5). Specimens from batches P3, P6 and P7 with diameters of 2.88 inches gave cumulative relative mass loss of 2.03%. These results are very good for small specimens in these extreme exposure conditions. For a civil engineering material, a relative mass loss of less than 30% is considered a success. The Paoli waste form was 15 to 20 times better in freeze/thaw resistance than the maximum allowable value for a structural material.

Table 5:	Resistance of solid materials to wet/dry and freeze/thaw tests	
Sample Diameter (Inches)	Wet/Dry Relative Mass Loss (%)	Freeze/Thaw Relative Mass Loss (%)
1.53	0.16	1.49
2.88	0.19	2.03

Microstructural Examination:

Microstructural examination by MRC of the wet/dry and freeze/thaw cycled specimens showed little or no evidence of microcracking at the center of the sample (see Figures 1 and 2). The development of microstructure in these exposed specimens was not different from the unexposed specimens (see Figures 6 and 8). Other results show no signs of any significant negative impact from freeze/thaw and wet/dry exposures. This further strengthens the surface damage argument as the root-cause of the few higher permeability measurements. No significant long-term damage is done to the waste form during freezing and thawing or wetting and drying.

Summary:

QualTEC's results showed that the Unconfined Compression Strength (UCS) of this proposed waste form increased from 727 psi to 833 psi and 847 psi after the wet/dry and freeze/thaw cycles respectively. In the case of permeability, the measured values remained in the 10^{-7} cm sec^{-1} range after the wet/dry and freeze/thaw cycles. There was an apparent increase in the permeabilities that was due to the damage to the specimen surfaces during testing.
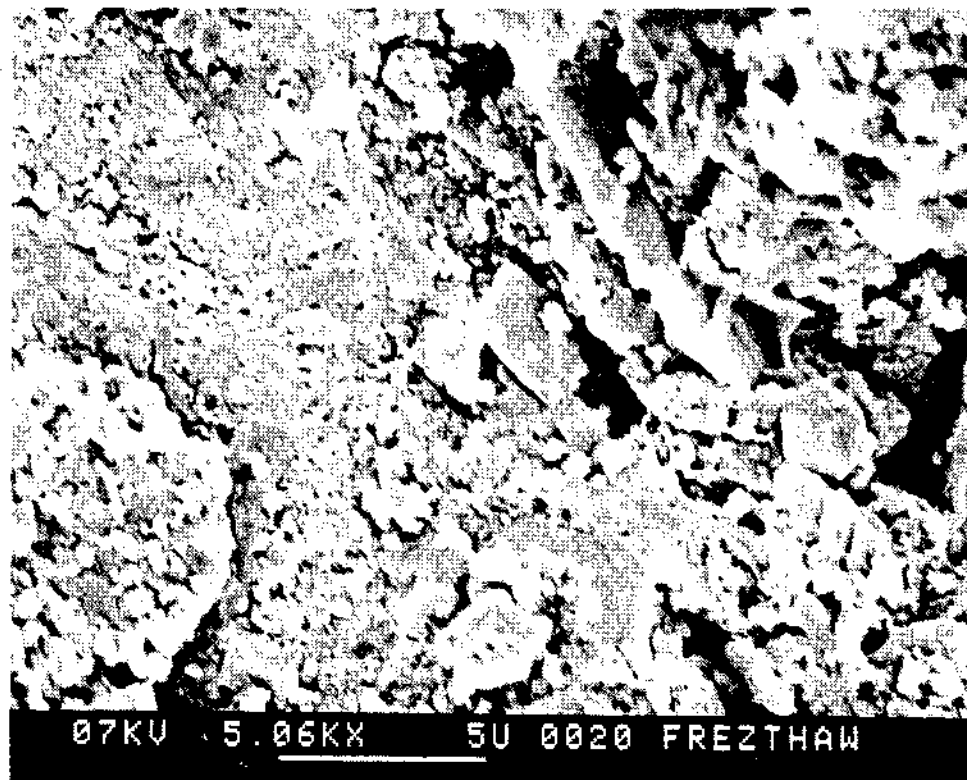
Figure 1:   Five-micron scale micrograph of a specimen exposed to freeze/thaw testing.
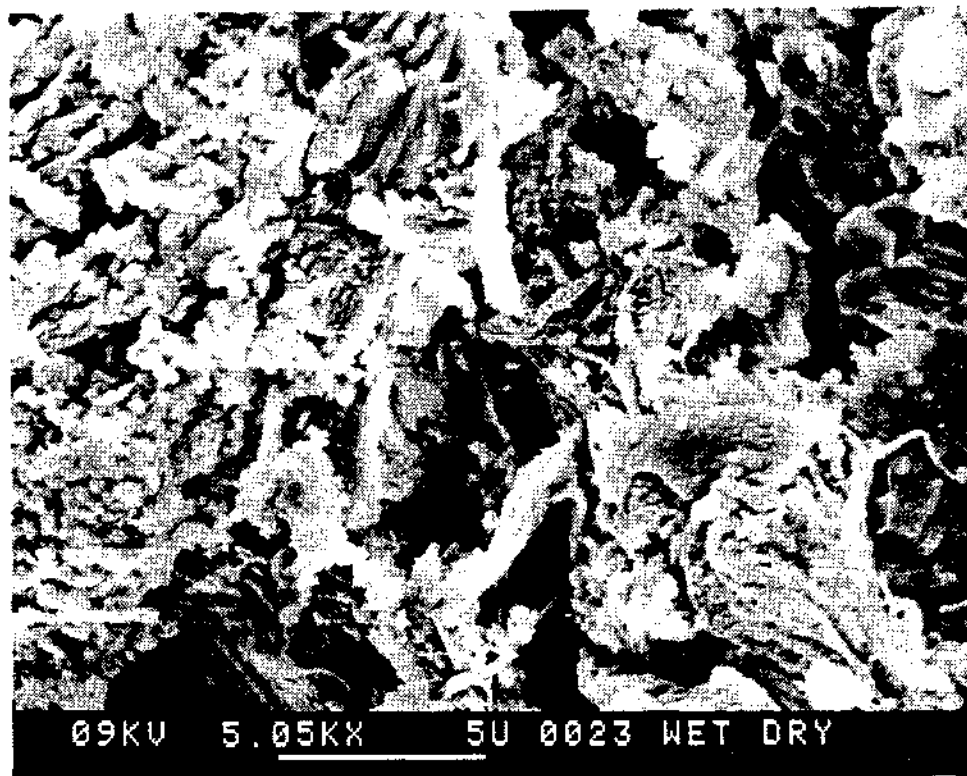

Figure 2:   Five-micron scale micrograph of a specimen exposed to wet/dry testing.

4.0 MATERIALS RESEARCH LABORATORY RESULTS

Specimens were prepared by QT, and were received at the MRL via Federal Express on February 19, 1992. In total, 27 cylindrical specimens measuring 2" X 4" were received. Test specimens were numbered P1-P3 and P5-P28. Specimens were prepared by QT personnel in a Hobart mixer and compacted by hand in 2" X 4" plastic molds on February 12, 1992. The specimens were placed in zip-lock bags with wet paper towels and shipped by overnight courier. Once they arrived at the MRL, the specimens were cured at room temperature in their plastic bags at 100% relative humidity (RH).

A series of tests were carried out after 7, 28, 56, 90 and 120 days. Three tests included unconfirmed compressive strength (UCS) of capped specimens deionized (DI) water permeability of 2" X 4" cylinders at 30-60 psi driving pressure, Hg-porosimetry to measure the percentage of porosity and the pore size distribution, scanning electron microscopy (SEM) and elemental dispersive x-ray analysis (EDX) for microstructure and chemistry, respectively, chemical analyses of PCB and ionic components of the leachates and permeating fluids and x-ray diffraction phase analyses.

In addition to the specimens cured at a 100% RH, additional tests were performed to determine what would happen if the specimen were immersed in rain water (RW) and pure water. To accomplish this, twelve specimens were demolded and six (P5, 7, 12, 15, 22, and 24) were immersed in simulated rain water, and six (P6, 13, 14, 16, 20, and 21) were immersed in deionized (DI) water. Table 6 shows the starting compositions of these immersion solutions.

Table 6:	Composition of Immusion Solutions (Mg L^{-1})	
Element	Rain Water*	Delonized Water
Al	0.13	0.04
B	<0.02	<0.02
Ba	<0.02	<0.02
Ca	0.36	<0.02
Cr	<0.02	<0.02
Fe	<0.02	<0.02
K	0.03	<0.02
Mg	0.08	<0.02
Mn	<0.02	<0.02
Na	0.16	<0.02
Ni	0.00	0.00
Si	<0.02	<0.02
Sr	<0.02	<0.02
Ti	<0.02	<0.02
Zn	<0.02	<0.02
pH	–	–

*Chemicals used to make 15 liters of simulated rain water: 3.91 mg NaOH, 5.00 mg Ca(OH)$_2$, 2.25 mg MgO, 3.03 mg Al(OH)$_3$, 3 mL 0.18 M H$_2$SO$_4$, 2 mL 0.159M HNO$_3$, and 1.33 mL 0.12M HCL

These specimens were 36 days old at the time of their immersion. Starting at 56 days, both the 100% RH and the immersed specimens were subjected to testing as described above. Immersion did not degrade properties, but generally tended to improve them. After immersion, most specimens had lower permeabilities and increased strength. Details of the testing are given below.

Task 7: **Effects of Immersion on Compressive Strength and Permeability**

Compressive Strength:

100% RH - The specimens prepared by QT were cured in sealed plastic bags containing wet paper towels. They were left in their plastic molds until the day before they required testing. At that point the mold was removed and the samples were capped using a commercial sulfur-based capping compound (ASTM C-617). After remaining overnight in their plastic bags, the compressive strength of the specimens was tested (ASTM C-39) using a Tinius Olsen testing machine. Two of the 100% relative humidity specimens were tested at each test date. Strength data and standard deviation are given in Table 7.

Table 7:	Compressive Strength of 2" X 4" Capped Samples (psi)				
	Sample Age (days)				
	7	**28**	**56**	**90**	**120**
100% RH	348 ±7	690 ±40	726 ±34	845 ±69	910 ±4
Rain Water (immersed at 36 days)			662	506	831
Deionized Water (immersed at 36 days)			683	777	958

Immersed Samples - In order to examine the potential deleterious effect of exposure to CO_2 saturated acid rain and CO_2 saturated ground water, six samples were immersed in simulated acid rain water and six were immersed in deionized water. Because the surface area of the cylinders were calculated to be 202.7 cm^2, each sample was immersed in 2,027 cm^3 of solution. Weight of the containers was monitored, allowing fluid losses were made-up at the end of the leach period. Immersion solution losses by evaporation (usually 5-10 grams) were compensated for DI water. The volume to surface area ratio was maintaining at 10:1, in keeping with conventional leach testing regimens. When a test was required, the leachate was decanted into two one-liter Nalgene HDPE bottles. At the end of the exposure service these solutions/leachates were sent out for analysis.

The cylinders were capped and tested as described above. Data for immersed samples is given in Table 7.

Discussion - A plot of the compressive strength development of the 100% RH specimens is given in Figure 3. This type of strength development versus time behavior is typical during cement hydration. The strength development in the RW and DI specimens also fall in this general range. However, the latter data are for only single cylinders and thus it is hard to judge if they are in fact significantly different.
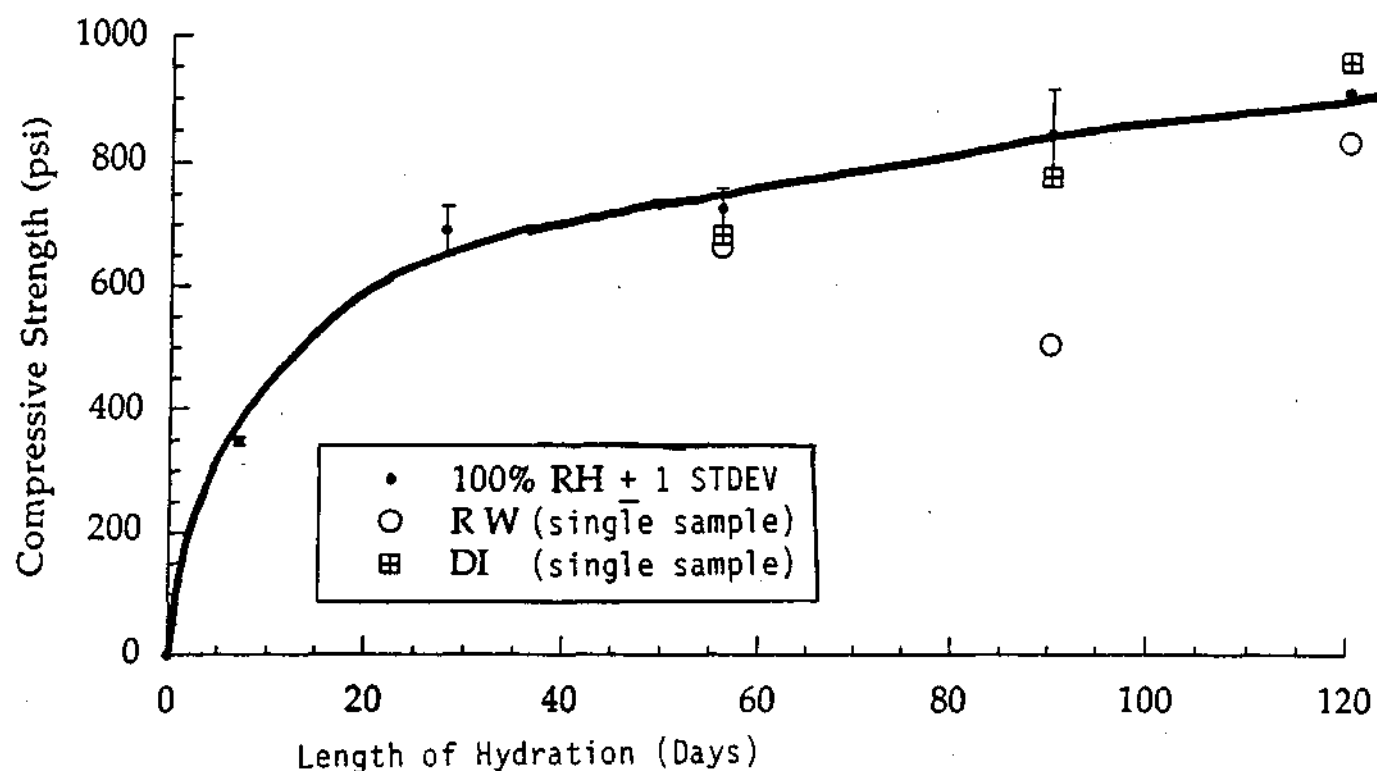

Figure 3: **Compressive strength of 100% RH and immersed samples (RW, DI)**

The achievement of 900 plus psi in 120 days of hydration shows that the cement/soil-ash combination is of high quality. Once the soil-ash is stabilized/solidified, it will support more than its own weight. It could support many building structures without crushing or cracking.

Permeability:

Both the 100% RH and the immersed specimens were tested using the same specimen preparation techniques and permeability apparatus. While conducting this test efforts were made to explore the idea of developing a new leach test which would reflect actual environmental conditions more accurately than leach tests now in use. The test described below was designed around an existing PSU-designed and built-permeability apparatus in which deionized water is forced through the sample's pores under pressure. The intent was to pass approximately one liter of solution through the specimen in a 24-48 hour period. As the water passed through the four-inch long cylinder it could interact with the solid phases present and potentially leach various components from them. Performing the test in this fashion provides a more environmentally accurate representation of leaching by a moving front of water while also providing the necessary data to permit calculation of the permeability of the test specimen.

Sample Preparation - The development of a suitable technique to contain the specimens during the test tended to prove difficult. The first attempts by MRL resulted in flow rates at least 100 times larger than those measured by QT using a constant head technique.

The sample cell prepared by MRL was designed to seal on the outer edges of a 2.25 inch cylinder. In the past MRL used brass sleeves and epoxies the samples into them. In the first attempts, the same epoxy (Aquatapoxy) was used but the brass sleeves were replaced with 2-inch PVC pipe. The inner clearances were too great and the adhesion to the pipe and moist specimen was poor. As a result, flow rates were higher than expected (compared to QT), most likely due to leakage along the epoxy-pipe or epoxy-sample

interface. Hydraulic conductivities of both the 100% RH and the immersed specimens were on the order of 10^{-5} versus QT's 10^{-7}

Table 8: Water Permeability of 2" X 4" Cylinders (cm sec^{-1})				
	28-days	56-days	90-days	120-days
100% Relative Humidity	*	*	1.5 X 10^{-6}	3.0 X 10^{-6}
Rain Water (immersed at 36 days)		*	4.1 X 10^{-6}	2.6 X 10^{-7}
Deionized Water (immersed at 36 days)		*	1.4 X 10^{-7}	7.2 X 10^{-9}
*Sample by-passed during test; invalid due to seal failure as discussed in text.				

The second attempt still used the white PVC water pipe, but instead of trying to slide a specimens into the pipe and fill the space with some type of adhesive, the pipe was cut in half length-wise. The specimen and the inner surfaces of the two half pieces of pipe were then coated with silicon-rubber sealer, and clamped together with screw-adjustable hose clamps. The silicon rubber cures in the presence of water. The seal was found to polymerize overnight and was normally tested the next day. The 90- and 120-day specimens were tested in this fashion (see Table 8).

Apparatus - The deionized water used to permeate the specimens was pressurized using N_2 gas and a moveable piston in a water-filled stainless steel cylinder. The specimens was contained in a O-ring sealed sample holder attached to the bottom of the cylinder, and water was collected in a HDPE bottle sitting on a load cell. The weight of the accumulating water activated a strip chart recorder, and the resulting plot allowed us to calculate the flow rate through the specimen from the slope of the plot.

The water collected during the experiment was sent for PCB and elemental analysis. See Appendix B.

Discussion - Once the new method of specimen preparation was adopted, the measure of hydraulic permeabilities was more in keeping with those measured by QT, ranging from 10^{-6} to 10^{-9} cm sec^{-1}. The immersed specimens tended to have lower permeabilities than their 100% RH counterparts.

Task 8: Mercury (Hg)-Porosimetery

Hg-porosimetery is a well-established technique whereby mercury (Hg) is forced into a test specimen under pressure (15-55,000 psi). By plotting the amount of Hg intruded versus pressure, one is able to observe not only the total amount of Hg intruded under pressure (reflects total porosity), but also which pore sizes are most prominent. The technique is described in many publications and the reader is requested to refer to one such publication for more details.[1]

Values obtained for both the 100% RH and the immersed specimens are given in Table 9. The standard deviations accompanying the 100% RH data reflects the fact that two specimens were tested. The single value for the RW and DI water samples reflects the fact that only one sample was tested for each condition--at 56, 90, and 120 days. At seven days, the porosity of the 100% RH specimen was approximately 25%. Considering the variability in standard deviations, the data suggest that porosities remained relatively constant, perhaps exhibiting a slight decrease with time (25.4-22.8). Likewise, the immersed specimens tended to exhibit similar porosities, but due to the lack of replicate specimens, it is difficult to gauge the significance of time dependant variations. However, it is safe to say that their porosities are not adversely affected by immersion in water.

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[1] S. Lowell and J.E. Shields, *Powder Surface Area and Porosity*, 2nd Ed., Chapman and Hall, NY (1984).

Table 9: Hg-Porosimetery of Freeze-Dried Samples (%)					
	Sample Age (days)				
	7	28	56	90	120
100% Relative Humidity	25.4 ±0.6	23.4 ±1.6	23.6 ±2.3	23.4 ±1.3	22.8 ±0.1
Rain Water (Immersed at 36 days)			24.4	22.8	24.3
Deionized Water (Immersed at 36 days)			22.7	21.2	22.4

Discussion - The porosity data to parallels the permeability data. As porosity decreases with time, so does the permeability. This suggests that existing pores are filling up with hydration products over time. Paths through the waste form matrix are becoming more tortuous. Water finds it more and more difficult and to move through the specimen as the specimen age.

Task 9:   Scanning Electron Microscopy and Elemental Dispersive X-ray Analysis
Microstructural development was monitored using an ISI DS 130 scanning electron microscope. Pieces of freeze-dried soil and broken compression test cylinders were mounted on brass sample stubs, and coated with a thin layer of gold (to make the specimens conductive to electrons). Both micrographs and chemistry on elemental compositions of the solids were recorded. Chemistry was obtained using an element dispersive X-ray (EDX) microprobe manufactured by Kevex.

Chemistry of the solidified/stabilized specimens is dominated by the presence of calcium (Ca), silicon (Si), aluminum (Al), and iron (Fe). Magnesium (Mg) is present in some instances and is attributable to the presence of slag in the soil. Figure 4 represents the microstructure of the original soil-ash mixture. The two photos suggest that the soil sample contains a wide variety of particle sizes with decidedly different textures. Some particles are very large, smooth and rounded (upper photo dominated by one particle) whereas others are agglomerations of smaller particles (lower photo). The EDX
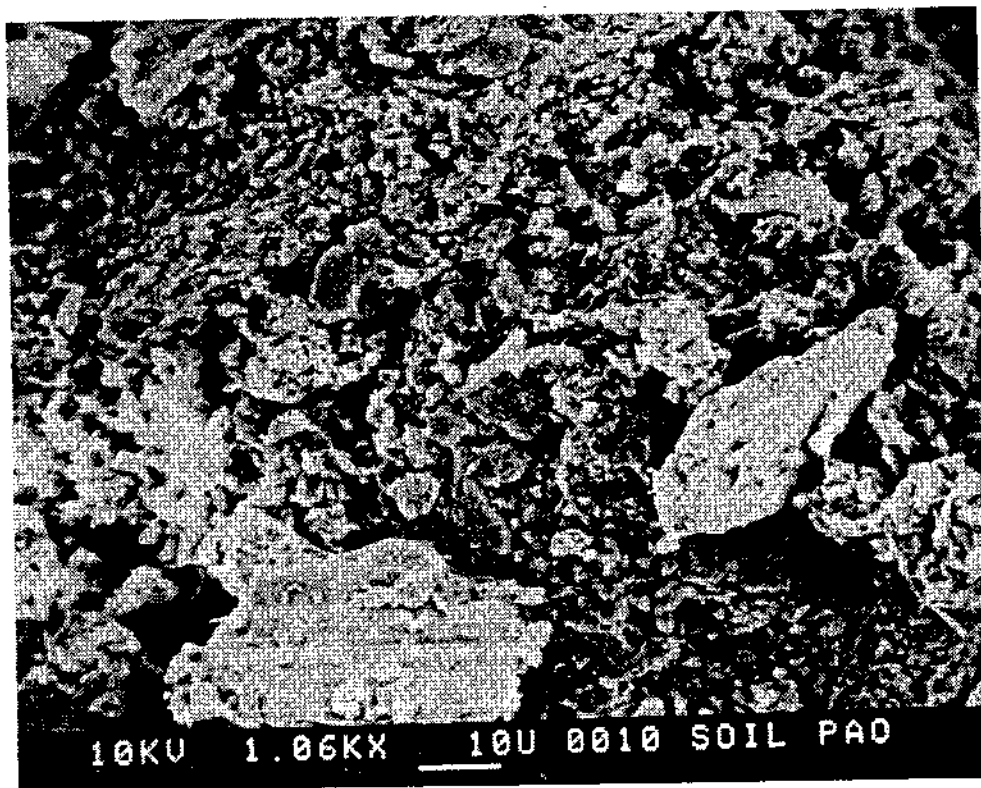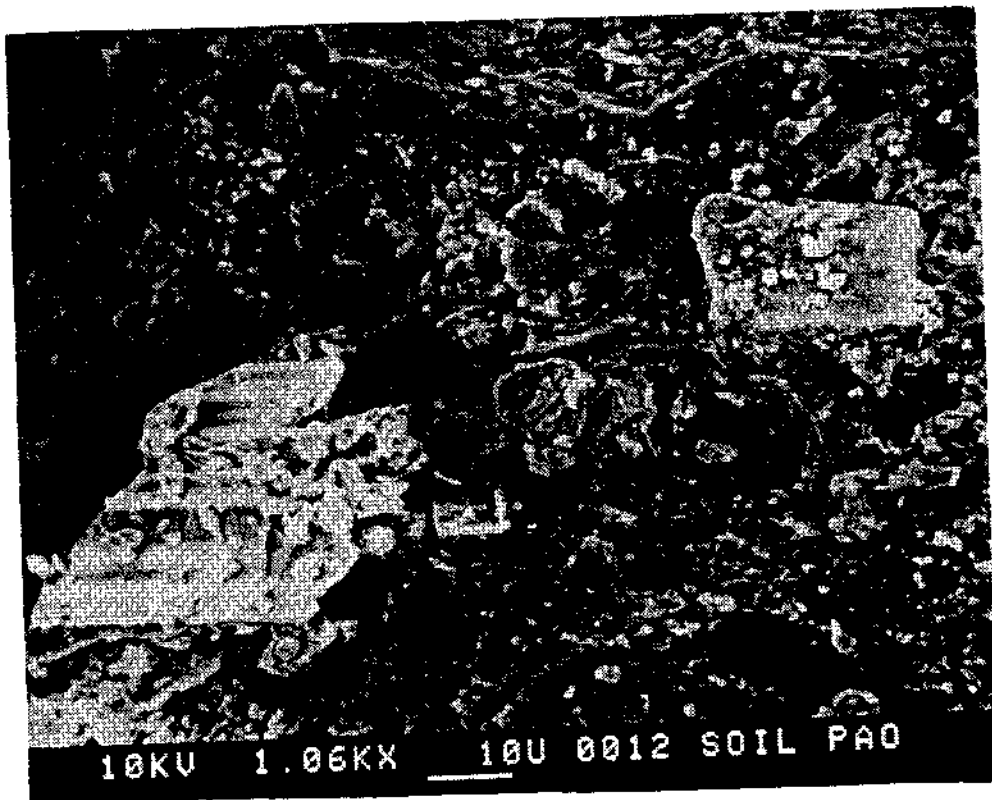
Figure 4: Scanning Election Microscope (SEM) micrographs of Paoli Rail Yard Soil Sample prior to treatment. Horizontal bars are 10μm long.
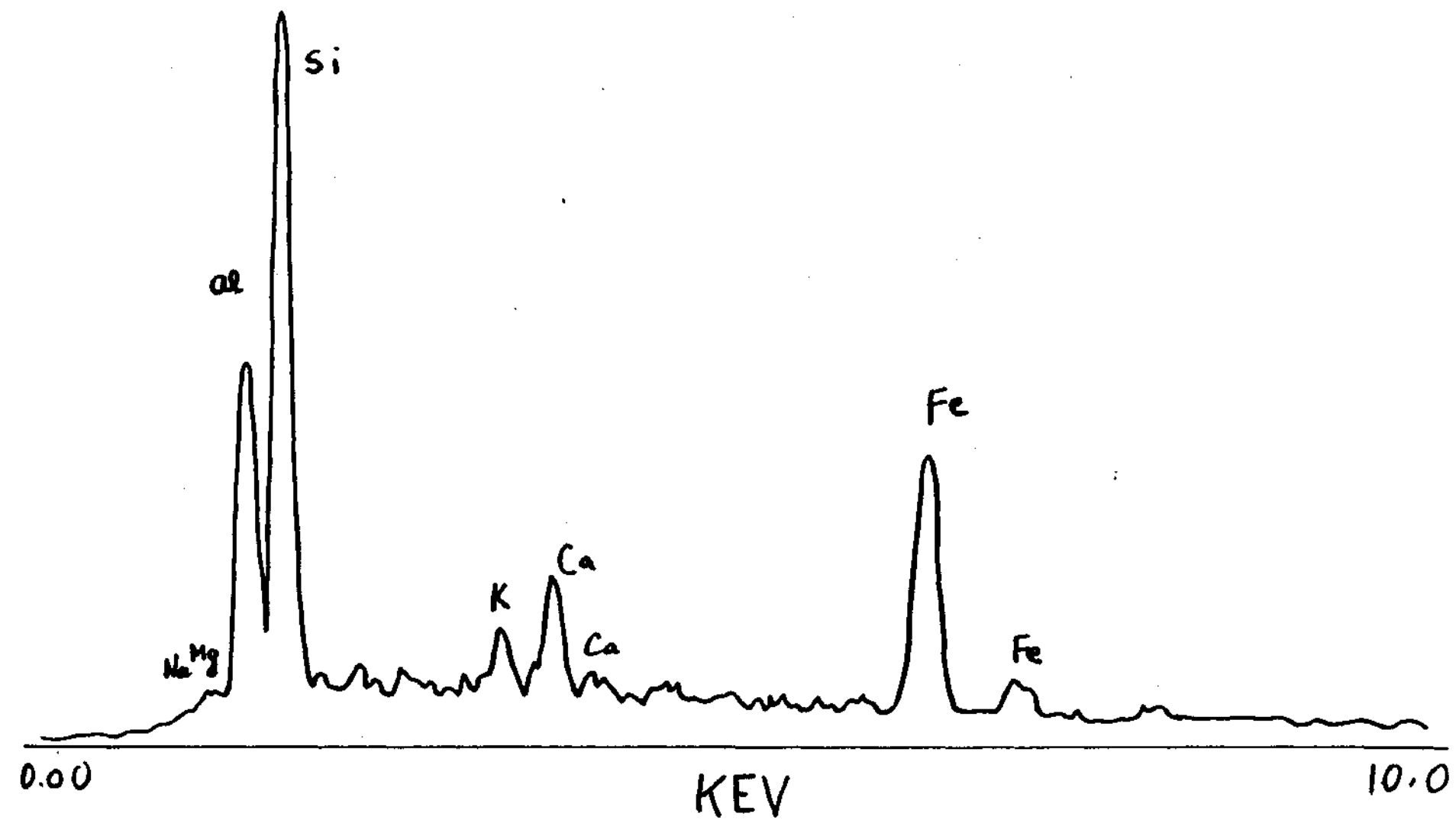
Figure 5:   Elemental Dispresive X-ray (EDX) of Microprobe Scans Paoli Rail Yard Soil Samples.

chemistry of the untreated soil is predominately Si, Al, Fe, Ca. Only small amounts of potassium (K), sodium (Na), and Mg are present (see Figure 5). Figure 6 represents the state of hydration present in the 7-day specimen cured at 100% RH. The microstructure is fairly typical of all of the specimens (including immersed) up to 120 days. The particles are becoming covered with needle-like and plate-like crystals. These crystals are unidentified, but are assumed to be some calcium silicate hydrate. These account for the strength development of the specimens with time. These crystals are bridging gaps between the particles and tying them together.

Figure 7 is an EDX spectra of the 7-day specimens. It is similar to the soil with the notable exception that iron is not present and calcium is more prominent. The calcium comes from the portland cement added to the soil. The lack of iron is due to soil inhomogeneity. Gold was used to coat the specimen, therefore gold becomes a major peak even though it is not present in the soil or binders.

Figure 8 represents a 100% RH specimen at 56 days. The needle-like and plate-like crystals seen earlier are still present, in fact they are better developed, and more crystals are seen filling the gaps between particles of soil and ash.

For the sake of comparison, Figure 9 represents micrographs of immersed specimens at the same starting magnification as Figure 8. The RW specimens are on the left and the DI specimens are on the right. Once again, calcium silica and hydrate crystals are seen to play a major role in binding larger particles together. In all cases, the excess Ca produced by the hydration of the cement is combining with soil-ash to form a calcium silicate hydrate. This cementing phase is normally associated with these curing reactions. It is noteworthy that immersion does not degrade the microstructure of the phases present; they look identical to the 100% RH samples. The microstructure of the 90 and 120 day specimens closely resembled the appearance of the 7 and 56 day specimens. The only real difference was a general densification of the matrix (lower porosity) with increased time of hydration. Also, in both instances, the outer surfaces of the immersed

specimen tended to carbonate. This was easily observed as the surfaces were covered with typical "dog-tooth" calcium carbonate crystals.

Task 10: PCB and Chemical Composition of Permeating Fluids

As part of the developmental aspect of the research, permeating solution were analyzed for PCB and elements normally associated with soil solidified/stabilized materials. The PCB content and chemical analysis of the 56 and 90 day fluids are given in Tables 1B and 2B of Appendix B, respectively. PCB contents were determined by GTEL (Milford, New Hampshire) and are less than 1-2 ppb. This is a very good indication that the solidification/stabilization procedure is not affecting the soil-PCB bonding already in place. The levels of PCBs in the leachates are below detection limits.

The elemental analyses (Table 2B in Appendix B) of the permeating solution were determined by MRL/PSU (University Park, Pennsylvania). The analyses are dominated by the lime contained in the system. Although the compositions vary quite a bit, the effect on the PCB content was minimal. This suggests that pore water composition may not in fact be a critical issue in guaranteeing the longevity of the solidified/stabilized material. The variability of the numbers suggest that one is not achieving equilibrium in one day. Also, possible channeling is occurring where one path gives you less Ca than if all pores of the entire sample are involved.
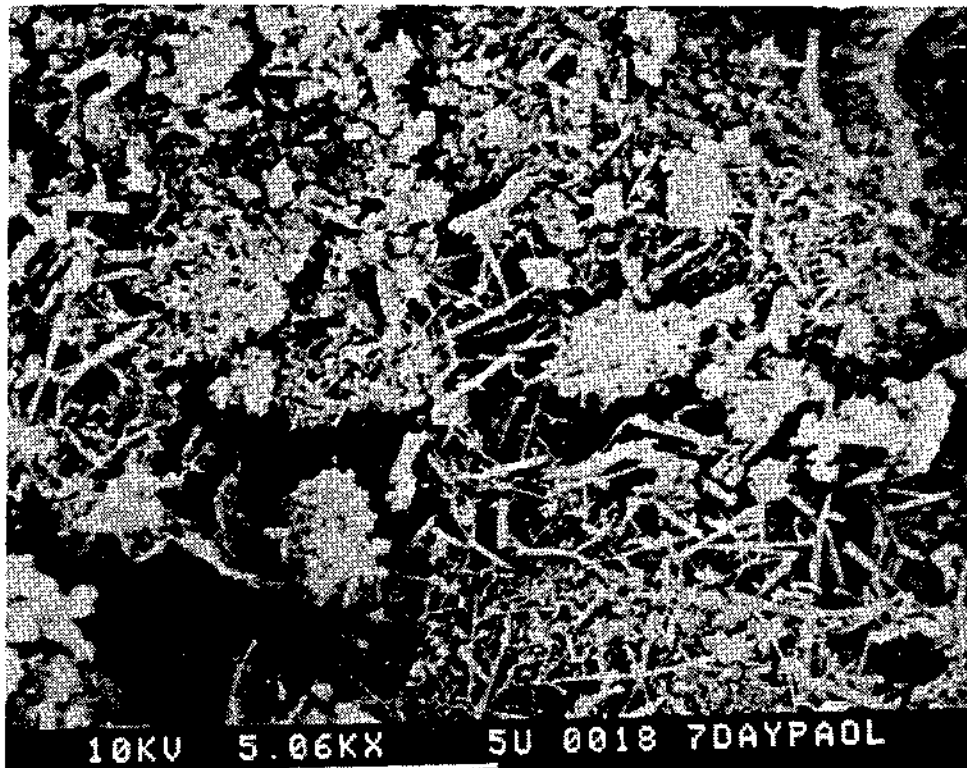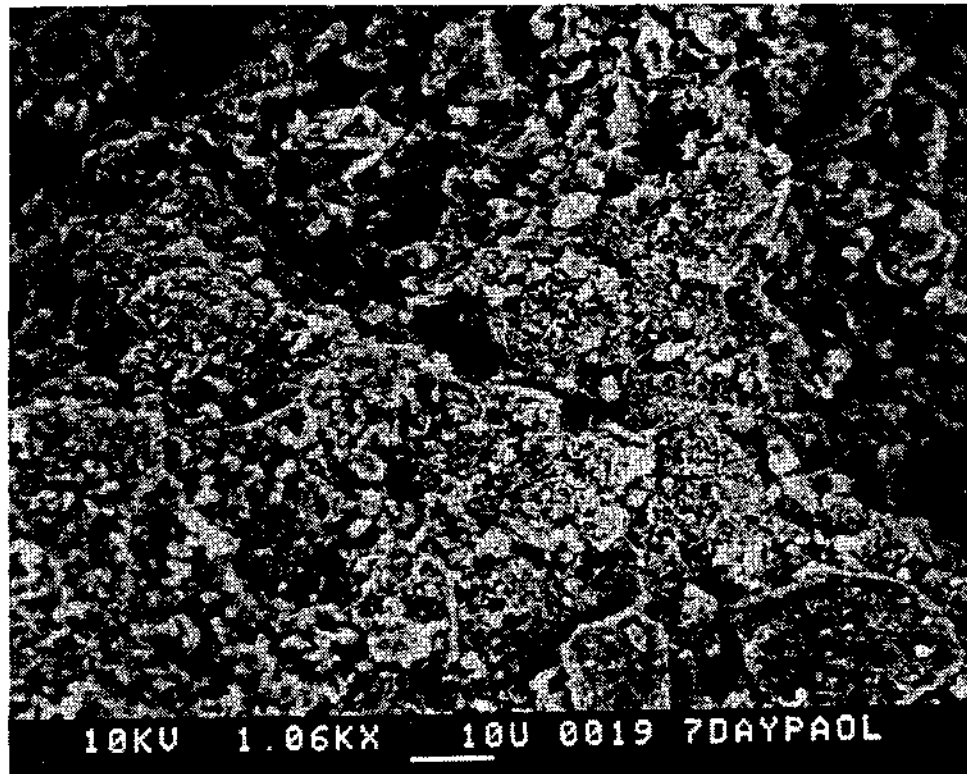
Figure 6:   7-day samples of solidified soil-ash/cement mixtures. Horizontal bars are
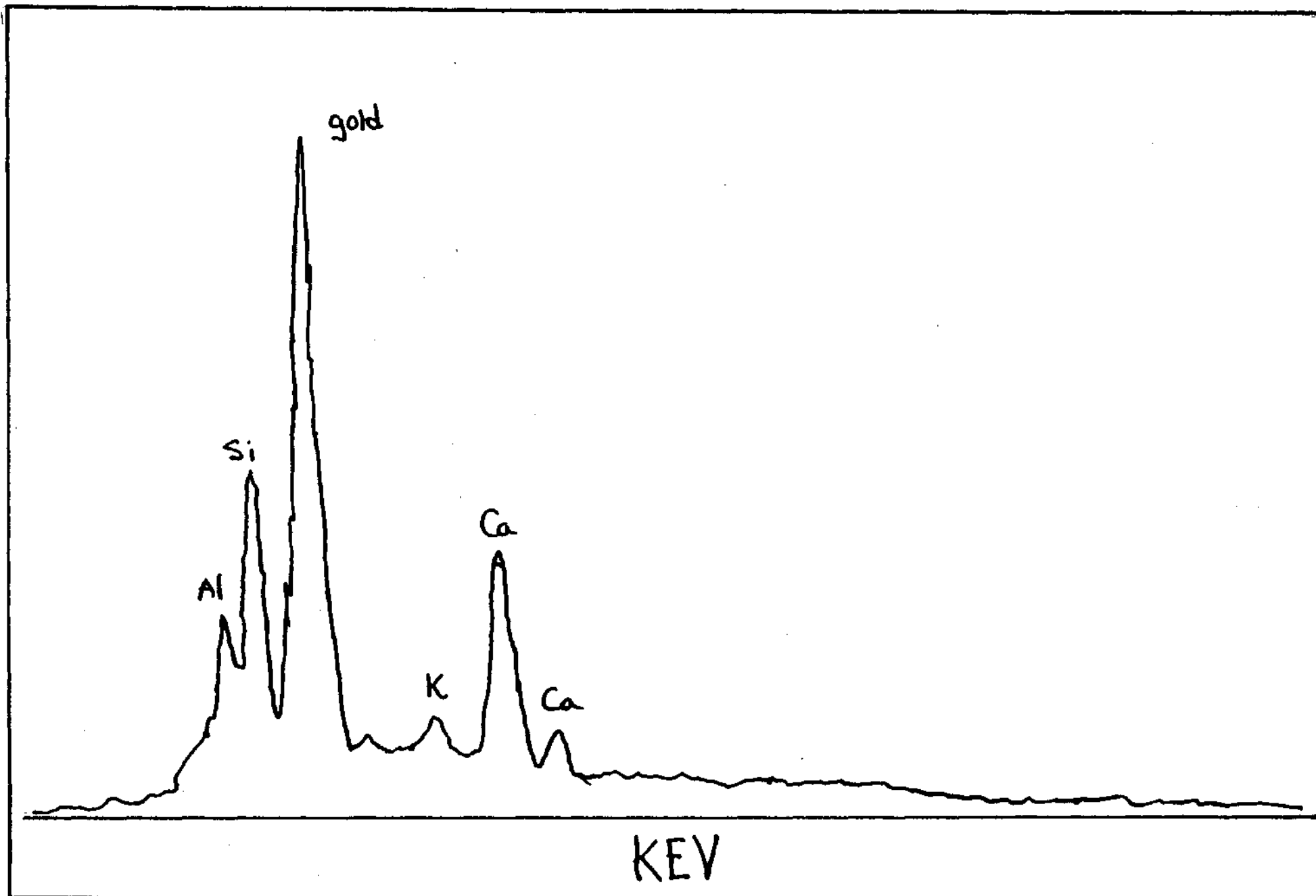   10 and 5 μm long (top, bottom) respectively.

Figure 7: EDX of Paoli soil stabilized with 10% Portland Cement. A thin film of gold was used to make the sample conductive to electrons. It is not normally present in the sample.
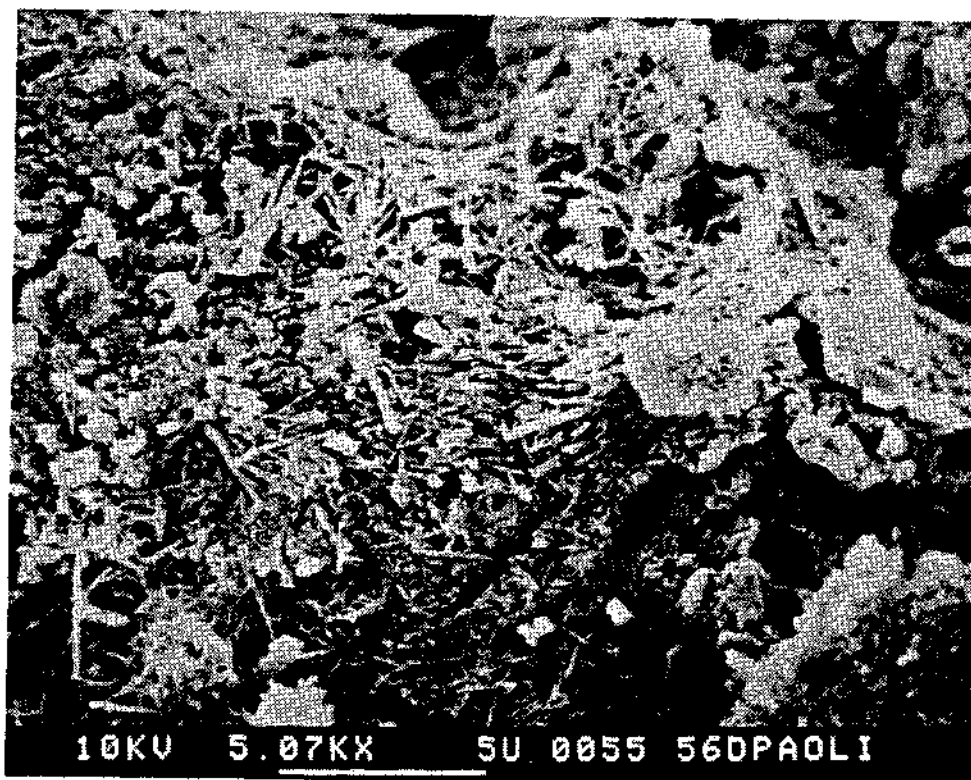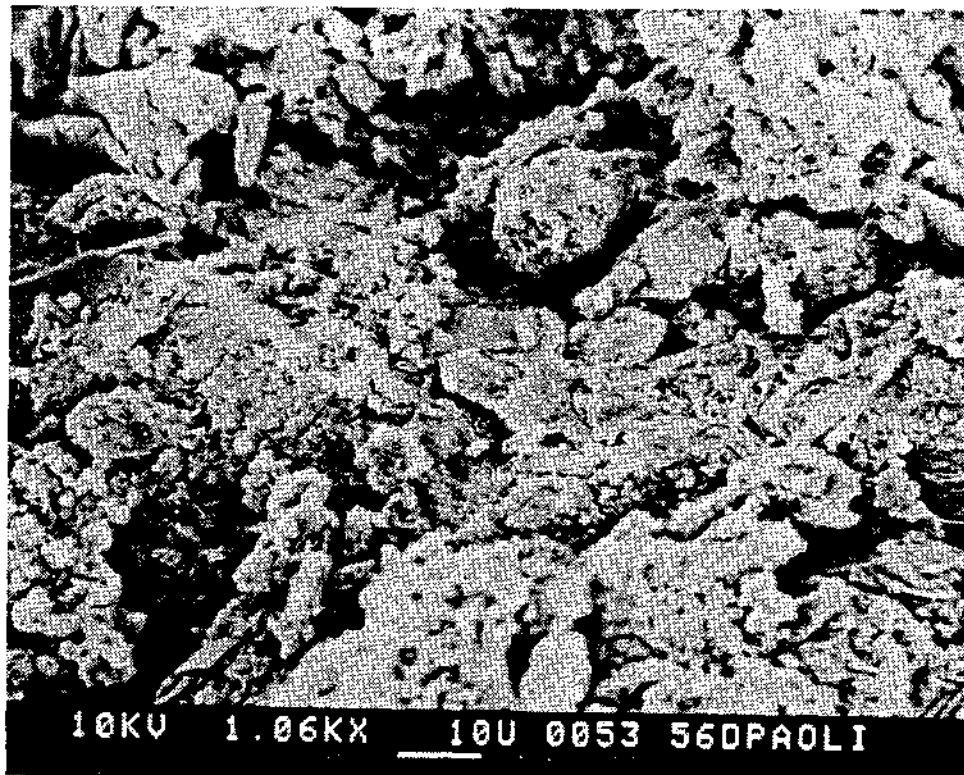
Figure 8:   56-day samples of solidified soil-ash/cement mixtures. Horizontal bars are 10 and 5 μm (top, bottom) respectively.
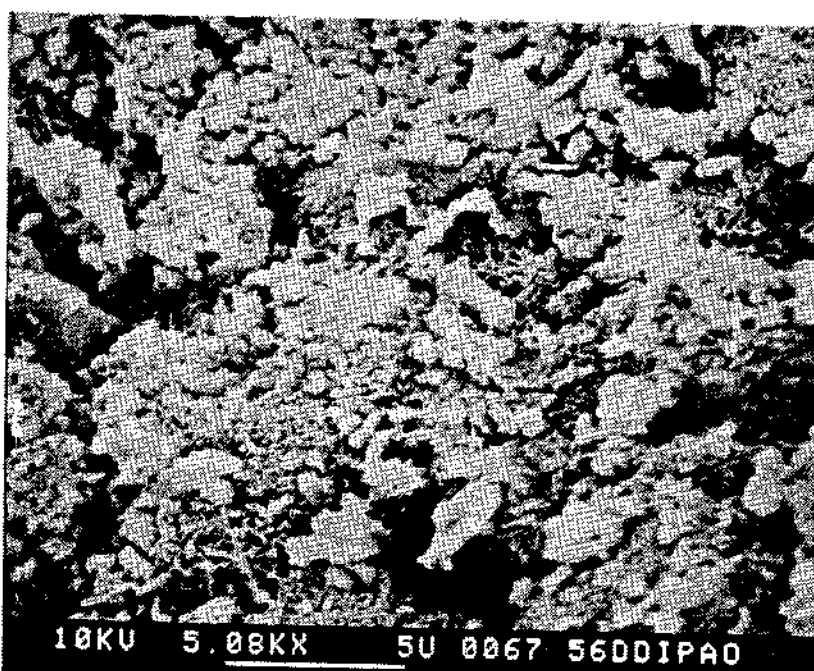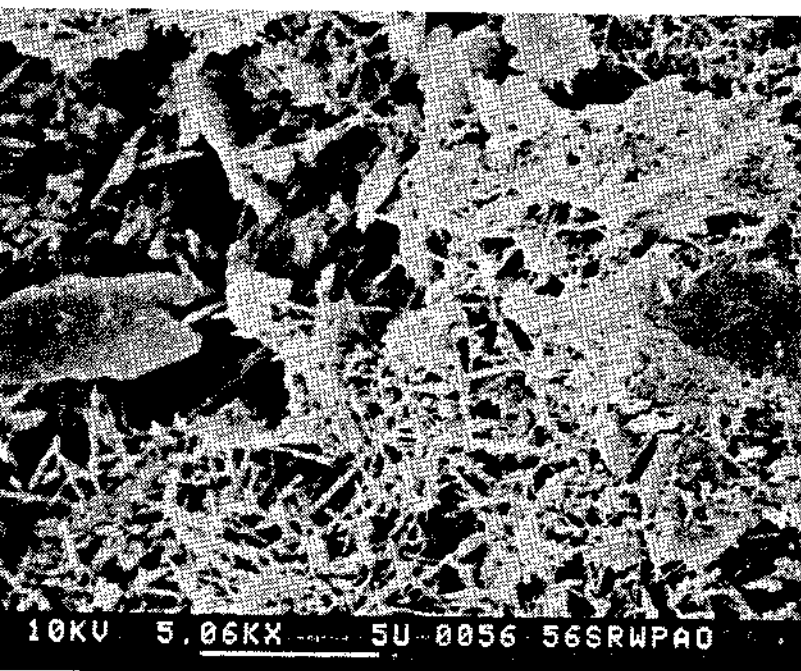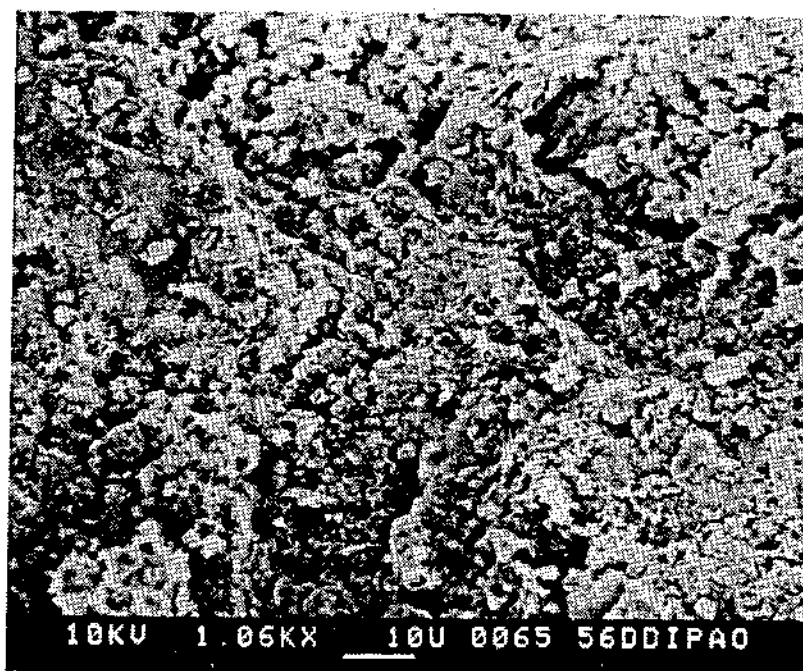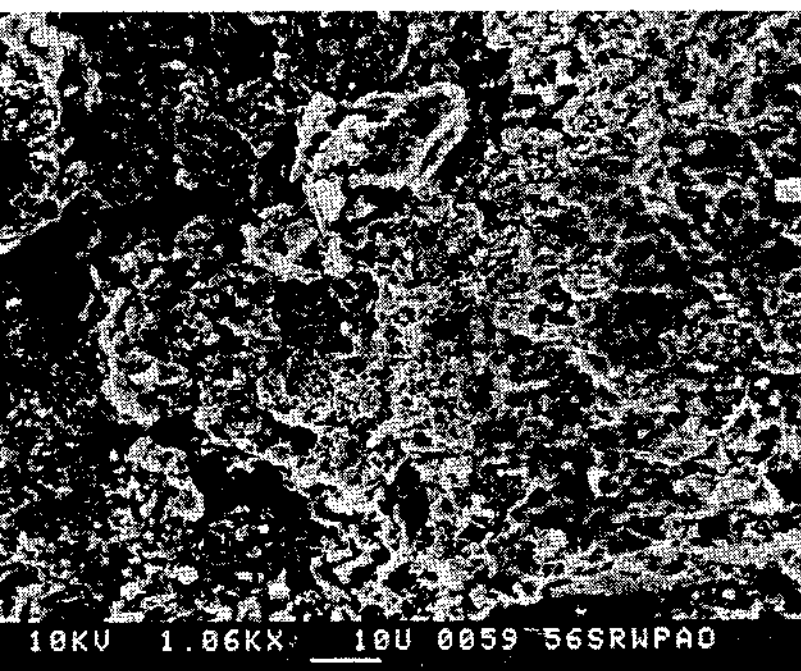
Figure 9:   56-day immersed samples (RW on left and DI on right) of
solidified/stabilized soil-ash/cement mixtures. Horizontal bars are 10 and 5
μm long, respectively.

Task 11:   PCB and Chemical Composition of Immersion Solutions

As part of the test protocol, specimens were immersed in simulated rain water and deionized water for 56 and 90 days (see Task 7). By analyzing the solutions after the samples had been removed for testing, it was possible to tell whether or not PCB was lost to the solution under static conditions. In fact, the PCB contents of the 56 and 90 day immersion solutions were below detectable limits (see Table 1C in Appendix C).

The consistency of the elemental analyses (Table 2C in Appendix C) reflects that the system had time to approach equilibrium in 56 to 90 days. At a given time, the RW and DI water samples have the same composition. The leachate is dominated by Ca > K > Na, with values for the four samples being relatively close to one another.

Task 12: X-Ray Diffraction Phase Analysis

X-ray diffraction is a simple yet effective technique useful for determining the identity of the crystalline phases present in the specimens. The present specimens are dominated by a quartz peak (quartz being present) in the soil, and smaller amounts of clay minerals such as illite, muscovite, phlogopite, kaolinite, as well as gypsum, and amorphous glass. See Figure 10.

Other peaks form during the hydration process. Some are attributable to carbonate and others are yet to be identified. There is not a great deal of crystallinity. But judging from the micrographs, some crystals are forming. One problem observed by MRL was inhomogeneity. Specimen to specimen variability was noticed, which made it more difficult to interpret x-ray patterns.

Figure 11a and 11b represent the 10 weight percent soil/ash-cement after 7 days of hydration at 100% RH. The quartz peaks remain. Also present are amorphous peaks. Many of the clay peaks are gone, because the clays may have reacted with the cement.
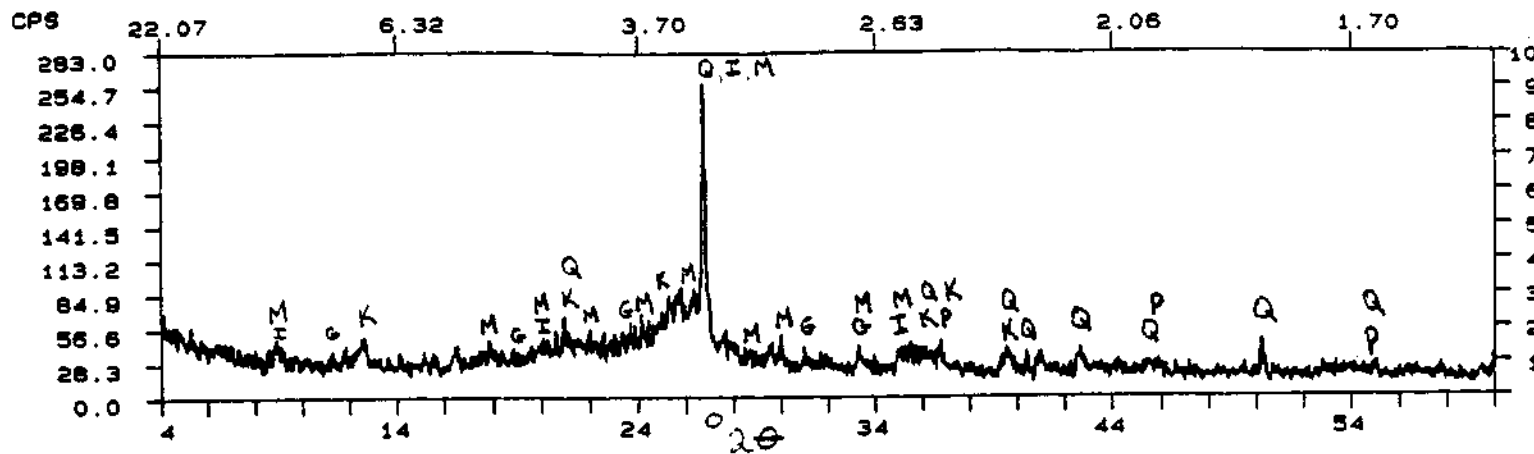
Figure 10: X-ray diffraction patterns of Paoli soil. Q = quartz; I = illite; M = muscovite; p = phlogopite; k = kaolinite; g = gypsum.
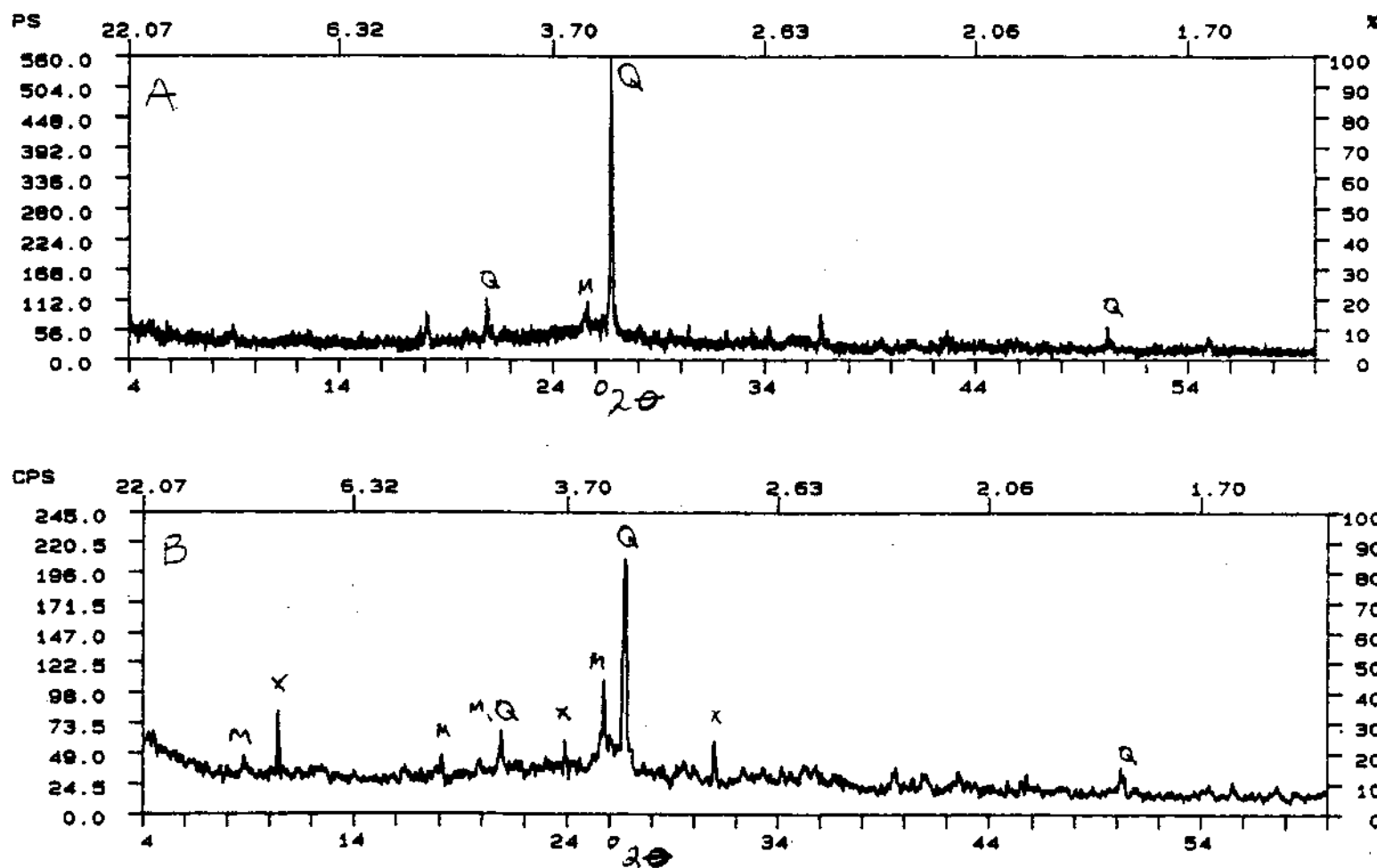
Figure 11: X-ray diffraction pattern of 7-day solidified/stabilized samples. Samples used to obtain patterns for A and B were taken from the same cylinder. Differences represent soil inhomogeneity. Q = quartz; M = muscovite, x = $4CaO \cdot Al_2O_3 \cdot 13 H_2O \cdot$

Figures 12-14 represent x-ray diffraction traces of the 56 day specimens (100% RH, RW, and DI). Patterns are reasonably similar to those observed at 90 and 120 days. Once again the patterns are dominated by residual quartz peaks, but little else. The amorphous hump at 20-28° 2ø represents remnant coal-ash particles, whereas the hump at 30-34° 2ø represents calcium silicate hydrate cement.
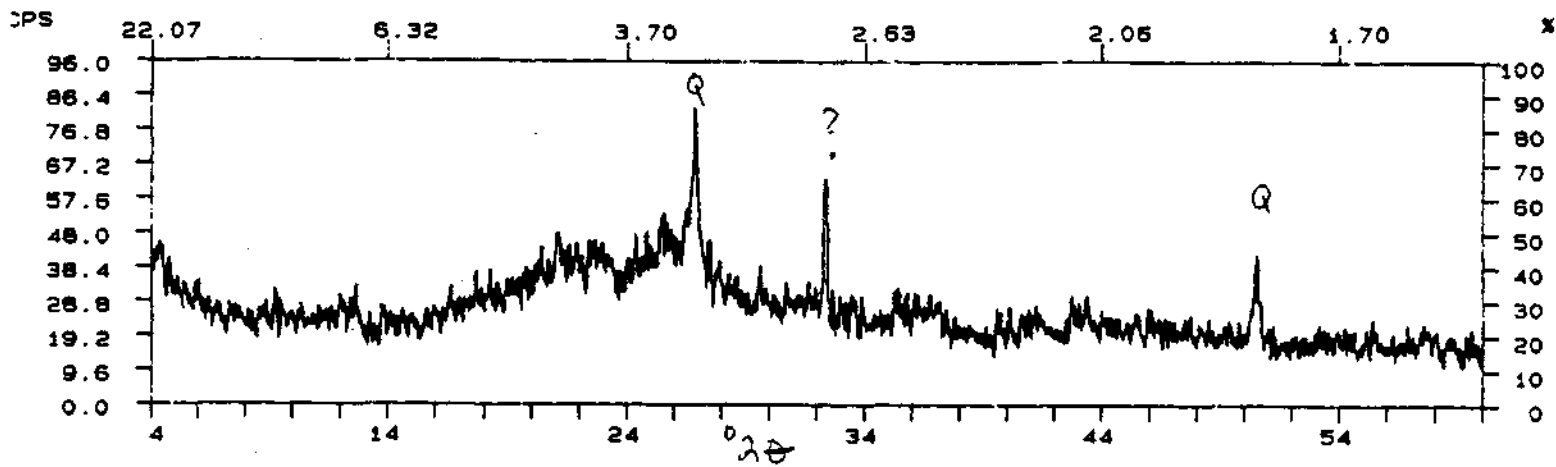
Figure 12:   X-ray diffraction pattern of 100% RH sample (56-day).
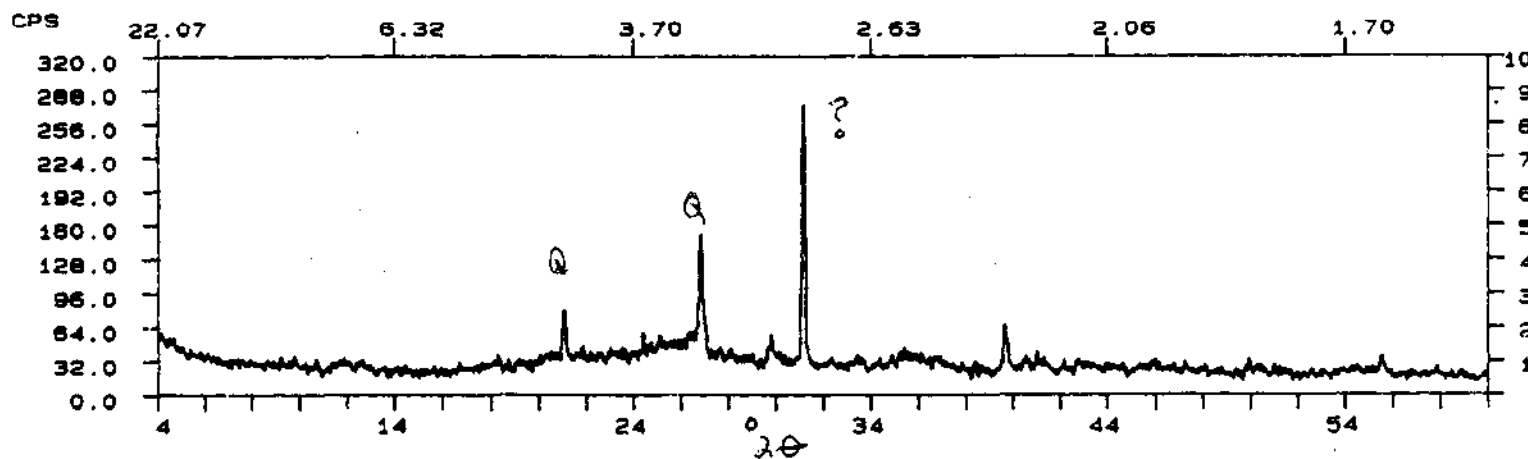
Figure 13:   X-ray diffraction pattern of RW sample (56-day).
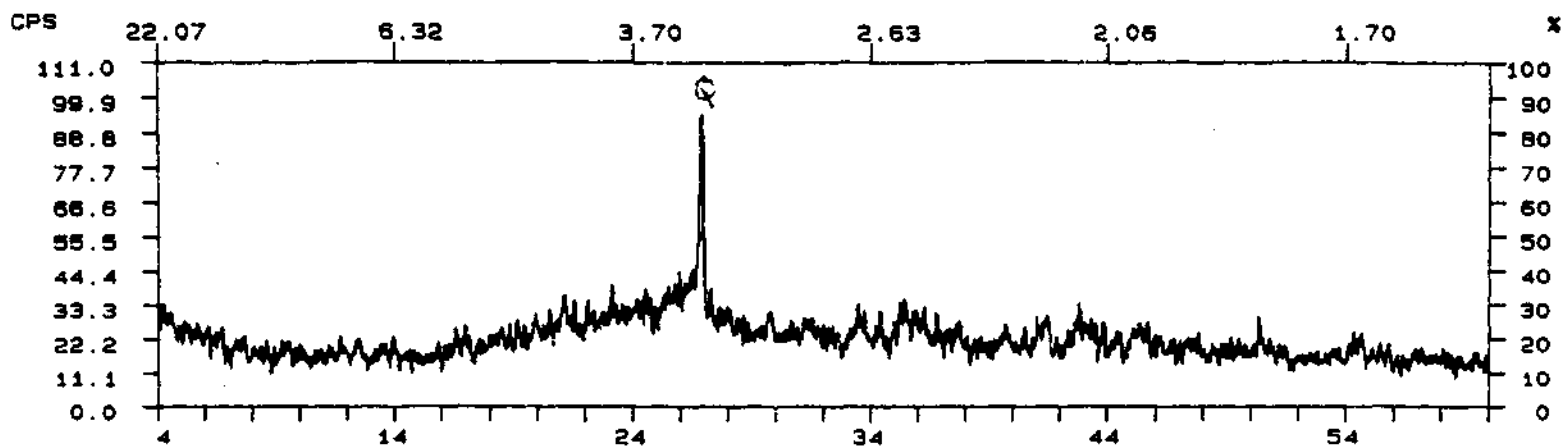
Figure 14:   X-ray diffraction pattern of DI sample (56-day).

Task 13: Thermodynamic Phase Stability Diagrams

A soil analysis was performed at MRL as part of this study. See Appendix A, Table 1B. The analysis is dominated by oxides of calcium (Ca), aluminum (Al), silicon (Si), and iron (Fe). Other oxides containing magnesium (Mg), alkalies (Na,K), and titanium (Ti) are present in smaller amounts. The analysis is rather typical of coal combustion products and slag which were presumably used as rail road track ballast. If the CaO, Al_2O_3 and SiO_2 content of the soil is plotted on a schematic diagram for the system CaO-Al_2O_3-SiO_2-H_2O (Figure 15, Paoli soil), it can be seen that the soil plots in an area of the diagram generally allotted to clays and zeolites. If one adds 8-10% portland cement to the soil and bulk composition moves a little closer to the CaO corner of the diagram (Paoli soil-cement mixture). This shift is not a major one, leaving the bulk composition of the solidification/stabilization mixture well within the area dominated by clays and zeolites. The only change in phase composition is the production of a small amount of calcium silicate hydrate (C-S-H), the material which gives portland cement its strength. Recent work by LaRosa et al.,[1] has shown that C-S-H and zeolites can coexist if bulk compositions fall in the same area of the diagram.

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[1] J.L. LaRosa, S. Kwan and M.W. Grutzeck, Zeolite Formation in Class F Fly Ash Blended Cement Pastes 75, 1574-80 (1992) and J.L. LaRosa, S. Kwan and M.W. Grutzeck, Self-Generating Zeolite Cement Composites, Mat. Res. Soc. Symp. Proc. 245, 211-16, Mat. Res. Soc., Pittsburgh (1992).

For sake of comparison, approximate compositions of ancient cements and mortars as well as more modern dam and bridge cements are also plotted on the figure. The Roman cements which have survived many hundreds of years without significant deterioration were mixtures of crudely burnt and slaked lime (calcium hydroxide) mixed with zeolitic material taken from the local pozzolanic deposits (altered volcanic ash). These recipes fall near the compositions of present day portland cement. The U.S. Corps of Engineer Dam compositions contained upwards of 24-32% pulverized fuel ash (fly ash). The bridges which span San Francisco Bay contain 25% calcined shale (clay). Based on the long-term performance of these materials, past experiments with similar materials, and the fact that clays and zeolites are among the most stable end products of chemical weathering, it seems highly likely that the present Paoli soil-cement waste form will also perform well into the future without significant damage (expansion/shrinkage due to ground water driven chemical modification).
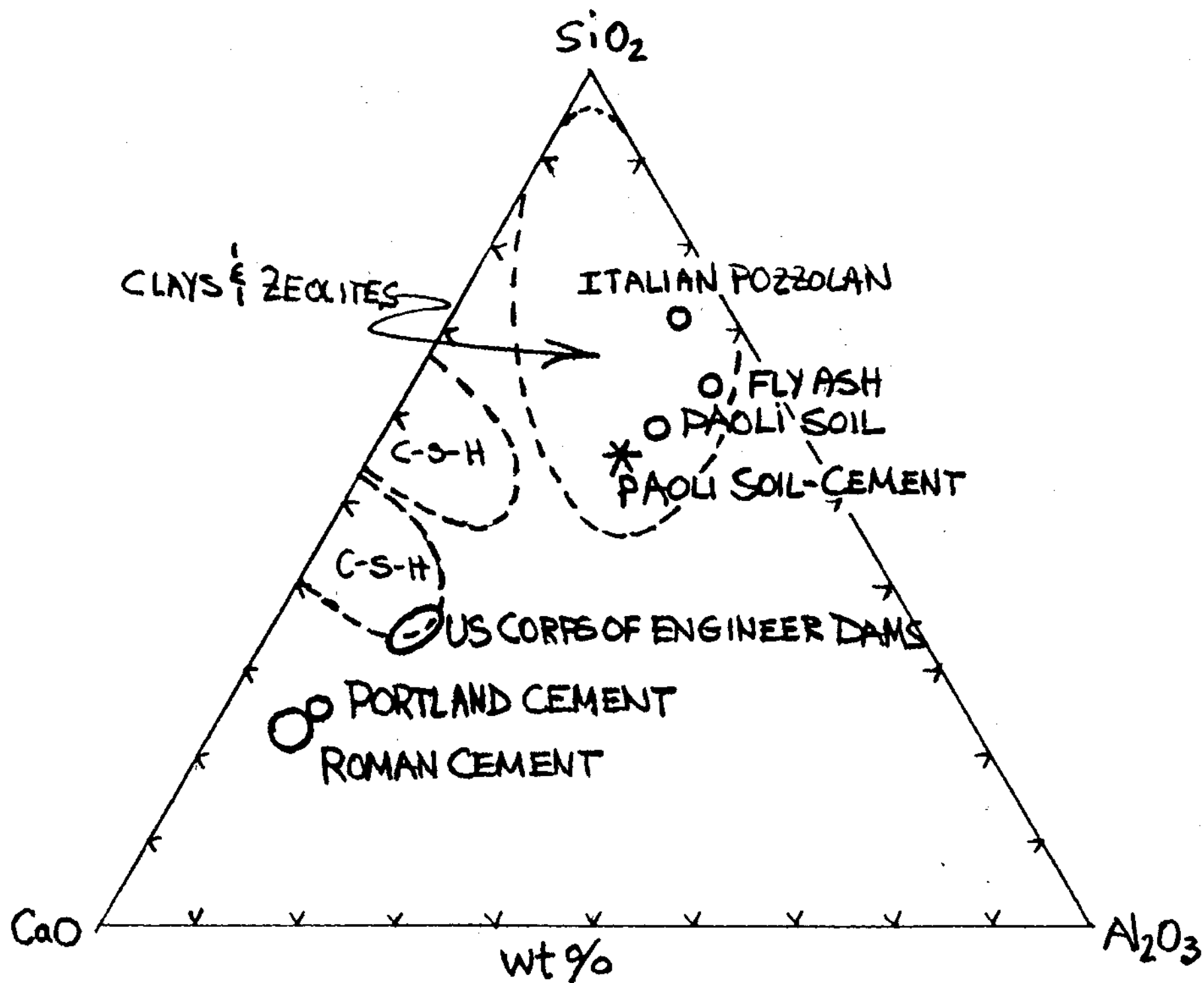
Figure 15.   Schematic diagram of the system CaO-Al_2O_3-SiO_2-H_2O showing the relative location of Paoli soil-cement to other cements with proven long-term performance. Data have bene projected onto the anhydrous base of the system.

5.0   CONCLUSIONS

This solidification/stabilization waste form is a good one. PCB soil bonding is not affected by the presence of cement and elevated concentrations of Ca, K, and Na from the cement. In fact, strength improves and porosity decreases as hydration continues. The soil is reasonably pozzolanic and has no free calcium hydroxide [$Ca(OH)_2$]. Some of the calcium hydroxide might have been converted to carbonate. However, none of these secondary reactions were found to affect the integrety of the matrix.

Phase equilibrium diagrams suggest that the solidified/stabilized Paoli soil should be stable (chemically and dimensionally) and will not degrade with time. This is based on the fact that the composition of the present material lies within compositional limits normally associated geochemically stable clays and zeolites. The latter materials are very durable, and by association, it is felt that the solidified/stabilized Paoli soil-cement will also be durable in terms of geological time.

In all cases, the strength of the waste form increased and the permeability decreased as the pozzolznic reactions continued throughout the durability exposure tests. The density and physical durability of this waste form improved continually with age. The waste form's ability to sequester PCBs was not lowered by exposures to these durability tests.

APPENDICES

APPENDIX A
SOIL ANALYSES

TABLE 1A

ANALYTICAL RESULTS
Polychlorinated Biphenyls in Soil
EPA Method 8080

GTEL Sample Number		02608-01	---	---	---
Client Identification		QUALT-1	---	---	---
Date Sampled		02/12/92	---	---	---
Date Extracted		02/25/92	---	---	---
Date Analyzed		03/11/92	---	---	---
Analyte	Detection Limit, ug/kg	Concentration, ug/kg			
Aroclor-1221	40	<48000	---	---	---
Aroclor-1232	40	<48000	---	---	---
Aroclor-1242(1016)	40	<48000	---	---	---
Aroclor-1248	40	<4800	---	---	---
Aroclor-1254	40	<4800	---	---	---
Aroclor-1260	40	780000[c]	---	---	---
Detection Limit Multiplier[b]		1200	---	---	---
Percent Solids, %		83.2			

a   Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Revision 0, US EPA November 1986: Extraction by EPA Method 3550 (low level sonication). Results are reported on a dry weight basis.

b   The detection limit multiplier indicates the adjustments made to the data and detection limits as a result of dilutions and percent solids.

c   High levels of this target analyte preclude detection of other PCBs at lower concentrations.

TABLE 1A. (Continued)

ANALYTICAL RESULTS
Polychlorinated Biphenyls in Soil
EPA Method 8080[a]

GTEL Sample Number	110152-01	---	---	---
Client Identification	PAOLI SOIL	---	---	---
Date Sampled	11/01/91	---	---	---
Date Extracted	11/10/92	---	---	---
Date Analyzed	11/17/92	---	---	---

Analyte	Detection Limit, ug/kg	Concentration, ug/kg			
Aroclor-1221	40	<23000 X	---	---	---
Aroclor-1232	40	<23000 X	---	---	---
Aroclor-1242(1016)	40	<23000 X	---	---	---
Aroclor-1248	40	<2300 X	---	---	---
Aroclor-1254	40	<2300 X	---	---	---
Aroclor-1260	40	5300000 X	---	---	---
Detection Limit Multiplier[b]		5800	---	---	---
Percent Solids, %		85.5			

a   Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Revision 0, US EPA November 1986: Extraction by EPA Method 3550 (low level sonication). Results are reported on a dry weight basis.

b   The detection limit multiplier indicates the adjustments made to the data and detection limits as a result of dilutions and percent solids.

X   Estimated concentration. Sample extraction performed beyond recommended holding time per client request.

TABLE 1B.
CHEMICAL ANALYSIS OF PAOLI SOIL

Date: November 10, 1992
To: Barry Scheetz/Mike Silsbee
From: Scott D. Atkinson
Subject: Spectrochemical Analysis of PQ and FlyAsh
           Samples

	Paoli (wt%)
Moist	14.70
LOI	37.60
AgO	
Al2O3	18.10
As2O3	
B2O3	0.76
BaO	0.08
BeO	
CaO	6.14
CdO	
CoO	0.01
Cr2O3	0.11
CuO	
Fe2O3	20.50
HgO	
K2O	1.38
MgO	1.34
MnO	0.52
MoO3	0.01
Na2O	0.80
NiO	0.01
PbO	
Sb2O3	
SeO2	
SiO2	48.20
SnO2	
SrO	0.06
TiO2	1.28
V2O5	0.05
ZnO	0.20
ZrO2	0.05
S	0.4

APPENDIX B

ANALYSES OF SOLUTIONS OBTAINED DURING PERMEABILITY TESTING

Table 1B:	PCB Content of Permeating Fluids*	56 day	90 day
100% RH	Aroclor 1221	<1.1	<1.1
	Aroclor 1232	<1.1	<1.1
	Aroclor 1242 (1016)	<0.70	<0.72
	Aroclor 1248	<1.1	<1.1
	Aroclor 1254	<1.1	<1.1
	Aroclor 1260	<1.1	<1.1
	Detection Limit Mult.	1.08	1.11
Rain Water (immersed at 36 days)	Aroclor 1221	<1.1	<1.1
	Aroclor 1232	<1.1	<1.1
	Aroclor 1242 (1016)	<0.74	<0.74
	Aroclor 1254	<1.1	<1.1
	Aroclor 1260	<1.1	<1.1
	Detection Limit Mult.	1.14	1.14
Deionized Water (immersed at 36 days)	Aroclor 1221	<1.1	<2.0
	Aroclor 1232	<1.1	<2.0
	Aroclor 1242 (1016)	<0.72	<1.3
	Aroclor 1248	<1.1	<2.0
	Aroclor 1254	<1.1	<2.0
	Aroclor 1260	<1.1	<2.0
	Detection Limit Mult.	1.11	20.0

*Analyte   Detection Limit, ug/L
Aroclor 1221   1.0
Aroclor 1232   1.0
Aroclor 1242 (1016)   0.65
Aroclor 1248   1.0
Aroclor 1254   1.0
Aroclor 1260   1.0

Table 2B:	Chemical Composition of Permeating Fluids (elemental % in Mg L^{-1})			
		Blank	56-Day	90-Day
100% RH	Al	0.04	0.76	1.2
	B	<0.02	<0.02	0.02
	Ba	<0.02	0.06	0.71
	Ca	<0.02	53.0	350.0
	Cr	<0.02	<0.02	0.12
	Fe	<0.02	0.02	0.04
	K	<0.02	4.8	39.0
	Mg	<0.02	0.04	<0.02
	Mn	<0.02	<0.02	0.02
	Na	<0.02	0.77	6.5
	Ni	0.00	0.01	0.04
	Si	<0.02	1.48	2.94
	Sr	<0.02	0.23	2.08
	Ti	<0.02	<0.02	<0.02
	Zn	<0.02	<0.02	0.03
Rain Water (immersed at 36 days)	Al	0.04	0.15	1.73
	B	<0.02	<0.02	0.03
	Ba	<0.02	<0.02	0.24
	Ca	<0.02	4.5	220.0
	Cr	<0.02	<0.02	0.04
	Fe	<0.02	<0.02	0.02
	K	<0.02	0.28	15.3
	Mg	<0.02	<0.02	0.07
	Mn	<0.02	<0.02	<0.02
	Na	<0.02	0.08	2.52
	Ni	0.00	0.00	0.02
	Si	<0.02	0.58	5.0

Table 2B: Chemical Composition of Permeating Fluids (elemental % in Mg L^{-1})		Blank	56-Day	90-Day
	Sr	<0.02	<0.02	0.84
	Ti	<0.02	<0.02	<0.02
	Zn	<0.02	0.06	<0.02
Deionized Water (immersed at 36 days)	Al	0.04	0.15	2.5
	B	<0.02	<0.02	<0.02
	Ba	<0.02	<0.02	0.36
	Ca	<0.02	2.75	220.0
	Cr	<0.02	<0.02	0.03
	Fe	<0.02	<0.02	0.04
	K	<0.02	0.16	35.0
	Mg	<0.02	<0.02	0.03
	Mn	<0.02	<0.02	<0.02
	Na	<0.02	0.04	6.6
	Ni	0.00	0.00	0.05
	Si	<0.02	<0.02	3.43
	Sr	<0.02	<0.02	1.46
	Ti	<0.02	<0.02	<0.02
	Zn	<0.02	<0.02	<0.02

APPENDIX C

ANALYSES OF SOLUTIONS SAMPLES WERE IMMERSED IN

Table 1C: Immersion Solutions (PCBs in Mg L^{-1})*		56 day	90 day
Rain Water (immersed at 36 days)	Aroclor 1221	<1.0	<1.0
	Aroclor 1232	<1.0	<1.0
	Aroclor 1242 (1016)	<0.67	<0.65
	Aroclor 1248	<1.0	<1.0
	Aroclor 1254	<1.0	<1.0
	Aroclor 1260	<1.0	<1.0
	Detection Limit Mult.	1.03	1.00
Deionized Water (immersed at 36 days)	Aroclor 1221	<1.1	<1.0
	Aroclor 1232	<1.1	<1.0
	Aroclor 1248	<1.1	<0.65
	Aroclor 1242 (1016)	<0.70	<1.0
	Aroclor 1254	<1.1	<1.0
	Aroclor 1260	<1.1	<1.0
	Detection Limit Mult.	1.08	1.00

*Analyte   Detection Limit, ug/L
Aroclor 1221   1.0
Aroclor 1232   1.0
Aroclor 1242 (1016)   0.65
Aroclor 1248   1.0
Aroclor 1254   1.0
Aroclor 1260   1.0

Table 2C:	Chemical Composition of Immersion Solutions (elemental % in Mg L⁻¹)			
		Blank	56-Day	90-Day
Rain Water (immersed at 36 days)	Al	0.13	1.3	1.6
	B	<0.02	<0.02	<0.02
	Ba	<0.02	0.37	0.68
	Ca	0.36	265.0	360.0
	Cr	<0.02	<0.02	0.03
	Fe	<0.02	0.03	0.06
	K	0.03	24.9	41.0
	Mg	0.08	<0.02	<0.02
	Mn	<0.02	<0.02	<0.02
	Na	0.16	4.0	6.7
	Ni	0.00	0.02	0.04
	Si	<0.02	0.59	0.87
	Sr	<0.02	1.2	2.13
	Ti	<0.02	<0.02	<0.02
	Zn	<0.02	<0.02	<0.02
Deionized Water (immersed at 36 days)	Al	0.04	1.2	1.55
	B	<0.02	<0.02	<0.02
	Ba	<0.02	0.41	0.66
	Ca	<0.02	260.0	320.0
	Cr	<0.02	<0.02	0.02
	Fe	<0.02	0.03	0.05
	K	<0.02	24.1	40.0
	Mg	<0.02	<0.02	<0.02
	Mn	<0.02	<0.02	<0.02
	Na	<0.02	3.66	6.6
	Ni	0.00	0.03	0.02
	Si	<0.02	0.99	0.66
	Sr	<0.02	1.31	2.0
	Ti	<0.02	<0.02	<0.02
	Zn	<0.02	<0.02	<0.02