QUALTEC, INC.

IN SITU IMMOBILIZATION OF PCBs AT THE PEPPER'S STEEL AND ALLOYS SITE: A SUCCESS STORY

By

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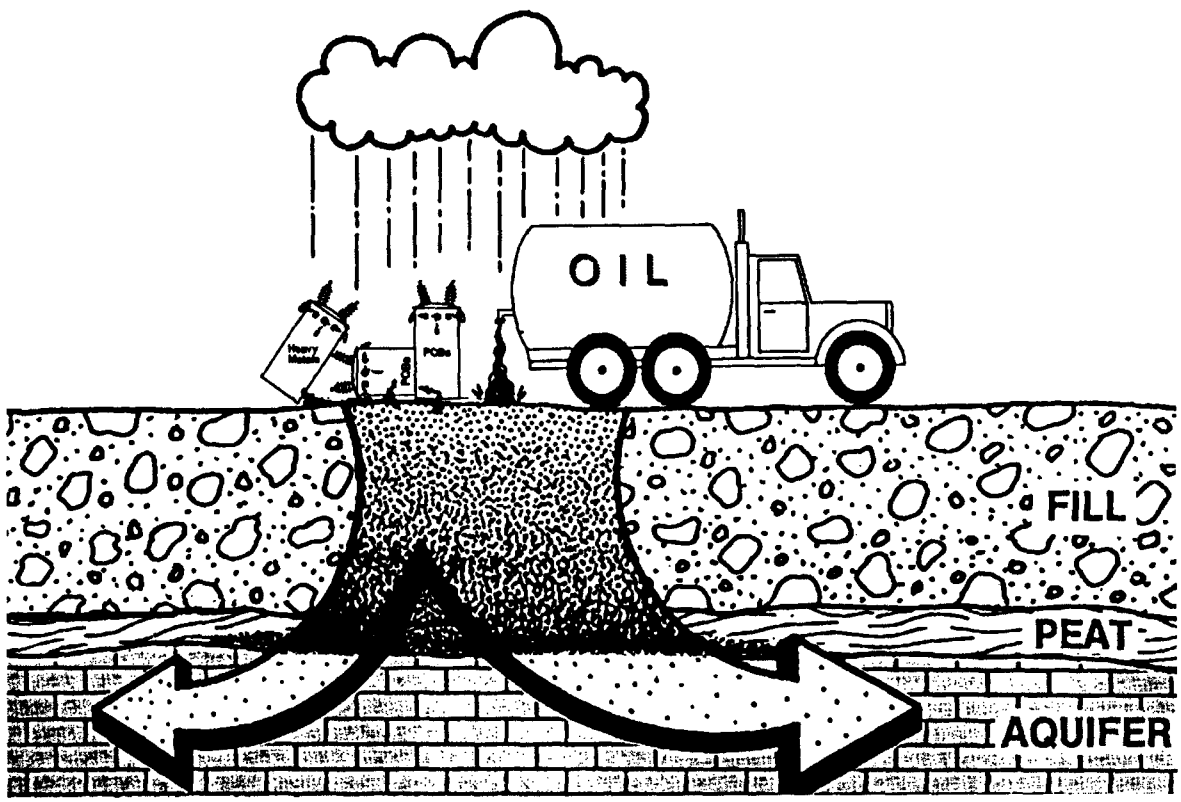

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1. Strategy Behind Pepper's Steel and Alloys Site Closure at Medley, Florida With a Pozzolanic Grout

1.1. Introduction

The Pepper's Steel and Alloys (PSA) Superfund site is located in Medley, Florida, 10 miles northwest of downtown Miami (see Figure 1). Until its June 1988 remediation, the PSA site was on the National Priorities List (NPL). Old transformers once owned by Florida Power and Light Company (FPL) were found on this 30-acre site, which was used for a junk-yard and scrap recovery operation. Subsequently, FPL became the major "deep-pocket" potentially responsible party.

The PSA soil was contaminated with lead, arsenic, and PCBs (polychlorinated biphenyls). Contamination extended from 2 to 8 feet into the soil and into the Biscayne aquifer, which is the sole source of drinking water for metropolitan Miami. Also, the PSA site is up-gradient and within 6 miles of Miami's well fields.

FPL—with full disclosure to EPA (Environmental Protection Agency) Region IV—planned and conducted a formulation, testing, and modeling program that showed the safety of pouring monolithic grout directly into this critical regional aquifer. The PSA development study established the feasibility and the

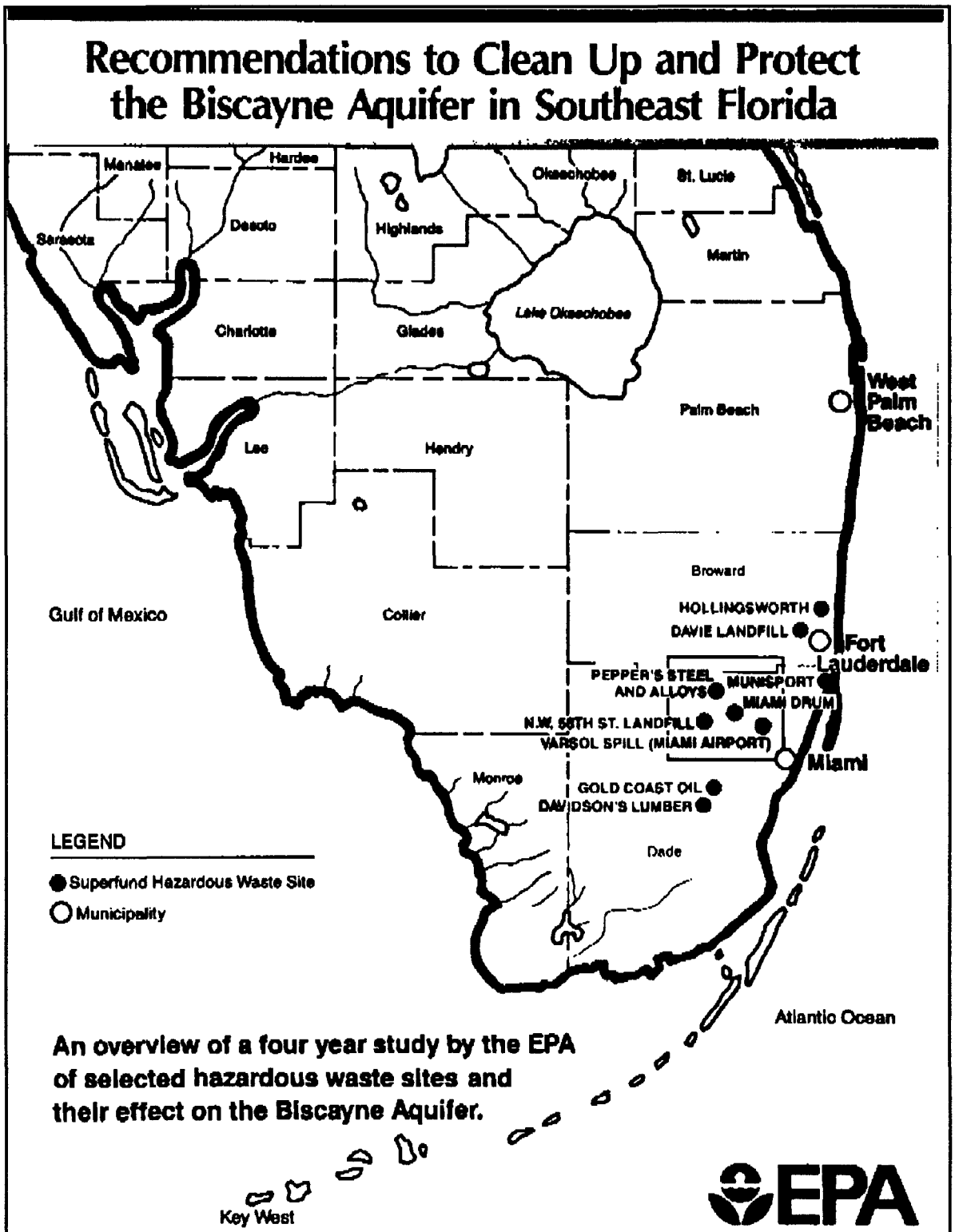

Figure 1 Northwest of Miami is a cluster of Superfund sites, including the Pepper's Steel and Alloys site.

performance characteristics of on-site, in-situ immobilization technology. This technology was then used for the remediation of 120,000 cubic yards of heavy metal and PCB-contaminated, transformer-oil-soaked soils at the PSA site.

The closure of the PSA site set several precedents for immobilizing both inorganic and organic contaminants simultaneously through the application of a cement and pozzolan waste form. This report reviews and summarizes the development strategy, performance data, and performance model. It also reports new, long-term aging and leaching data on waste form samples collected during the Quality Assurance program. Finally, it discusses maintenance and future land use at the PSA site.

1.2. Current Regulatory Status of Immobilization

In the recent reauthorization of 40 CFR (Code of Federal Regulations) Part 300 of the National Oil and Hazardous Substance Pollution Contingency Plan (NCP),[1] immobilization as an alternative to thermal or chemical remediation is addressed. That document gives qualitative guidelines for the acceptance of solidification as an alternate remediation technology.

[1] 40 CFR Part 300, National Oil and Hazardous Substance Pollution Contingency Plan (NCP), United States Environmental Protection Agency, February 1988.

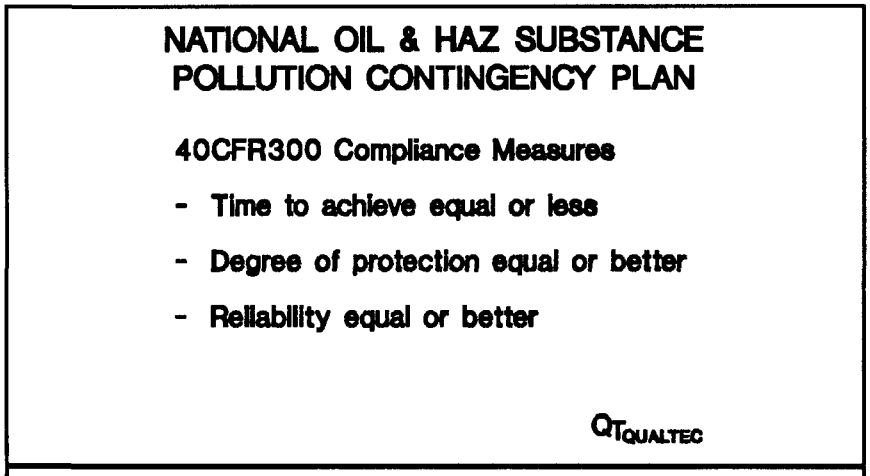

Figure 2 Conditions to be met relative to destruction technologies.

Three conditions must be met in order for the solidification technology to be accepted (see Figure 2).

The conditions set for the performance criteria of alternate technologies are expressed as three comparisons to ideal destruction technologies. These alternatives must

- perform as well as or better than incineration,
- be as reliable as or more reliable than incineration, and
- take no longer than incineration.

No quantitative engineering guidance or formal approval procedure is specified in the NCP.

Although the PSA solidification alternative development study was executed before these guidelines were adopted, the results of the PSA study showed

that in-situ immobilization meets and exceeds these new performance criteria for alternate technologies. The PSA study anticipated the growing use of risk and consequence analysis in evaluation of disposal alternatives. It set an example of how to execute and apply such principles at the Medley, Florida, site.

1.3. Selection of Immobilization for the PSA Site

The application of immobilization technologies to hazardous wastes is a new and developing area. Many contaminated soils, like those at the PSA site contain both metal (inorganic) and nonmetal (organic) toxic compounds. For wastes with both classes of hazards, immobilization offers one-step treatment advantages of speed and economy. Otherwise, two or more processes would be used to treat these classes separately. Soil washing and thermal/chemical destruction can treat only the organic hazards. Further treatment steps are then required to mitigate the remaining inorganic elements and compounds before either land or sea disposal is acceptable.

Without any treatment, such contaminated soils require special landfills with double plastic and clay liners and leachate collection systems. These lined hazardous waste landfills are difficult and expensive to install. They require long-term monitoring (30 years) and show high rates of failure in the first decade.

Additionally, the use of these landfills mixes your wastes with those of other customers. You then join them in perpetual partnership for the future liabilities of their wastes. Also, there are very high costs and risks for trucking the contaminated soils many hundreds of miles to a lined storage facility.

To move the 120,000 tons of contaminated soils over 850 miles from the PSA site to Emile, Alabama, would have taken 7,622 truck loads. At $2.00 per mile, the transportation costs alone would have been $12,920,000. In addition, this transportation route was up I-75, a heavily traveled traffic corridor in the eastern United States. This route traverses high population centers and major vacation areas, including Fort Lauderdale, the Palm Beaches, and Disney World.

Instead of the landfill alternative, in-situ immobilization with a cement-based pozzolanic grout was used, and the total cost of the PSA site closure was less than $8,000,000. This cost included development, permitting, site preparation, excavation, on-site immobilization operation, Quality Assurance/Quality Control programs, site drainage systems, monitoring wells, and cover. In other words, the whole on-site closure was done with no operational risk to the public for less than the cost of transporting the contaminated soils to Emile, Alabama.

Florida Power & Light Company presented data to EPA from a careful set of site-specific physical and chemical tests. After extensive peer review, EPA Region IV accepted the remedy. This NPL site within a few miles of one of Miami's well fields was then closed using a pozzolanic monolith.

1.4. PSA Waste Form Development Objectives

The development of the technologies for the in-situ remedy of the PSA soils had three goals, shown in Figure 3. The first goal was to seal the waste contaminants into an impermeable, durable monolith. This prevents direct contact by potential leachates, like groundwater and percolating rain. Diffusion through the waste form's mass is then the only mechanism by which a contaminant can reach the biosphere.

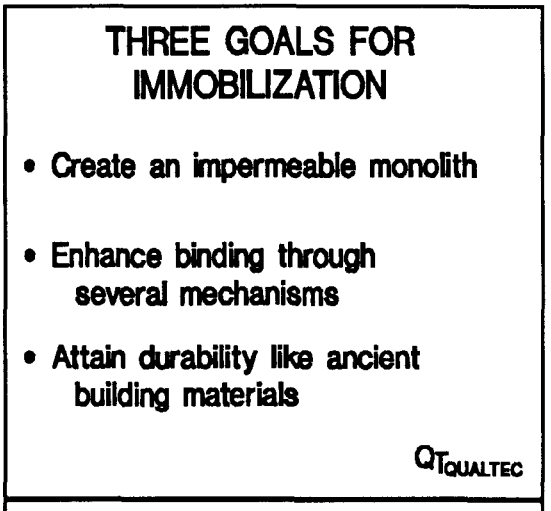

Figure 3 The three goals of immobilization.

Therefore, in the first phase, the PSA waste form development program[2] focused on developing a processable grout that had the following properties:

- no bleed-water after set,
- a 72-hour set-time,
- an unconfined compressive strength greater than 21 psi,
- a very low permeability of less than 10^{-6} Darcy (cm/s)

Figure 4 shows the steps taken to develop the PSA wasteform.

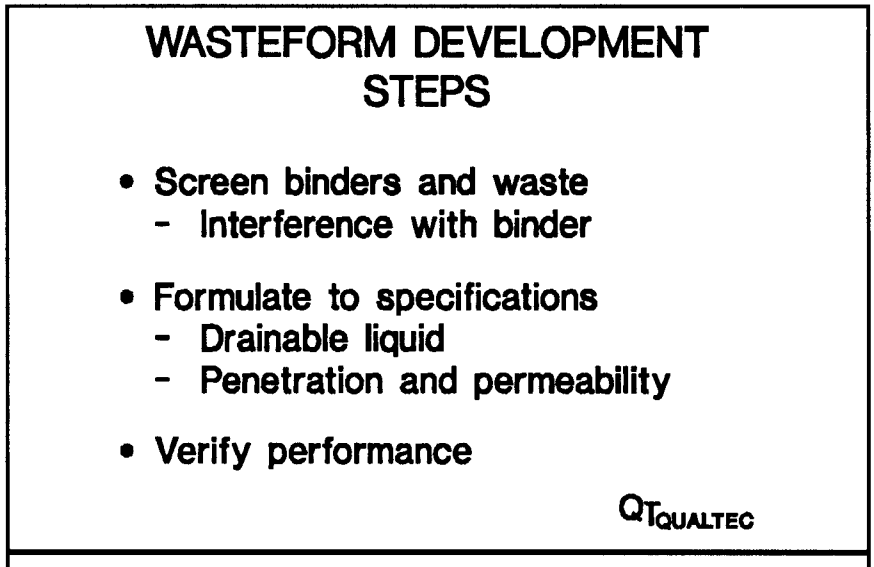

Figure 4 Steps to developing, optimizing, and proving performance of the PSA soil-grout.

[2] "Fixation/Stabilization Final Report: Pepper's Steel and Alloys Site," Medley, Florida, Volumes 1 and 2, Florida Power and Light Company, P. O. Box 14000, Juno Beach, FL 33408, November, 1985.

The second goal of the waste form development program was to design a solid matrix so that it binds with the lead, arsenic, and PCBs. Several mechanisms were used in the physical and chemical binding of contaminants in the PSA soil-grout matrix. These mechanisms include partitioning, co-precipitation, ion exchange, mole-sieve effects, and chemical reactions and they reduce the mobility of the hazards within the monolith. Figure 5 summarizes these binding mechanisms.

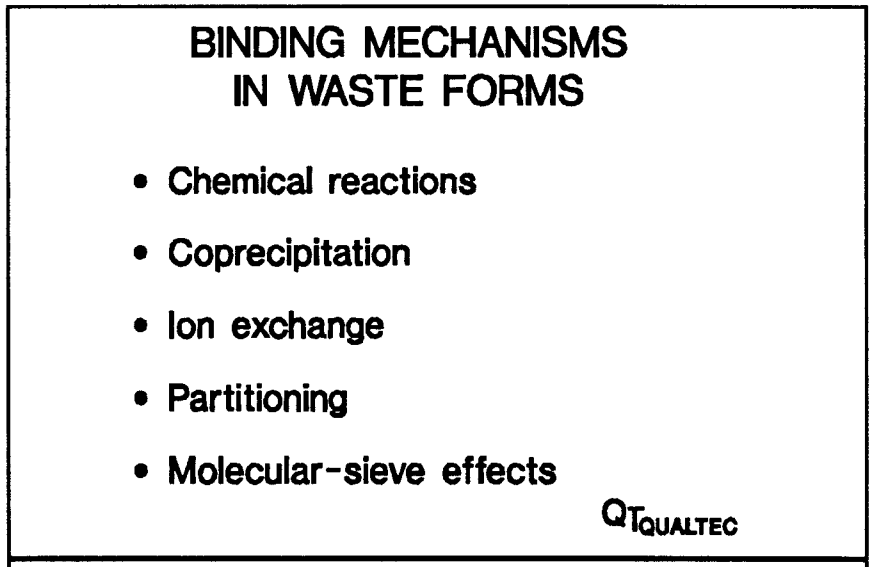

Figure 5 A summary of major binding mechanisms in the soil-grout mixture.

When combinations of these mechanisms are at work in the grout matrix phases, the hazards are effectively retained. In worst-case scenario analyses, verification leach data and site modeling show that the maximum leaching of contaminants into the biosphere does not result in concentrations above detection limits.

The third goal of the PSA program was to make a durable monolith that withstands environmental stresses at this Medley, Florida, site. These stresses could include immersion in groundwater, the mechanical loads of the cap, and the subsequent weight of a dock-level warehouse. For the PSA monolith, 21 psi was chosen as the design compressive strength because it is adequate to support such medium construction footers.

Because environmental performance requirements are site-specific, the waste form's specifications depend on each site's climate, geology, site operations, and final land use. To meet these criteria, the PSA study chose the most durable material from the oldest man-made structures, which were made of high-silica pozzolans.

1.5. Choosing the Pozzolanic Binder

Using ancient building materials from Rome, Greece, and Cyprus as models, modern material scientists can formulate durable, impermeable monoliths. For example, high-silica pozzolans endured between 2,500 to 5,000 years of weathering. Thus, this type of waste form will remain competent for millennia in

various geochemistries throughout the United States.[3]

The PSA monolith is buried and will not be directly exposed to weathering. Any spills from surface activities at the site will be buffered by a crushed limestone cap. Also, the high carbonate soils and groundwater at the PSA site promote the stability and durability of the cement/pozzolanic binders used to form the impermeable monolith. The PSA monolith will endure and protect the Miami water supply for many millennia.

1.6. Physical and Chemical Testing to Verify Performance

Existing handbook tests were insufficient to verify the monolith's expected performance, for several reasons. First, handbook tests only measure engineering properties that describe short-term performance rather than the very long-term strength and integrity that was the goal at the PSA site. Second, these tests are also material specific (i.e., metal, plastic, concrete) and do not address the specific cement/pozzolanic blends that were used at the PSA site. Finally, handbook tests do not consider the site-specific environment. Therefore, these handbook

[3] D. M. Roy, M. W. Grutzeck, and L. D. Wakely, *Selection and Durability of Seal Materials for Bedded Salt Repository: Preliminary Studies,* ONWI-479 prepared by the Materials Research Laboratory of the Pennsylvania State University, University Park, PA 16802, 1983.

tests alone could not be used without modification for evaluating long-term performance on pozzolans at the PSA site.

After modifying existing handbook tests to consider these factors, five classes of protocols were developed to verify performance of the monolith. These protocols addressed (1) the interactions between the binders and the waste constituents in site soils, (2) the process and emplacement characteristics, (3) the physical and mechanical stability of the monolith, (4) regulatory compliance, and (5) the determination of the in-situ leaching performance. The combination of these tests is summarized in Figure 6. This combination of tests assured complete chemical, physical, and mechanical compatibility with the soils, the process equipment, the emplacement method, and future land uses at the PSA site.

Whenever possible, slight variations of standard American Concrete Institute (ACI), American Society for Mechanical Engineers (ASME), EPA SW-846 methods, U.S. Army Corps of Engineers (USACE) standard engineering methods, and U.S. Nuclear Regulatory Commission (NRC) tests were applied. The formulations were tested at various points in the curing process.

Sometimes, these test protocols were modified to simulate more closely the PSA site conditions and the planned remedial operations. The testing protocols

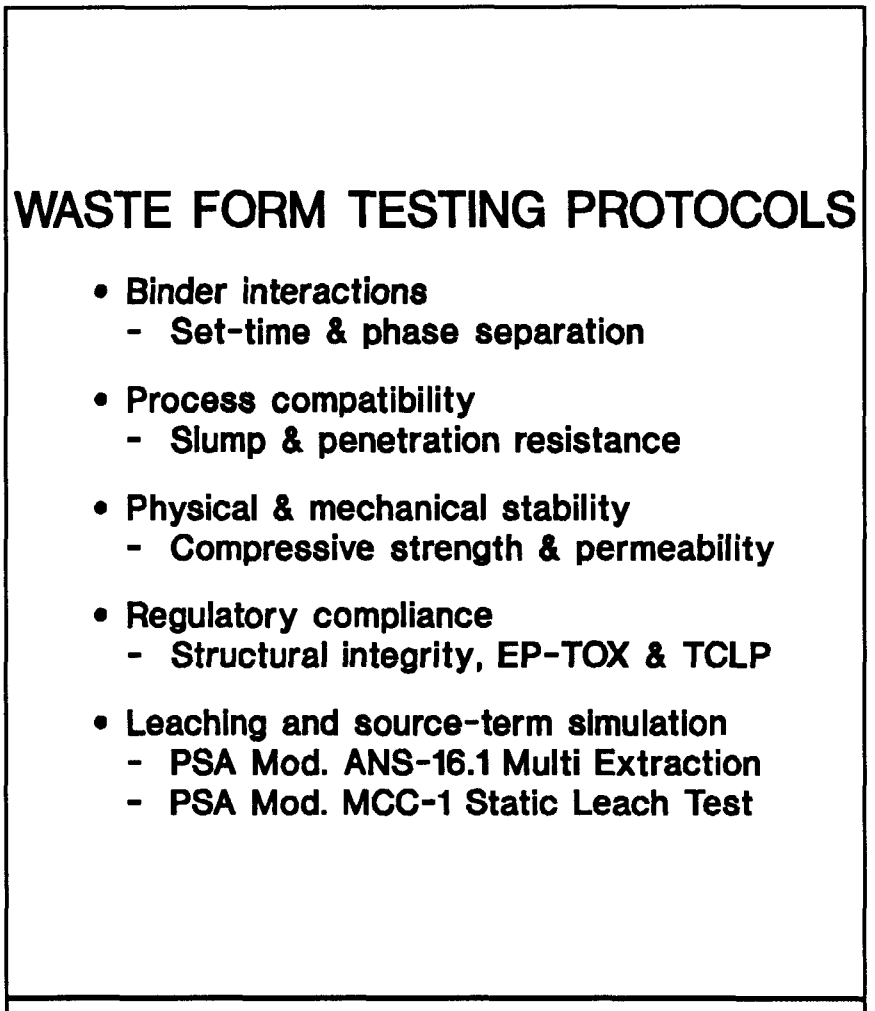

Figure 6 Protocols used to select grout formulas and to prove the performance of the monolith.

and the results underwent stringent peer review by US EPA Region IV and its consultants before the Enforcement Decision Document was issued that approved the planned remedial action. The results of this treatability study, previously provided to EPA, are summarized in Section 2.

2. Review of the PSA Treatability Study and Resulting Data

2.1. Introduction to the Treatability Study

Cleanup levels were established at the PSA site for lead (1,000 ppm), PCBs (10 ppm), and arsenic (5 ppm) only. The PSA pozzolanic mix was designed to retain other inorganic and organic waste constituents also present in the PSA site soils. The areas encompassed by these cleanup levels were established through a combination of coring and Kriging contours. This is a geostatistical method for defining iso-concentration lines and their associated confidence levels. When this method was applied at the site using the 95% confidence level, it identified approximately 62,000 cubic yards of contaminated soil. Subsequent site operations identified and treated 120,000 cubic yards.

The first step in the treatability study was to set up a soil collection plan which was developed and conducted under the direction of Dr. Benjamin Mason. Collected soil samples then were analyzed by Residual Management Technologies (RMT). After this phase of the treatability study was completed, the collected PSA samples were forwarded to Canonie Engineers to be used in the development of stabilization/solidification formulas.

The locations of the soil sample sites for PCB and metals analysis were selected because of the results of previous field investigations. The types of soils collected were (1) dry fill, (2) oily fill, and (3) oily peat. Table I describes representative analytic data from these three soil materials.

TABLE I - Summary of PSA Soil Data

% Solid	Dry Fill	Oily Fill	Oily Peat
Water	17.0	45.0	107.0
Oil and Grease	1.2	0.6	3.8
PCBs,* ppm	42.0	116.0	44.0
Lead, ppm	16980.0	1030.0	836.0
Arsenic,ppm	76.1	35.6	nd

*PCBs were Aroclor 1260

2.2. Treatability Study Tasks

Performance objectives[4] for the proposed in-situ monolith at PSA addressed (1) mixing and emplacement characteristics, (2) curing rates and the timely development of adequate physical properties, and (3) effective binding of waste constituents within the monolith. The program focused on developing a processable grout that had these properties: (1) no bleed-water after set, (2) a 72-hour set-time, (3) an

[4] L. R. Dole, "Overview of the Application of Cement Based Immobilization Technologies at US-DOE Facilities," Volume 2 of *Proceedings of Waste Management 85,* Editor Roy Post, Tucson, Arizona, pp. 455-563, March 1985.

unconfined compressive strength greater than 20.8 psi, and (4) a Darcy permeability of less than 10^{-6} Darcy (cm/s). A design compressive strength of 20.8 psi was chosen because it was adequate to support planned future construction activities on the monolith. Figure 4 (page 8) shows the overall development performance evaluation strategy of the PSA grout development program.

More broadly, the formula screening and treatability study tasks[5] included the following:

Task 1 Screening available materials from South Florida, based on their availability, cost, workability, and physical properties.

Task 2 Testing compressive strength, penetration resistance, and permeability.

Task 3 Testing for leaching and durability:

-Structural Integrity and EP-TOX (EPA SW-846)

-PSA Mod. MCC-1 Static Leach (US DOE-5820)

-PSA Mod. ANS 16.1 Dynamic (NRC 10 CFR 61)

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[5] "Remedial Alternative Fixation/Stabilization Work Plan," Florida Power & Light Company, P. O. Box 14000, Juno Beach, Florida 33408, March 1985.

2.3. Screening Studies

The completion of Task 1 was reported in the Interim Status Report,[6] and the results of the remaining tasks are reported in the Final Report. These studies selected the dry-solids blend summarized in Table II.

TABLE II - PSA Soil-Grout Formula Used To Form the In-Situ Monolith

Component	Weight	(Weight %)
1. Soil Solids	1,680	(55%)
2. Soil Water	340	(11%)
3. Cement, Portland-I	300	(10%)
4. ASTM Class F Ash	450	(15%)
5. Mix Water	260	(9%)

Solids Blend:Soil Ratio: 0.45
Volume Ratio of Fixed Soil: <1.1

2.4. Physical Testing

In the treatability study, the overnight penetration resistance and 28-day unconfined compressive strength of the soil-grout specimens were over 500 and 20.8 psi, respectively. These strengths are sufficient to allow traffic over and medium construction on the monolith.

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[6] L. R. Dole, "Interim Status Report: Fixation and Stabilization Remedial Action Alternative for the Pepper's Steel and Alloys Site located at Medley, Florida," Energex R85-003, Energex Associates, 575 Oak Ridge Turnpike, Oak Ridge, Tennessee 37830, July 1985.

Using a modified triaxial apparatus, the constant-head permeabilities on specimens of spiked dry-fill and oil-peat grouts cured for 28 days are summarized in Table III. These permeabilities are at least 1,000 to 100,000 times lower than the 10^{-2} to 10^{-4} permeabilities of the PSA site soils. Therefore, these grouts will be so impermeable relative to the site soils that groundwater or precipitation cannot percolate through these stabilized masses.[7]

TABLE III - Summary of Triaxial Permeability and Hydraulic Conductivity of PSA Soil Grouts

Soil Grout	Darcy Permeability (cm/s)	Hydraulic Conductivity (cm/s)
Dry Fill	1.6E-8	1.5E-11
Oily Peat	6.5E-8	6.2E-11

2.5. Leaching Tests

Two series of leach-test specimens were prepared with spiked PSA soils (see Appendices A and B). A composite PSA soil sample was prepared from known areas of high heavy-metal concentration. The soils were spiked with oil collected at the PSA site in the summer of 1983 to raise their oil content to 10 percent. Other oils containing Aroclor 1260 were also

[7] A. Atkinson, "The Influence of Waste Form Permeability on the Release of Radionuclides from a Repository," *Nuclear and Chemical Waste Management*, Vol. 5, pp. 203-214, 1985.

added. The resulting soil sample had a PCB concentration of 216 ppm. Some sample characteristics of the spiked soils are shown in Table IV.

TABLE IV - Parameters Of Interest in the Spiked PSA Soils Used in the Treatability, Grout Development, and Leaching Studies

Water	**15.6%**
Oil & Grease	**10.0%**
PCBs*	**490 ppm**
Lead	**31,490 ppm**

***PCBs are Aroclor 1260**

Two series of right-circular leach specimens were prepared from the spiked soil for use in the PCB and heavy-metal leaching tests. These specimens had surface areas of 100 cm^2 and 30 cm^2, respectively. The specimens were leached in PSA groundwater by the Modified MCC-1 and ANS 16.1 methods (see Appendices A and B). Also, the 40 CFR 261 structural-integrity and EP-TOX (Extraction Procedure-Toxicity) tests were applied, and they both passed by wide margins. Both the Modified MCC-1 and ANS 16.1 methods (Appendices A and B) can measure an effective diffusion coefficient (D_e, cm^2/s) that conser-

vatively estimates the maximum credible release rates of waste constituents from the monolith.[8]

The concentration of the waste constituent in the monolith specimen, the leachate, and the leach time are used to decide the D_e (summarized in Table V) for the soil grout used in the PSA monolith.

TABLE V - The Leach Indices (LI) and Effective Diffusion Coefficients of Metals and PCBs From Short-Term Tests on the PSA Soil Grout

ANS 16.1 Leachability Indices Soil Grouts

Element	Leach Index LOG [D_e]	Coefficient D_e (cm^2/s)
Arsenic	15.9	1.26×10^{-16}
Barium	>13.0	$<1.00 \times 10^{-13}$
Cadmium	>11.9	$<1.26 \times 10^{-12}$
Chromium	>12.8	$<1.58 \times 10^{-13}$
Lead	13.5	3.16×10^{-14}
Mercury	>9.2	$<6.31 \times 10^{-10}$
Selenium	>9.8	$<1.58 \times 10^{-10}$
Silver	>8.4	$<3.98 \times 10^{-9}$
PCBs*	>14.0	$<1.00 \times 10^{-14}$

*PCBs were Aroclor 1260

[8] T. M. Gilliam, L. R. Dole, and E. W. McDaniel, "Waste Immobilization in Cement-Based Grouts," *Hazardous Solid Waste Testing and Disposal: Sixth Volume,* ASTM STP 933, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket, and W. J. Stacy, Eds., American Society for Testing Materials, Philadelphia, PA, pp. 295-307, 1986.

Barium, cadmium, chromium, mercury, selenium, silver, and PCBs were below the detectable limits after 28 days of leaching on these small cured specimens. Therefore, the diffusion coefficients were calculated based on the detection limit to establish a worst-case D_e. In fact, the D_e overstated the actual diffusion coefficients for these waste constituents.

The PSA soil fixation blend development and testing program successfully identified a formula to fix the waste constituents at the PSA site. The formula achieved the goals of the fixation/stabilization work plan. Using materials available in South Florida, an initial blend of 60/40 fly-ash/cement was selected based on its engineering properties of cost, mixability, set time, compressive strength, and permeability.

2.6. Monolith Performance

The leach test results were used in a conservative computer model based on the following general equation for diffusion from an semi-infinite solid body. There it was easily demonstrated that the monolith's in-situ performance would be effective to meet all goals of the remediation. This model always predicts the conservative upper-bound release:

Equation 1: Conservative General Equation for Diffusion from a Semi-Infinite Solid Body

Model

$$F_i = 2 \cdot \frac{S}{V} \cdot \sqrt{D_e \cdot \frac{t_i}{\pi}}$$

Where:

F = Cumulative Fraction Released of i

S = Specimen Surface Area

V = Specimen Volume

De = Diffusion Coefficient of i

t = Time of Leaching Interval

Based on Equation 1 and the effective-diffusion coefficients (D_e) in Table V, Figure 7 shows the integrated leach fraction of the lead, PCB, and arsenic present in the PSA monolith that could be released over 2,400 years.

The fractional releases predicted from the leach test results were derived from the Source-Term Model (STM) presented in Appendix C. This model considers the worst-case hydrology for an isolated panel of the PSA monolith. This panel is 300-feet long and 20-feet wide, with a depth of 8 feet. The model assumes that the entire monolith is immersed in moving groundwater and that its longitudinal axis is oriented in the direction of the hydrologic gradient. This configuration minimizes the dilution of released

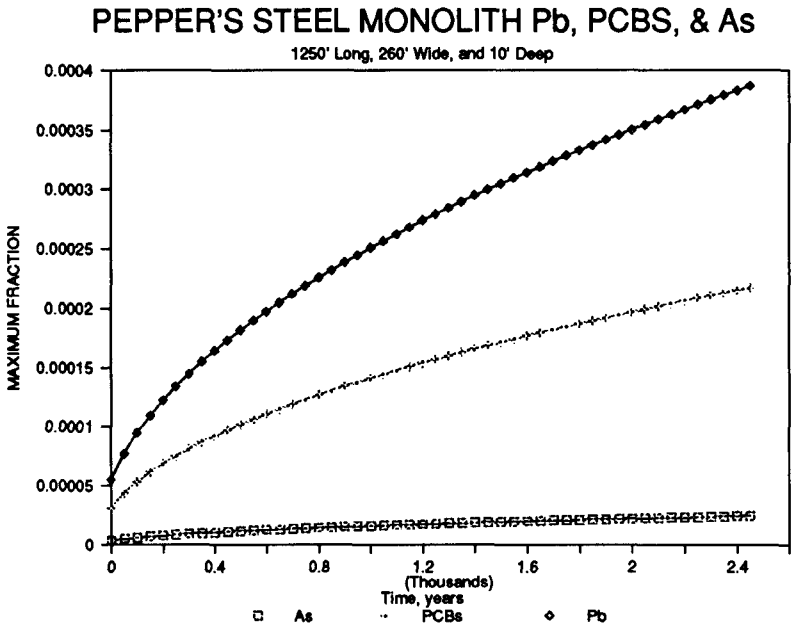

Figure 7 Using Equation 1 and the diffusion coefficients from Table V, the maximum credible integrated or cumulative release fractions are calculated for 2,400 years.

waste constituents by groundwater and maximizes the calculated waste constituent concentrations.

The model also counts only one-half the dilution expected from the effects of local precipitation. South Florida's average rain fall of 60 inches per year in the model was reduced by subtracting 30 inches per year for evapotranspiration.

The STM also purposely does not count rainfall falling beyond 5 feet of the monolith boundaries. Therefore, the potential dilution factor for rain falling on adjacent areas is understated.

The model assumes that the entire surface of the monolith is exposed. Yet, the crushed limestone cap that covers the monolith already has formed a solidified mass that has sealed the upper surface of the monolith.[9] The model ignores occlusion at the points of contact with the soil or cap material and over-predicts the surface available for mass transport.

Significantly, the model also assumes that the 28-day diffusion rates do not change, however, in fact, the pozzolanic material continues to develop binder phases that further reduce the diffusion potential over time. The combination of these conservative assumptions in the Appendix C Source-Term Model probably overestimates the release of waste constituents by 25 to 120 times.

Using the STM, the small fractional releases from Figure 7 were integrated into the PSA site hydrology and annual tropical rainfall for the first 1,000 years[10] (Appendix C). The resulting maximum credible average groundwater concentrations of lead (Pb), PCBs, and arsenic (As) using this very conservative model are summarized in Table VI.

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[9] See "Evaluation of Drainage Structure, Pepper's Steel and Alloys Site, Medley, Florida," Canonie Environmental, December 1988, which appears elsewhere in the Final Report.

[10] L. R. Dole, "Leach Testing on In-Situ Immobilized Soils Contaminated with PCBs and Lead," *Papers Presented at the 194th National Meeting of the American Chemical Society Symposium on Leach Testing for Radioactive and Chemically Hazardous Waste: Mass Transport and Chemical Reactions,* New Orleans, Louisiana, p. 283, August 30-September 4, 1987.

TABLE VI - Maximum Credible Concentrations Over the First 1,000 Years, Using the Conservative Model in Appendix C

Element	Concentration, ppm
Lead (Pb)	0.001
PCBs	0.0004
Arsenic (As)	0.00005

In these leach tests, the diffusion coefficients and leach rates for the waste constituents were extremely low. In fact, even when the monolith is dug up and crushed, the soil-grout's performance would not be impaired. Appendix D presents the modeling of 8,000-year releases of PCBs or lead from small pieces of PSA monolith between 8 feet and 1/8 inch in diameter. These results show that a piece of crushed grout the size of a pencil eraser will take over 4,000 years to release 83 percent of these waste constituents, even under the conservative assumptions used in the model.

3. New Data Taken on Archived Samples of PSA Grout

3.1. Background

During the PSA site operations, both quality control (QC) and quality assurance (QA) samples were taken periodically by Dr. Benjamin Mason or Dan Giffin (GeoTrans). The process control parameters routinely measured were the slump and UCSs (unconfined compressive strengths). Twice or more daily, QC samples were taken from random batches processed in the two high-shear grout mixing machines used during the PSA site remediation. These measurements and results are reported in the PSA Quality Assurance/Quality Control Report by Dr. Benjamin Mason. They appear in Section Three of the Final Report.

Besides the routine daily QC samples, randomly selected duplicate QA samples were also taken and submitted to a referee laboratory. Independent slump measurements were taken on these QA samples by Mason or GeoTrans. Using these QA samples, the referee laboratory, Wastech, Inc., verified the UCS measurements recorded by the laboratory performing UCS testing on site QC samples. Wastech, Inc. also measured the permeability and the PSA Modified Leach indices (Appendix A) of lead, arsenic, and PCBs on QA samples. These QA and QC measurements are discussed by

Mason in his report. They confirm that the product produced at the PSA site met or exceeded design criteria for the PSA monolith.

3.2. Archived Development Study and QA Samples

The additional QA samples taken by Mason and Giffin were archived by Wastech, Inc. These samples were stored under 100% relative humidity (RH) at room temperature until the site operations were concluded. At the completion of the on-site operations, these samples were 300 to 600 days old. They have since been analyzed for their strength and permeability, and the results are discussed in Section 3.3 and Section 3.4.

Samples retained from the development study conducted in July 1985 were also archived by RMT, which had done the original leach studies. These archived samples had been immersed in PSA groundwater since August 1985. The leachate solutions were analyzed in February 1989. The results, which are also discussed in Section 3.5, show the performance of the PSA grouts after more than 3 years of immersion.

3.3. Unconfined Compressive Strength Measurements on Archived QA Samples from PSA On-Site Operations

Appendix E reports the results of the UCS measurements conducted by Wastech on archived QA samples taken during field operations. The first table in Appendix E compares the 7-day, 28-day, and the 300- to 600-day strengths. Figures 8 through 10 illustrate the development of compressive strengths with time.

The y-axis in Figures 8 through 10 represents UCS. The scale on the y-axis in these figures had to be adjusted graphically to fit the increase in UCS as the

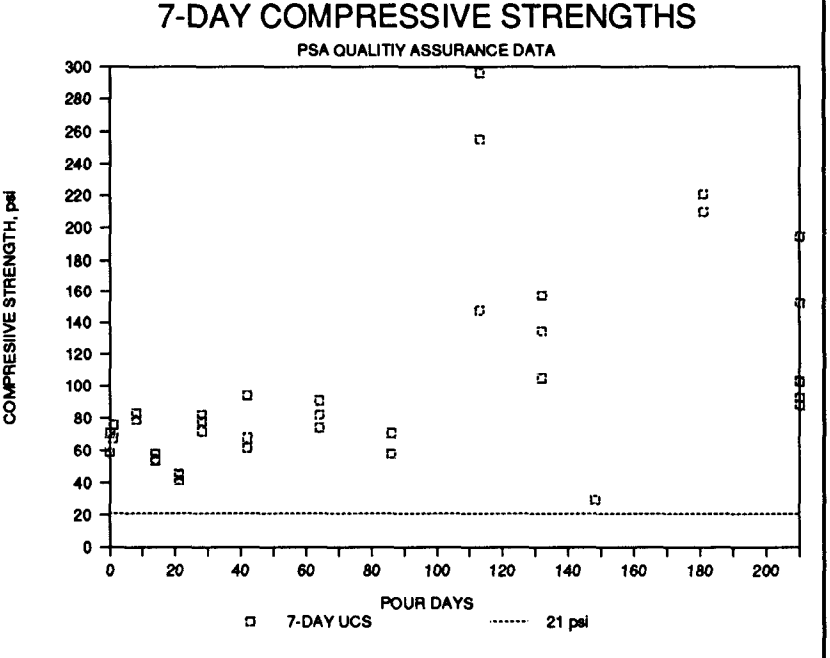

Figure 8 UCSs of archived samples after 7 days of curing.

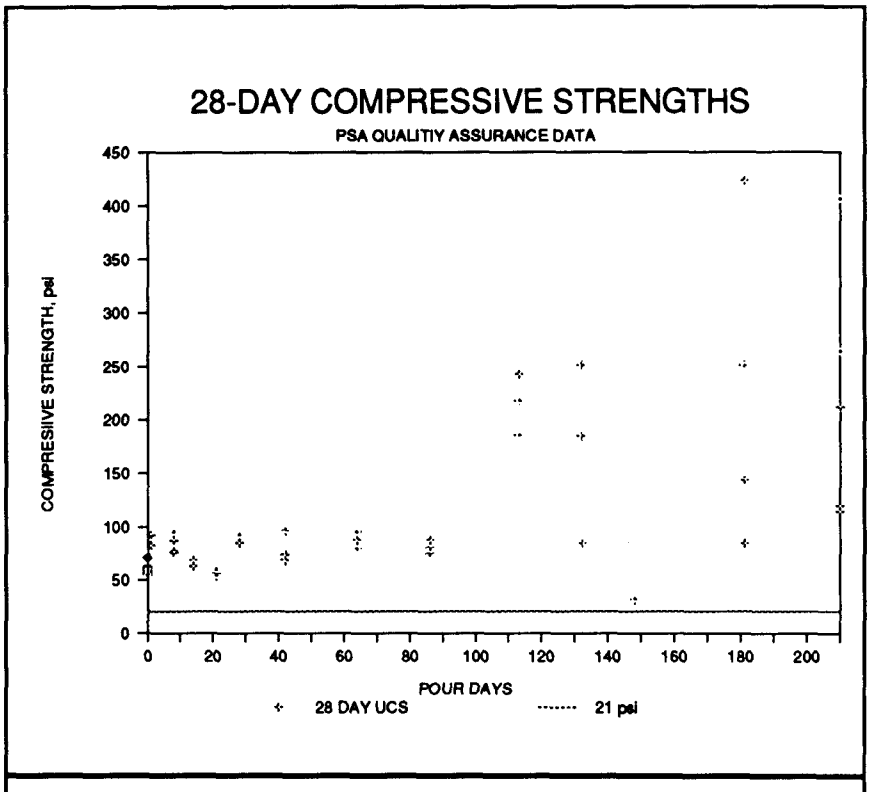

Figure 9 UCSs of archived samples after 28 days of curing.

archived samples aged (see Appendix E). The design basis strength of 20.8 psi is marked with a horizontal line in each figure. As discussed previously, this UCS was chosen because it was adequate to support medium construction such as dock-level warehousing. The x-axis, labeled "pour days," represents the date during the project that the sample was collected.

From the QA sample UCS testing, even the 7-day UCSs (Figure 8) met the design criteria. This study was conducted at laboratory room temperature. Because the PSA site is in a tropical climate, these early strengths are higher than were predicted by the development study. In the warm weather of South

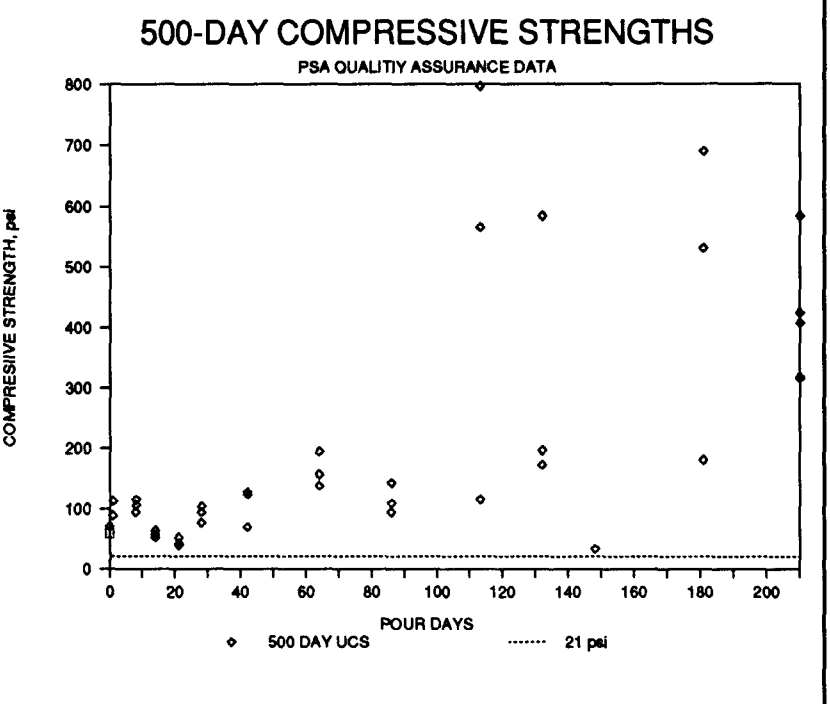

Figure 10 UCSs of 300- to 600-day old archived samples.

Florida, the high temperatures (90 to 120° F) of the raw materials used in the mixture accelerated the curing reactions of the cement and pozzolans. Also, the actual field mixtures were set at an approximately 10 percent higher cement/pozzolan-to-soil ratio than the laboratory ratio to ensure that the final product exceeded the grout design specifications

In addition, the dry-solid feeds for the cement and pozzolan in the soil processing equipment were metered with a lead-lag controller that tracked the soil feed. The cement and fly ash feeds came up faster and shut off slower than the soil feed to ensure that no untreated soil could get through the mixers. Fluc-

tuations in the soil feed—for example, because of clumping or debris—reduced the amount of soils flowing into the plant mixer. Under these circumstances, higher binder-to-soil ratios resulted.

During operations, fixed materials from cleaning equipment, truck wash areas, or other sources had to be reprocessed. Reprocessed material had a greater UCS. These factors would help to explain the upward skew in the distribution of compressive strengths shown in Figures 8 through 10.

The curing of the PSA grout has continued long after 28 days. As Appendix E shows, UCS increases slowly with the age of the archived samples. The excess pozzolan in the formula will continue to react for many hundreds of years, ensuring that the monolith will be mechanically stable for millennia.

Figures 11 and 12 show the relationship between slump (workability) and UCS from the QA archived samples. The water content of the grout mixes was lowered to make blends with slumps that were lower than the initial design basis mix. The initial design slump was for 4-inch to 6-inch workabilities. In the field, stiffer mixes (i.e., lower slumps, lower workability) of 1-inch to 3-inch were preferred to reduce the loss of grout while it was transported by dump-trucks to the excavated trenches. This water reduction resulted in higher UCSs than the original design-basis PSA grout. Again, the physical proper-

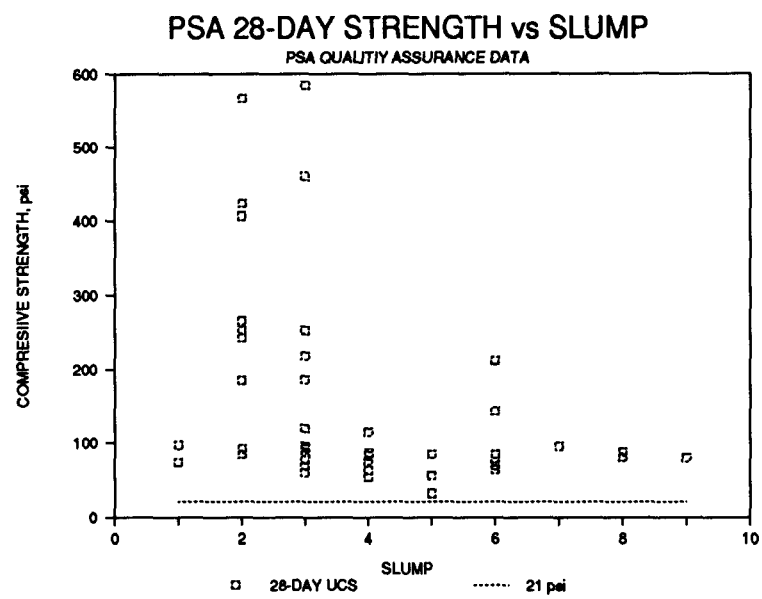

Figure 11 The 28-day UCSs as a function of slump, which is a measure of the soil-grout's workability.

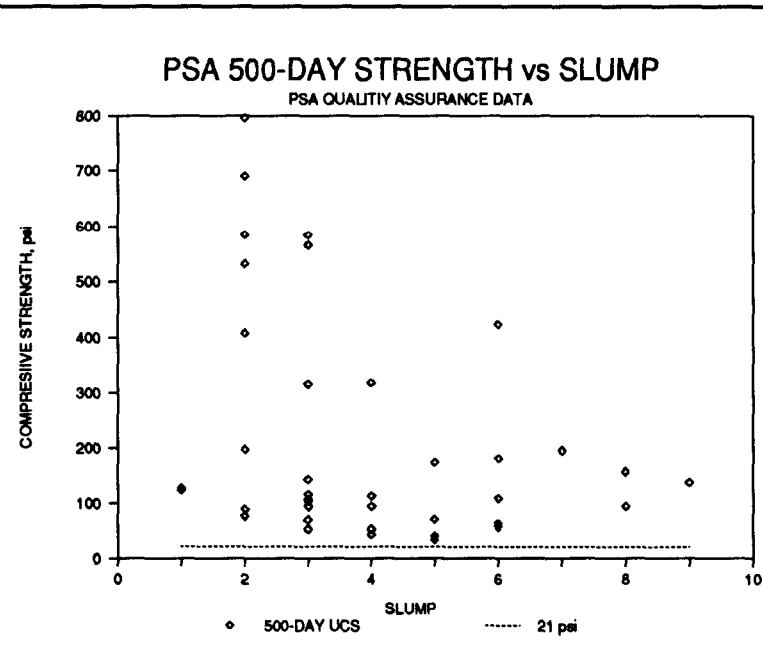

Figure 12 The 300- to 500-day UCS of archived samples as a function of slump, which is a measure of the soil-grout's workability.

ties of the "as-built" PSA monolith exceeded all design requirements.

3.4. Permeability Measurements on Archived QA Samples

The design requirement for the PSA soil grout was that the monolith be two orders of magnitude (100 times) less permeable than the host soil to ensure that rain or groundwater could not percolate through the monolith. The soils at the PSA site range from coarse sands with a Darcy permeability of 10^{-2} cm/s to fine "sugar" sands with a permeability 10^{-4} cm/s. In a monolith with a Darcy permeability of 10^{-6} cm/s, there is no advection through the treated waste. The release of waste constituents is then diffusion controlled.

Two permeability samples were archived as a QA measure. The two samples were formed on the PSA site on April 21, 1987, and were tested on February 22, 1989, 673 days later. The results of their permeability measurements are reported in Appendix F. Table VII compares these results.

TABLE VII - This Comparison Of Permeability With Age Confirms That Permeability Drops Significantly With Long-Term (>100 Days) Curing

7-Day Average	28-Day Average	500-Day Two Samples
3.6×10^{-6}	2.0×10^{-6}	7.0×10^{-7} 9.7×10^{-9}

The first sample (8940HL1-4) actually had been broken and was pieced together in the triaxial cell before the permeability test. Still, despite having been broken, this first sample had a permeability of 7.0×10^{-7} cm/s after two years of curing. The second sample (8940HL1-5) had pieces of battery casing and spacers at its surface. Permeability can be affected by surface roughness or defects. However, the second sample had a permeability of 9.7×10^{-9} cm/s after two years of curing. These are remarkably low permeabilities. These data show that the PSA monolith matrix is 1,000 to 100,000 times less permeable than the host soils at the PSA site, exceeding the design criteria for the PSA soil-grout mixture.

The long-term, slow pozzolanic reactions in the PSA monolith continue to reduce the permeability of the grout after emplacement. After a few hundred days, the permeability typically drops by at least an order

of magnitude from that measured at 28 days. This phenomenon is well documented.[11] The continuing pozzolanic reactions mean that the phases making up the bulk of the monolith will become more dense and impermeable over hundreds of days of aging.

The effective diffusion coefficients that were measured after only 28 days of curing have also dropped with the densification of the monolith's matrix. Because all the site release modeling discussed in Section 2 was done using these 28-day diffusion coefficients, all the subsequent predictions of waste constituent release are extremely conservative over-estimates. The actual maximum concentrations will be much lower than those predicted in Table VI and Appendices C and D.

3.5. Three-Year PSA Modified MCC-1 Leaching and Immersion Results on Archived Samples from the Original Treatability Study

On September 18, 1985, after a 28-day cure, RMT began static leach tests on samples from the original treatability study using PSA groundwater. These samples (Table VIII) have remained immersed in the PSA groundwater in the RMT laboratory since this original leach testing work was begun. RMT analyzed

[11] R. W. Crawford et. al., "Diffusion Mechanisms and Factors Affecting Leaching of Caesium-134 from Cement-Based Waste Matrices," *Radioactive Waste Management and the Nuclear Fuel Cycle,* Vol. 6(2), pp. 177-196, June 1985.

the leachates on February 28, 1989. The results of these analyses are reported in Appendix G.

TABLE VIII—Identification of Archived PSA Soil-Grout Samples Used for PSA Mod. MCC-1 Static Leach Tests After 1269 Days

Sample	RMT #	Description
308	12732-B(3)	Peat and 10% Oil
314	12733-B(2)	Dry-Fill Blank
337	12732-B(5)	Peat and 10% Oil
342	12731-A(17)	Dry-Fill and 10% Oil
366		Site Groundwater Blank
406	12731-A(16)	Dry-Fill and 10% Oil
410	12732-B(4)	Peat and 10% Oil

These leach tests ran for 1269 days (3.45 years). RMT photographed these specimens after removing them from the leachate. Figure 13 shows the condition of leach specimens after nearly 3.5 years of immersion in PSA groundwater.

All the samples were intact after 1269 days in the PSA groundwater. The only apparent damage to these specimens was chipping at the corners. This occurred during the handling of the leach vessels when they were moved to and from storage because samples swung against the wall of the teflon leach vessels, causing the corners to be chipped in a few places. Otherwise, the samples were physically unaffected by this long-term immersion.

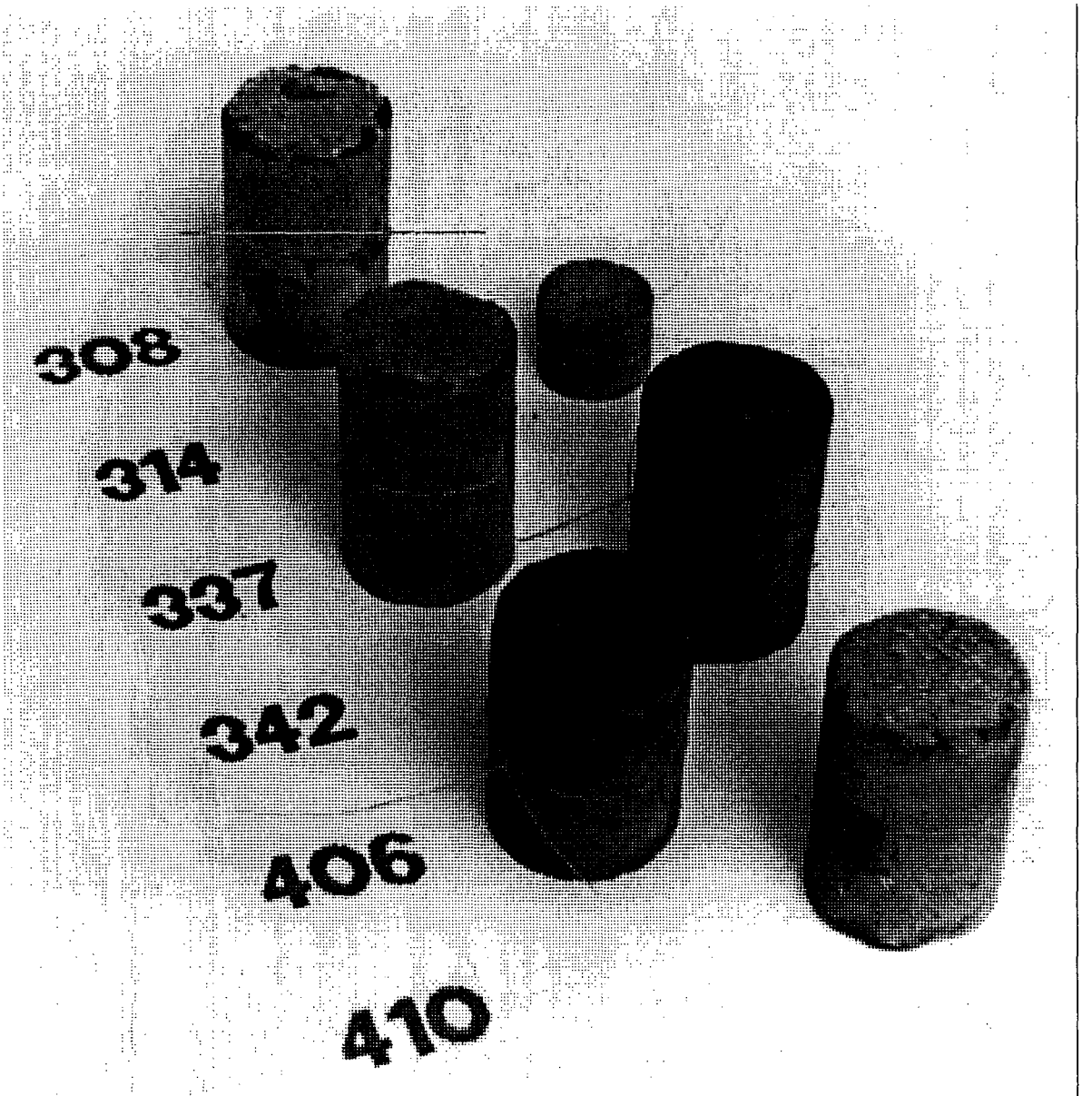

Figure 13 Photograph of PSA soil-grout after 3.45 years of immersion in PSA groundwater.

Table IX summarizes the PCB analyses of these long-term tests. After 3.45 years in a small closed volume, only the "spiked" peat samples showed any measurable concentration of Aroclor 1260 (PCB) in the leachate. When originally prepared for testing in 1985, the spiked soil-grout specimens contained

15,043 and 6,521 micrograms of PCBs for the fill and peat samples, respectively. In 3.45 years, only 0.2 to 0.44 micrograms (including plateout absorbed on the walls of the teflon leach vessels) leached out of these small specimens. These specimens had a large surface-to-volume ratio (1.4 cm^{-1}). Therefore, the fractional releases from these specimens were 6.1 x 10^{-5} to 1.3 x 10^{-5} mass fractions of Aroclor 1260 (PCBs). Considering the large surface to volume ratio, this loss is infinitesimal.

TABLE IX—Summary of PCB Analysis of 1269 Day PSA Mod. MCC-1 Leach Tests

Sample Number	Description	Leachate (ppb)	Plateout (micro g)	Total (micro g)
334	Site water	<0.2	nm	<0.2
314	Dry-fill blank	<0.2	nm	<0.2
342	Spiked dry-fill	<0.2	0.5	0.5
406	Spiked dry-fill	<0.2	nm	0.2
308	Spiked peat	0.2	0.04	0.24
337	Spiked peat	0.2	nm	0.2
410	Spiked peat	0.4	0.04	0.44

nm = not measured

Appendix H shows the diffusion model for a 1.5-inch diameter by 2.5-inch high specimen. Using the conservative assumptions discussed in Section 2, the model predicts that the upper bound of the fractional release after 3.5 years could be 1.6 x 10^{-3} mass fractions. This upper bound is depicted in Figure 14. The diffusion model predicted a fractional release that is 25 to 120 times higher than the 6.1 x 10^{-5} to 1.3 x 10^{-5}

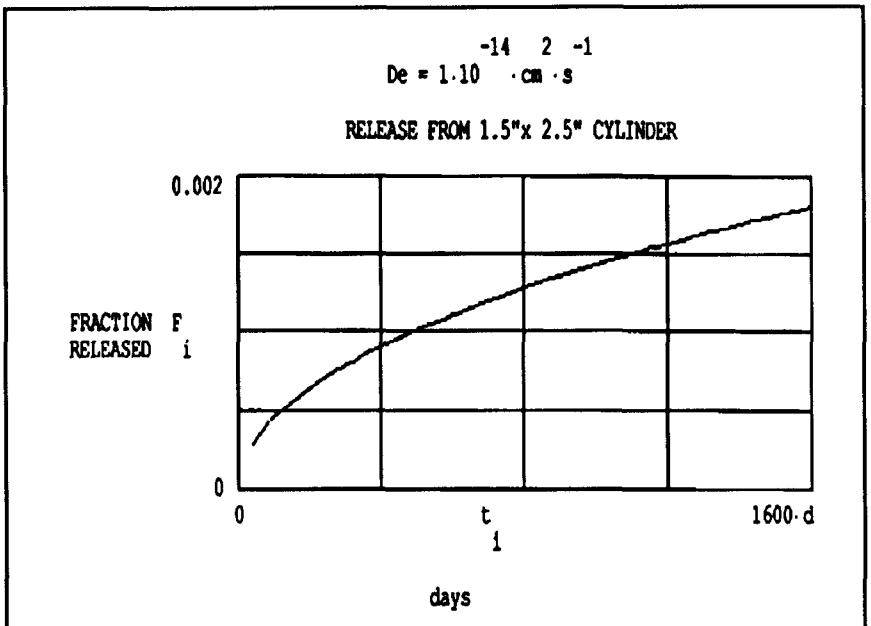

Figure 14 Results of the model for the maximum release of PCBs from a 1.5-inch diameter by 2.5-inch high soil-grout cylinder based on 28-day diffusion coefficients (See Appendix H).

mass fractions that were actually measured in the 3.5-year PSA Modified MCC-1 tests.

Therefore, the predicted performance of the monolith based on the short-term (28-day) leach test results significantly understates the actual performance of the monolith matrix shown by these long-term leach tests. Additionally, the original diffusion coefficients that guided the selection of the grout mixture were based on the 28-day leach test results. In view of the extraordinarily low fractional releases from the spiked samples in this long-term test, the PSA monolith has effective diffusion coefficients for PCBs that are over 100 to 10,000 times lower than the original estimates.

Table X gives the results for the 1269-days leachates. Here, the detection limit for the laboratory was 0.001 ppm. After 28 days, the leachates from the spiked peat samples had lead concentrations of 0.027 to 0.81 ppm, and the leachates from the spiked fill had concentrations of 0.036 to 0.077 ppm. After 1269 days, the lead levels were 0.006 to 0.098 for the spiked peat, and 0.015 to 0.19 for the spiked fill. These ranges overlap; thus, no indication is made that significant further release of lead occurred after the first 28 days. In these static MCC-1 leaching tests, the lead concentrations are controlled by the solubility or equilibrium ion exchange reaction with one or more of the phases that form during the curing of the soil-grout specimen.

TABLE X—Summary Of Pb Analyses Of 1269 Day PSA Mod. MCC-1 Leach Tests

Sample Number	Description	Leachate (ppm*)	Plateout (mg)	Total (mg)
334	Site water	0.004	nm	0.004
314	Dry-fill blank	0.034	nm	0.034
342	Spiked dry-fill	0.019	nm	0.019
342A		0.015		
406	Spiked dry-fill	1.1	0.7	1.8
406A		0.82		
308	Spiked peat	0.054	nm	0.054
337	Spiked peat	0.006	<0.1**	0.006
337A		0.015		0.015
410	Spiked peat	0.098	nm	0.098

nm = not measured

* = measured with AA graphite furnace

** = detection limit with ICP

For the dry fill with a De of 3.14 x 10^{-14} cm^2/s, the predicted fractional release from the 1.5-in. diameter by 2.4-in. high cylinder would be 0.002 cumulative mass fractions. This small cylinder started with about 128,000 micrograms of lead and lost only 15 to 19 micrograms in 1269 days. The fractions of lead lost were 1.2 x 10^{-4} to 1.5 x 10^{-4} fractions. This is 15 to 19 times less than predicted by the conservative diffusion model used in Appendices C and D.

One set of lead analyses on spiked dry-fill sample No. 406 showed higher lead concentrations of 0.82 to 1.1 ppm. Sample No. 406 is a duplicate of sample No. 342. The leach results from sample No. 406 for lead are inconsistent with the lead analyses for the duplicate

MCC-1 test sample No. 342 that had lead concentrations between 0.006 to 0.054 ppm. The results on sample No. 406 are also at odds with all other data on lead leaching, including the initial leach study and the two studies on the archived samples. Therefore, this leachate sample was probably contaminated during the filtration step (see Appendix A). With such a high-lead soil-grout concentration (32,000 ppm), a microscopic piece of grout specimen could produce this anomalous result. A high-lead grout particle probably bypassed the filter and caused a "flyer" in the leachate lead analysis.

As with the PCB results, this evidence confirms that the binder phases in the PSA monolith have a phenomenal capacity to limit the diffusion and solubility of the immobilized lead ions. This result is consistent with the performance seen in ancient pozzolans[12] that are similar to those used in the PSA monolith. Such pozzolans have held their trace-metal "finger prints" for millennia in cisterns and aqueducts.[13]

Table XI gives the results for the arsenic analyses of the leachates from the 1269-day PSA Modified MCC-

[12] D. M. Roy and C. A. Langton, *Characterization of Cement-Based Ancient Building Materials in Support of the Repository Seal Materials Studies,* ONWI-523, Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201-2693, December 1983.

[13] D. M. Roy, M. W. Grutzeck, and L. D. Wakely, *Selection and Durability of Seal Materials for Bedded Salt Repository: Preliminary Studies,* ONWI-30, Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201-2693, 1983.

1 static leach tests. After 28 days, the original study[4] measured arsenic concentrations of 0.003 to 0.008 ppm for the peat specimens and 0.004 to 0.037 ppm for the dry-fill specimens. The long-term study measured 0.005 to 0.015 ppm for the peat and 0.02 to 0.03 ppm for the dry fill specimens.

TABLE XI—Summary Of As Analyses Of 1269 Day PSA Mod. MCC-1 Leach Tests

Sample Number	Description	Leachate (ppm)	Plateout (mg)	Total (mg)
334	Site water	<0.003	nm	<0.003
314	Dry-fill blank	0.006	nm	0.006
342	Spiked dry-fill	0.029	nm	0.029
406	Spiked dry-fill	0.021	<0.003	0.021
308	Spiked peat	0.005	nm	0.005
337	Spiked peat	0.005	<0.003	0.005
410	Spiked peat	0.015	nm	0.015

nm = not measured

These changes in arsenic concentrations over 1200 days are not statistically different from the original results after 28 days. In such a static leaching system, these results mean that (1) the system reached an equilibrium concentration in the early stages after immersion, and (2) additional arsenic releases have not occurred. This equilibrium concentration for arsenic is probably controlled by the solubility of

mineral phases within the monolith matrix that capture the arsenic or by the partitioning of arsenic between the leachate and an ion-exchange mineral within the monolith matrix. Equilibrium conditions likely exist or will occur for all the waste constituents in the PSA monolith.

The diffusion model used to calculate the maximum concentrations in Table VI in Section 2.5 and the fractional releases seen in Appendices C, D, H, and I purposely ignores the existence of equilibrium in a static groundwater environment. This is another reason this model overstates potential release rates from the PSA monolith.

3.6. Conclusions

The results of these long-term measurements on the QA and original treatability archived samples establish two important conclusions. First, the "as-built" PSA monolith exceeds the physical design requirements that were set in the development study. Second, the long-term permeability and leaching results were significantly better than the results on which the remedy was designed and approved (which served as the basis for modeling the predicted monolith performance). Actual monolith performance is significantly greater than was established in remedial design.

4. PSA Monolith Matrix Reactions in Relation to Maintenance and Future Land Uses

4.1. Introduction

The outstanding results of the long-term physical and leach testing discussed in Section 3 were expected. These results confirm that the capacity of the cement-based PSA pozzolanic matrix to immobilize waste constituents increases with the passage of time. This long-term reaction is characteristic of ancient plasters and pozzolans[14] and, of course, served as the premise used in the development and selection of the solidification and stabilization remedy. Section 4 explains (1) why the PSA monolith binds waste constituents so effectively for millennia without maintenance and (2) why the monolith will support construction activity or other positive land uses without restriction.

4.2. Monolith Matrix Reactions

Figure 15 shows the normal reaction of cement paste without additives. For cement paste, these reactions are 80 to 90 percent complete between 30 and 90 days under normal curing conditions. In this curing process, the waste form (the mixture of binder

[14] J. Ragai, "Surface and Bulk Properties of Ancient Egyptian Mortars, Part III: X-Ray Diffraction Studies (b)," *Cement and Concrete Research,* Vol. 18, pp. 9-17, 1988.

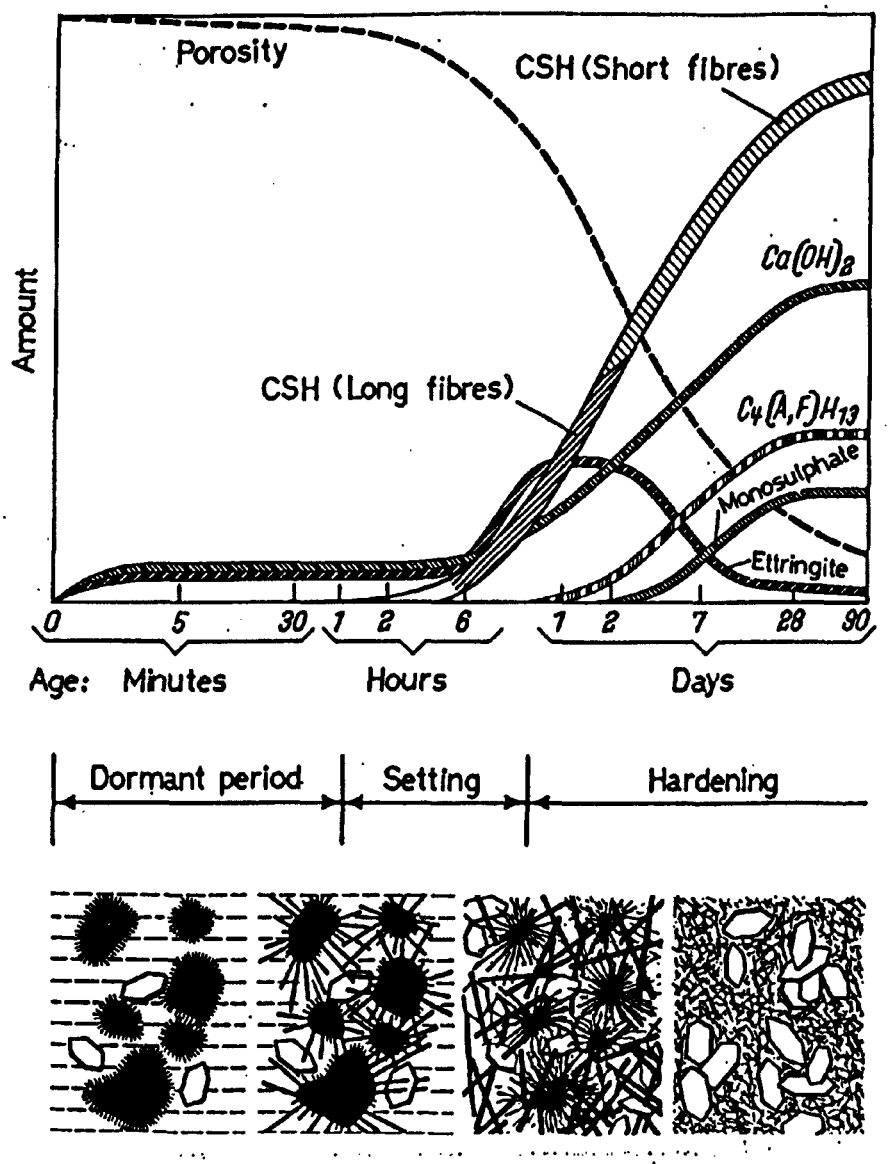

Figure 15 Early hydration reactions and structural developments in cement pastes (Source: I. Soroka).

material and soils) starts out as colloidal paste. While setting, it goes through a transition into a contiguous solid body. The mass initially is very porous. Then the fibers of calcium hydrosilicates (see the progression in the panels of Figure 15) grow together, locking the mass into a mechanically ridged structure. Over 7 to

90 days, the mass hardens into a more impermeable matrix as the binder phases become more dense (i.e., the interstices between the soil and cement particles become filled with calcium hydrosilicates).

Normal cement reactions produce calcium hydroxide [$Ca(OH)_2$] crystals as a reaction product.[15] These crystals are the hexagonal ones shown in the last panel in Figure 15. In simple cements, the calcium hydroxide phase is the most soluble phase in the solid matrix when exposed to water. When the calcium hydroxide becomes soluble, it opens the internal structure of the matrix, making it more porous. This is one reason simple cements are not effective binders of waste constituents over long periods of time.

Pozzolan additives suppress the formation of calcium hydroxides and result in denser calcium silicate hydrogels (CSH). The calcium hydroxide slowly reacts with the pozzolanic additives to form CSH,[16] which makes the matrix effective in retaining waste constituents despite long-term immersion in groundwater or exposure to rainfall.

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[15] I. Soroka, *Portland Cement Paste and Concrete,* Chemical Publishing Company, Inc., 121 Fifth Avenue, New York, NY, p. 35, 1980.

[16] L. R. Dole, "Overview of the Application of Cement-Based Immobilization Technologies Developed at U. S. DOE Facilities," *Proceedings of the Symposium on Waste Management,* Tucson, Arizona, March 24-28, 1985, Ed. Roy Post, pp. 455-463.

Pozzolanic reactions are slow. This slowness is a great advantage in forming large monoliths because pozzolans retard "hot" cement reactions. The initial cement reactions in a monolith are very exothermic[17] (100 to 200 calories per gram). The pozzolans dilute and retard the "hot" cement reactions, thus allowing very large monoliths to be cast without concern for excessive heating, which would be followed by cooling and shrinkage. Therefore, the presence of the pozzolan additives avoids steam explosions and cracking of the monolithic masses.

Because the pozzolanic reactions are slow, the monolith matrix fully develops its final characteristics of high strength, low permeability, and infinitesimal diffusion coefficients well beyond the civil engineering standard curing reference of 28 days. That is why the 28-day tests used in the PSA matrix development study are conservative. They were performed on partially cured specimens that had not even come close to completing the final matrix-forming reactions.

4.3. Control of Release Mechanisms

The test results in Section 3 show the relationship between age, strength, permeability, and leachability of monolith matrix samples using spiked PSA soils

[17] W. Czernin, *Cement Chemistry and Physics for Civil Engineers,* Chemical Publishing Company, Inc., 121 Fifth Avenue, New York, NY, p. 80, 1962.

along with QA samples prepared during the remediation. Those results proved that—over time—the PSA monolith grew stronger, became less permeable, had lower release rates, and exceeded the performance requirements of the remedy. An understanding of the relationship between permeability, leachability, and age requires a discussion of (1) concepts of release mechanisms from a multi-phased monolith matrix such as the one that exists at the PSA site, and (2) the relationship of those mechanisms to the calculation of D_e.

Figure 16 presents the serial and parallel leaching mechanisms that could occur in a monolith matrix. In a general sense, a diffusion coefficient, or diffusivity, is a statistical entity describing the shift in random molecular movement relative to a concentration gradient within a fluid or solid. The effective diffusion coefficient (D_e) numerically summarizes these release mechanisms, thus allowing one to describe the leaching potential of the monolith matrix. A smaller D_e means a lower release potential for a matrix.

Equation 2[18] describes the effective diffusion coefficient as a function of the interactions with the phases of a monolith is as follows:

[18] H. W. Godbee and D. S. Joy, "Appendix B: Solution of Mass Transport Relations for the Case of Diffusion and Instant Development of Cementitious Grouts for the Incorporation of Radioactive Wastes, Part I: Leach Studies," J. G. Moore et al., Oak Ridge National Laboratory, Oak Ridge, TN 37831, April 1975.

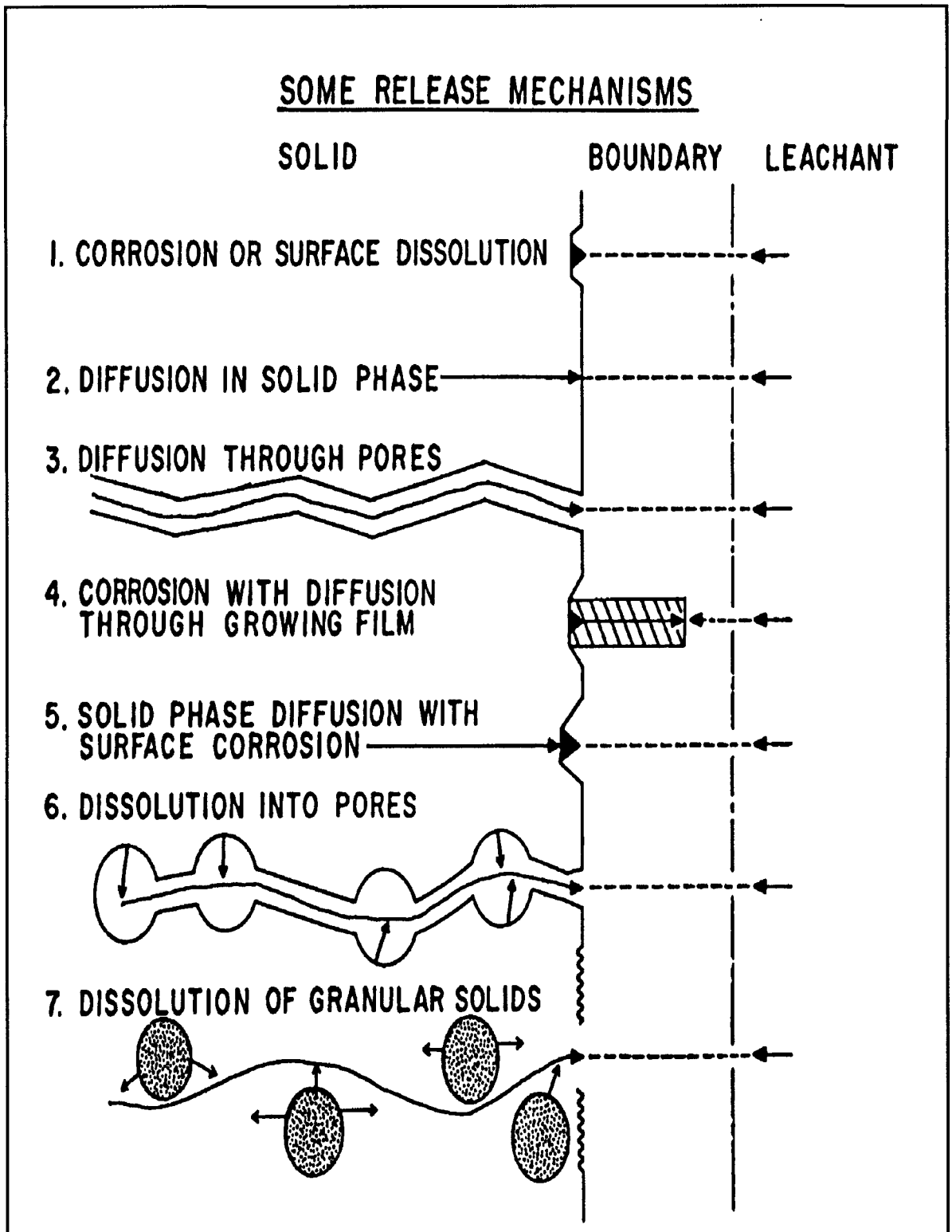

Figure 16 Summary of serial and parallel leach mechanisms that are represented by the general effective diffusion coefficient (D_e).

Equation 2: Simplified Definition of the Effective Diffusion Coefficient

$$D_e = \frac{D}{1 + K_e,}$$

Where:
D_e = Effective Diffusion Coefficient
D = Diffusion Coefficient, and
K_e = Partition Coefficient

The most effective modification to the intrinsic diffusion coefficient (D) in this equation is to add materials to the matrix that increase the ad/absorption or partitioning of materials or phases (K_e) with specific waste constituents or compounds. Adding a small fraction of materials with a large affinity for specific waste constituents can reduce the specific D_e by many orders of magnitude (i.e., factors of 10). Through the testing protocols for development of the PSA remedy, a determination was made that these materials were already present in the site soils. Therefore, the binder formula required no special additives to create this affinity.

However, the simplified equation for the effective diffusion coefficient (Equation 2) does not consider the progressive physical changes in the cement-pozzolan matrix that influence the release mechanisms from a matrix. Therefore, a more sophisticated

general model is needed to more accurately determine D_e.

Equation 3 correlates the D_e with the ad/absorption coefficient (K_e) and the physical parameters of tortuosity (τ), constrictivity (φ), porosity (ε), and density (ρ). These are the physical parameters that are used to describe the effects of continuing pozzolanic reactions on the soil grout's microstructure, which controls the release of waste constituents.

Equation 3: General Equation for the Effective Diffusion Coefficient

$$De := \frac{D}{\left\{\frac{r^2}{\varphi}\right\} \cdot \left\{1 + \left\{\frac{1-\varepsilon}{\varepsilon} \cdot \rho \cdot Kads\right\}\right\}}$$

Where:

D = Diffusion coefficient in pore water

τ = Tortuosity

φ = Constrictivity

ε = Porosity

ρ = Density

β = Dimension constant

Kads = Adsorption coefficient

$D_e = 3 \, x \, 10^{-14} \, x \, cm^2 \, x \, s^{-1}$

$- \log (D_e \, x \, \beta) = 13.5$

Tortuosity (τ) is the ratio of the length of the actual diffusion path to the surface divided by the shortest geometric distance to the surface. As the solid needle

phases of CSH grow together, the matrix becomes a diffusion labyrinth. This labyrinth effectively creates obstructions in the direct path to the surface of the matrix, forcing the molecule to "detour" throughout the labyrinth, where additional obstructions will be encountered. The tortuosity increases with the monolith's age and density.

Constrictivity (φ) is a transmission coefficient. As the CSH gels in a monolith matrix form more extensively, the macroporosity (about 0.1 micron) of the matrix becomes completely encircled with CSH gel. This gel becomes a diffusion barrier that acts like a molecular sieve. Small ions like cesium (Cs) may move more freely in the gel walls. But large nonpolar molecules like PCBs and metal hydroxide complexes cannot. These large organic or inorganic molecules are effectively stopped and cannot easily pass through the CSH pore walls.

With age, the soil grout's density (ρ) increases because of continued reactions within the matrix. The effective porosity (ε) correspondingly decreases with increases in the density. In the long term, the effect of adding a pozzolanic additive is to reduce the final effective porosity greatly and to tighten the molesieve effect in the pore walls.

Permeability expresses the ability of a liquid to penetrate a mass. The physical changes induced by the pozzolan additive effectively reduce the per-

meability of the monolith matrix. At the PSA site, this reduction was dramatic: 1,000 to 100,000 times less permeable than host soils (see Section 3). The combination of these reactions results in a formidable barrier to the diffusion of waste constituents.

Using these physical parameters, the D_e for a monolith matrix can be calculated more precisely. The negative log base 10 of the D_e is called the Leach Index (LI). The higher the LI, the lower is the leaching potential of a monolith.

Appendix I presents calculations of D_e and LI for a monolith matrix with and without pozzolanic additives. Table XII summarizes the calculations in Appendix I using the typical values for τ, ε, φ, K_e, and ρ. Table XII illustrates the effects of pozzolanic and other additives on the D_e.

TABLE XII—Typical Leach Indices*

Waste Form	τ	ε	φ	K_e	Leach Index
Cement	1.4	0.28	0.9	2	6.5
Cement/Pozz	2.5	0.2	0.3	10	8.3
Cement/Pozz-Additive #1	2.6	0.18	0.15	40,000	12.3
Cement/Pozz-Additive #2	2.6	0.18	0.15	2,000,000	14.0

*Assumes: Porewater, $D = 7 \times 10^{-6}$ cm^2/s and Density, $\rho = 1.8$ g/cc

Pozzolanic additives increase the tortuosity and decrease the porosity and constrictivity. Also, poz-

zolans can have a very large K_e for transition metals[19] and alkali metals.[20] Therefore, the LI is highest for the cement/pozzolan matrix with additives that increase K_e. This matrix would most effectively control release mechanisms for waste constituents.

This model explains why the diffusion coefficients are reduced during the long-term aging of cement-based, pozzolanic-monolith matrixes, like the one used at the PSA site. Over hundreds of days and years the monolithic mass slowly becomes denser and more effective at retention of waste constituents.

Not only do the changes in these physical parameters prevent the escape of waste constituents, they also prevent the intrusion of substances from the monolith's emplacement environment. Combined with its impermeability, the monolith is a self-sustaining matrix.

The changes in these physical parameters are at work within the fabric of the monolith matrix on a microscopic to an atomic scale. Therefore, no matter how finely divided the monolith becomes, the mechanisms described by these parameters still con-

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[19] P. W. Schindler, B. Furst, R. Bick, and P. U. Wolf, "Ligand Properties of Surface Silanol Groups, Surface Complex Formation with Fe (2+), Cu (2+), Cd (2+), and Pb (2+)," *Journal of Colloid and Interface Science,* Vol. 55, No. 2, pp. 469-475, May 1976.

[20] F. M. Lea, *The Chemistry of Cement and Concrete,* Third Edition, Chemical Publishing Company, Inc., 121 Fifth Avenue, New York, NY, pp. 574-575, 1971.

trol the leach performance of the basic matrix material.

4.4. Monolith Maintenance

The PSA monolith requires no maintenance. Unlike other remedial alternatives, the monolith has no operating parts that must be maintained or replaced over time and has no ongoing activity that requires operational attention. Once the pozzolanic reactions are started within the monolith matrix, they will continue on their own. In fact, the carbonate aquifer environment at the PSA site will contribute to the formation of a calcite (limestone) rind or shell around the outer surface of the monolith which, although unnecessary for effective performance of the monolith, provides it with added protection.

4.5. Effects of Constructive Land Uses on Monolith Integrity

Besides the monolith not requiring maintenance, the monolith also will accommodate constructive land uses, even if they impact its integrity. As explained previously, the effects of the pozzolan additives occur even in small fragments of the monolith matrix. All the testing done during the development study and since completion of remediation used small specimens of monolith material. As discussed in Sections 2 and 3, these small specimens demonstrated empirically the ability of the pozzolan additives to effectively restrict waste constituent transport from

the monolith matrix. The progressive physical changes in the monolith matrix that are described earlier in this section occur just as effectively in small particles of a monolith as they do in the monolith as a whole.

Therefore, pulverization of the monolith caused by foundation drilling or footer excavations, for example, will not affect the performance of the monolith. In addition, the UCS of the monolith exceeds 20.8 psi and will support many types of construction activity, including warehouses that are common in the Medley area.

Using the worst-case diffusion model in Equation 1, Appendix D calculates the upper-bound release rates from small pieces of monolith that range from 8 feet to 1/8 inch in diameter. Because the diffusion model is a semi-infinite, solid model, it is not accurate above a fractional release of 0.2 or greater. Therefore, Appendix D also uses a geometry-specific model that describes the diffusion from cylinders and spheres.[21] Figure 18 presents this model based on Nestor's solution in cylindrical coordinates.[22]

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[21] H. W. Godbee, J. E. Morchek, C. W. Nestor, Jr., and O. U. Anders, "Application of the NEWBOX Computer Program to an Analysis of the Leaching Data for Several Alkali Metals and Phenol from Cementitious Waste Forms," preprints of the papers presented at the 197th American Chemical Society Meeting, Vol. 29, No. 1, Dallas, TX, pp. 184-185, April 9-14, 1989.

[22] C. W. Nestor, Jr., "Diffusion from Solid Cylinders," ORNL/SDTM-84, Oak Ridge National Laboratory, Oak Ridge, TN 37831, January 1980.

Equation 4: Geometry Specific Model for Diffusion from a Cylinder or Sphere (Source: Nestor, 1980)

$$FC(t) = 1 - \frac{32}{\pi^2 \cdot a^2} \cdot \sum_n \sum_m \frac{e^{-\left[D_e \cdot \left[\alpha_m^2 + (2 \cdot n - 1)^2 \cdot \frac{\pi^2}{4 \cdot L^2} \cdot t \cdot s\right]\right.}}{(2 \cdot n - 1)^2 \cdot \alpha_m^2}$$

Where:

FC = Cumulative Fractional Release from Cylinder

D_e = Effective Diffusion Coefficient

t = Time of Leach Interval

α_m = Dimensionless Radial Diffusion Coordinate

a = Radius of Solid Waste Form

L = One half the height of the cylinder

s = units of seconds

Table XIII summarizes the upper bound release rates for these monolith fragments as derived from the model. For example, according to the model, it would take 6 years for a 1/8-inch diameter fragment to release 5 percent of its PCB and lead waste constituent inventory and 400 years to release 35 percent of that inventory. Considering the amount of potential waste constituent inventory in such a small fragment, when measured against time in years, the actual waste constituent release predicted by the model is insignificant.

As was explained in Section 3, this model predicts release rates that are at least 25 to 120 times greater than release rates actually measured on the small PSA monolith specimens used in the original treatability study and the QA testing. That is, in the emplacement environment of the PSA monolith, no apparent justification exists for restricting constructive land uses that impact integrity.

TABLE XIII—Releases From Small Cylinders

Diameter	First 5%	F_{400}	$F_{4,000}$
8'	3.0×10^{6}y	0.0005	0.0017
6'	2.0×10^{6}y	0.0007	0.0023
3'	4.8×10^{5}y	0.0014	0.0046
2'	2.1×10^{5}y	0.0022	0.0068
1'	5.4×10^{4}y	0.0045	0.0137
6"	1.3×10^{4}y	0.0086	0.027
3"	3,345y	0.017	0.055
2"	1,487y	0.026	0.082
1"	372y	0.052	0.16
1/2"	93y	0.10	0.33
1/4"	23y	0.19	0.53
1/8"	6y	0.36	0.86

Assumes $D_e = 3.0 \times 10^{-14}$ cm^2/s

5. Appendices

Appendix A— PSA Modified ANSI/ANS 16.1-1986 Leach Method

Appendix B— PSA Modified MCC-1 Static Leach Method

Appendix C— Source-Term for the PSA Monolith

Appendix D— Leach Model for a Small PSA Waste Form Core

Appendix E— Unconfined Compressive Strength of Archived PSA QA Samples

Appendix F— Wastech, Inc. Permeability Data on PSA Archived QA Samples

Appendix G— RMT Analyses of Archived PSA Modified MCC-1 Static Leachates

Appendix H— Cylinder Diffusion Model of a 1.5-inch Diameter by 2.5-inch High Specimen

Appendix I— The Effective Diffusion Coefficient Model

Appendix J— L. R. Dole, Ph.D., Vita and Publications

Appendices referred to in this report are available upon request from: Dr. Leslie R. Dole, Director of Technology, QUALTEC, Inc., 725 Pellissippi Parkway, Knoxville, Tennessee 37932-3363.

6. Further Information

Please see the EPA report describing remedies at Pepper's Steel Site. It is available from any of the QUALTEC offices.