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26
The Fixation of Incineration Residues

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ABSTRACT

Incineration ash from three operational facilities within the New York Metropolitan area were stabilized with various portions of additives (lime, gypsum, Portland cement and sodium carbonate) to produce a concrete-like material suitable for both marine disposal and use in the construction industry. Curing parameters were adjusted to maximize the structural integrity of the experimental mixes. Certain mix and curing designs produced proctor sized samples exhibiting a compressive strength of approximately 1,600 psi.

Stabilized composite residues (containing both fly ash and bottom ash) did not exceed EPA leachate limits. New York City fly ash, stabilized without any bottom ash did exhibit significantly higher elemental concentrations and exceeded EPA leachate limits for cadmium and lead.

Permeabilities of the stabilized mixes ranged from 10^{-5} - 10^{-8} cm/sec with the stabilized composite residues yielding the lowest permeabilities. Following submersion in seawater, stabilized composite residue samples experienced no decline in their structural integrity while significant expansion and loss of strength was observed for the New York City fly ash samples.

The results of this investigation indicate that incineration ash possesses significant pozzolanic activity and may be a suitable substitute for aggregate in the manufacture of cement blocks for use by the construction industry in this region. In addition, blocks having excellent structural properties relative to marine disposal have been fabricated.

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Section 1

INTRODUCTION/OVERVIEW

PROJECT DESIGN

This project, entitled "The Fixation of Incineration Ash: Physical and Leachate Properties", is a one year laboratory study which began in May 1985. This work is sponsored by the New York State Legislature with the New York State Legislative Commission on the Water Resource Needs of Long Island as the lead agency. Investigators at the Waste Management Institute of the Marine Sciences Research Center of the State University of New York at Stony Brook are conducting the investigation. Motivation for the project stemmed from a desire to examine the feasibility of fixating incineration ash and demonstrate the use of the stabilized material in a constructive manner as an alternative to landfilling.

PROJECT OBJECTIVES

This project focussed on two main objectives:

Objective 1 - To investigate incineration ash fixation by means of chemical additives and controlled curing environments.

Objective 2 - To determine the permeability and leachate characteristics of several "optimum" mixtures of incineration ash and fixation additives.

Objective 1 was addressed during the first stage of the project.

The incineration ash utilized in this study was secured from three operational incinerators. New York City's Southwest Brooklyn facility twice provided a source of fly ash. On two separate occasions the Town of Huntington incinerator located in East Northport, Long Island was visited to remove composite samples of both bottom and fly ash. Composite ash samples were also acquired from the Westchester Resource Recovery facility in Peekskill, New York.

The incineration wastes were initially characterized by determining the moisture content of the samples, particle size distribution and pH. The concentration of organic constituents was determined by measuring the loss on ignition and X-ray diffraction provided information as to the major mineral phase found within the incineration wastes.

Calcium hydroxide (lime), Portland cement (Type 1), gypsum and sodium carbonate served as fixation additives during the fabrication of ASTM proctor sized cylinders of incineration ash. The proctors were cured in various controlled temperature-humidity environments for varying periods of time.

At the end of the curing period, proctors were subjected to compressive strength testing (ASTM C39). Relative compressive strengths were used as a criterion for comparing various mixes of incineration wastes and fixation additives in order to determine an optimum formulation. Mixes containing 15% Portland cement were selected as optimum.

The next stage of the project addressed the second objective; to determine the permeability and leachate characteristics of the optimum mixes. Portions of proctors were sealed into PVC pipe. The rate and quantity of water which permeated through the proctors was recorded, enabling calculations of permeability constants.

The leachate characteristics of starting materials and optimum mixes were studied using both EPA and ASTM protocols. Additional physical tests were performed on the optimum mixes and starting materials. Density/porosity (ASTM C 642) of the optimum mixes was measured. Optimum mixes and starting materials were analyzed for major, minor and trace components. Samples were digested in hydrofluoric acid prior to analysis by atomic absorption spectroscopy. X-ray diffraction was used to identify the principal cementitious phases. Table 1.1 summarizes the overall scope of the project.

Table 1.1. "The Fixation of Incinerator Residues: Physical and Leachate Properties" - A summary of activities.

Objective 1: To investigate incineration residue fixation by means of chemical additives and controlled curing environments.

- Initial research and development of proctor fabrication techniques,
- determination of physical properties of incinerator residues,
- determination of optimum water content for making proctors,
- full scale production of test proctors for all of the test mix types studied,
- selection of an "optimum" mix to be used during the investigation of the second objective.

Objective 2: To determine the permeability and leachate characteristics of optimum mixes of three incinerator residues plus fixation additives.

- Darcy falling head permeability measurements of the optimum mixes,
 - EPA and ASTM chemical leachate tests of optimum mixes and starting materials,
 - determination of the bulk chemical composition and mineralogy of the optimum mixes and starting materials,
 - additional physical testing of the optimum mixes and starting materials,
 - preliminary fabrication of "cement blocks" incorporating incineration residue in place of natural aggregates,
 - determination of the flux of calcium from the optimum mixes and a preliminary evaluation of block longevity,
 - initial evaluation of the impacts from marine disposal of fixated incineration residues.
-

PROJECT RESULTS

This report is the final product of the first phase of this investigation. It includes a tabulation of all data and a description of methods. A brief discussion of the results with suggestions for future work is included.

Section 2

PROJECT SUMMARY AND CONCLUSIONS

STATEMENT OF PRINCIPAL CONCLUSIONS

This project provided data to support the following principal conclusions:

- Incineration residues contain sufficient pozzolanic ingredients to support lime fixation.
- Fixation additives affect the physical and chemical properties of proctors.
- Both physical and chemical properties of proctors determine the chemical composition of leachate.
- Higher temperature generally accelerates the curing process. Compressive strength increases with curing time.
- Chemical fixation of incineration residue is capable of reducing the rate of release of trace metals.
- Structural integrity is significantly affected by particle size and organic content of the residue.
- Proctors of stabilized combined ash maintain their structural integrity following their placement in the sea.
- For fixated combined ash proctors, EPA leachate limits were not exceeded for parameters which were tested.
- For fixated incinerator fly ash, EPA leachate limits were exceeded for Cadmium and Lead.

- Preliminary results indicate that stabilized blocks of combined incineration residue will maintain their structural integrity in the marine environment for prolonged lengths of time.
- Incineration residues may be a suitable substitute for natural aggregates in the production of cement blocks.
- Proctors fabricated with New York City fly ash and Portland cement experience significant expansion upon seawater submersion resulting in failure of the samples structural integrity.
- If the New York Metropolitan region were to elect marine disposal of all the projected incineration residue (2.2×10^6) it would require 10 years to construct one artificial fishing reef.

A SUMMARY OF PHYSICAL AND CHEMICAL OBSERVATIONS

Fabrication Techniques and Mix Types

Proctor fabrication was accomplished following the ASTM D698 method "Standard Test Moisture-Density Relations of Soils and Soil-Aggregate Mixtures using 5.5 lb. Rammer and 12 inch Drop". While modifications of this test were investigated, proctor fabrication could not be improved.

A water content of 17% was found to be optimum for fabrication of proctors containing Westchester residue. In general optimum water content is a function of median particle size, increasing as particle size decreases.

The maximum observed compressive strength was 1592 psi for a 67% Westchester residue and 15% Portland cement mix with 18% water content cured for 21 days at ambient temperatures. Additions of sodium carbonate (Na_2CO_3) found to improve the structural integrity in fixated coal ash, resulted in no improvement for the incineration ash proctors. Gypsum, calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) another commonly used additive significantly deteriorate the compressive strength and produced the lowest compressive strengths measured during this investigation.

The three optimum mixes selected for additional physical and chemical testing were:

- 62% New York City fly ash with 15% Portland cement and 23% moisture cured at 49 C for 72 hours. [Proctor series COA2].
- 67% Huntington combined residue with 15% Portland cement and 18% moisture cured for 14 days at Ambient temperatures. [Proctor series HA3].
- 68% Westchester combined residue with 15% Portland Cement and 17% moisture cured at 49 C for 24 hours. [Proctor series WAE6].

Physical and Chemical Tests

Tables 2.1 and 2.2 summarize the results of the physical, chemical and mineralogical tests performed on optimum mixes.

Physical testing disclosed the need for either calcium hydroxide (lime) or Portland cement and increased curing time to insure the development of sufficient reaction products to insure the physical integrity of the stabilized mix. No significant differences were observed in either the top or bottom portions of the proctor with the one exception that the bottom edges of the New York City proctors were sometimes chipped in removal from the mold. Basically uniform values for both porosity and permeability suggest that the compaction effort was homogeneously distributed during proctor fabrication. For each of the optimum mixes, the permeability initially declined very rapidly, then stabilized experiencing a minor trend toward lower values during the four week period of the investigation.

Mineralogical and chemical analyses provided an interesting comparison of the fly ash and composite residues used in this study. Elemental constituents were found in higher concentration in the fly ash, when compared to the composite residues.

Comparison of the chemical composition of the ASTM and EPA leachate revealed that:

- EPA leachate concentrations were significantly higher than the ASTM values. It is important to note that the pH of the EPA leachate is adjusted with acid prior to the test.
- For composite ash proctors leachate concentrations did not exceed EPA limits for those parameters which were examined.
- Modelling of leachate diffusion from a hypothetical disposal site indicates that water column chemistry is unaltered beyond 1000 meters from the disposal site. For most elements the distance is less than 100 meters.

Table 2.1. Summary of physical tests performed on optimum mixes.

Test	New York City Fly Ash	Huntington Composite Residue	Westchester Composite Residue
Proctor fabrication data (Modified ASTM D698 method)	62% Ash 15% Portland Cement 23% Moisture	67% Residue 15% Portland Cement 18% Moisture	68% Residue 15% Portland Cement 17% Moisture
Proctor compressive	228 (± 43)	455 (± 51)	1230 (± 59)
Proctor wet density, ASTM D698 (modified) (kg/m^3)	1533	1712	1744
Darcy falling head permeability (cm/sec)	Top of Proctor: 10^{-7} Bottom of Proctor: 10^{-5}	T: $<10^{-7}$ B: $<10^{-5}$	T: 10^{-8} B: 10^{-8}
Density/porosity, ASTM C642:			
Apparent specific gravity	2.32	2.53	2.51
Water absorption	36%	21%	18%
Voids	47%	39%	36%

Table 2.2. Summary of chemical and mineralogical tests performed on optimum mixes.

Test	Optimum Mixes
<u>Bulk Chemical Composition</u>	
Major Constituents	Aluminum Silicon Magnesium Iron Calcium Zinc
Minor Constituents	Copper Chromium Lead Manganese
Trace Constituents	Cadmium Arsenic Cobalt Mercury Nickel
<u>Mineralogy</u>	
Major Crystalline Phases	Anhydrite Gypsum Quartz Calcite
Minor Crystalline Phases	Ettringite

SUGGESTIONS FOR FUTURE WORK

The following suggestions are provided as an aid for planning future investigations:

- undertake toxicity bioassays on selected organisms representative of the project site following the procedures described by the US EPA for the ocean disposal permit program,
- develop methods for the mechanical, high speed fabrication of SAI blocks using existing equipment and technology provided by the concrete block industry,
- construct small test structures, simulating an artificial fishing reef, at our marine test site located in Conscience Bay, an embayment of Long Island Sound,
- examine the chemical, physical and biological interactions of SAI blocks submerged in Conscience Bay as a function of marine exposure,
- evaluate the suitability and engineering properties of construction grade cement block using incineration residues as a substitute for natural aggregate.

Section 3

INCINERATION WASTE CHARACTERISTICS

INCINERATION RESIDUES USED IN THE PROGRAM

Ash from three operational New York State facilities was utilized in this study. The Southwest Brooklyn plant operated by the City of New York, the Signal - RESCO facility in Westchester County, and the Town of Huntington incinerator located in East Northport were selected. Ash was collected on two separate occasions from each site and returned to our facility in steel 55 gallon drums. The total amount of residue collected from each site was, approximately, 4,200 lbs from Westchester, 600 lbs from the New York City plant and 1,200 lbs from the Town of Huntington facility. Distinction between the use of first and second trip ash is indicated in the remaining sections of the report.

Composite ash, a combination of bottom and fly ash, was collected at the Westchester and Huntington facilities, and only fly ash was collected at New York City. Different types of ash are produced due to the varied descriptive parameters of the plants, and some of these parameters can be found in Table 3.1.

BULK PROPERTIES

Particle-size Analysis

The distribution of particle size in the incineration wastes was determined by sieving a sample of approximately 6 kg of Huntington residue, 1 kg of Westchester residue and 0.5 kg of New York City fly ash. We secured ash twice from Huntington and New York City and following each collection event particulate size distribution analysis was undertaken. The analysis followed ASTM D422-63 using a series of U.S. Standard Sieves 3 in, 1.5 in, 0.75 in, Numbers 4, 10, 18, 40, 60, 100 and 200. For the three larger size sieves the residues were sieved dry and shaken by hand. The smaller sieves were placed into a Ro-Tap sieve shaker.

Table 3.1. Comparison of incineration ash facilities.

Statistics	Westchester	Huntington	NYC Southwest Brooklyn
Start-up	1984	Unit#1-1956 #2-1960 #3-1962	1961
Area served	Westchester Cty 850,000 people	Huntington 210,000 people	Varies ~300-500,000
Plant capacity	2250 tons/d	***	750 tons/d
Average throughput	1800 tons/d	Unit#1&2-100tons/d #3 -200tons/d	600 tons/d
Combustion temp.	2500°F+	1400°F+	1400-1600°F
Type of system	Mass burning with waterwall boilers	Mass burning	Mass burning
Operation	24 h/d 7 d/week	24 h/d 6 d/week	24 h/d 7 d/week
Materials recovery	Ferrous, Aggregate	Aggregate ¹	None
Precipitators	Electrostatic, 3	Electrostatic, 1	Electrostatic, 4
Power generation	Electric power	None	None
Power generation capacity	60 MW, ongoing	***	***
Customer	Consolidated Edison Co.	***	***

¹ Material is sorted at the plant before burning and the metallic fraction is disposed of in a landfill located on the premises.

The results of the particle-size analysis are illustrated in Figures 3.1 - 3.3 which shows the composition of the different size fractions. The composite ash from Westchester and Huntington was more heterogeneous than the New York City fly ash, as expected. In the larger size groups glass was predominant. In the Huntington samples fragments of rags, paper and wood shaving were observed.

The quantitative contributions of the different size fractions to the samples are given in Table 3.2. From the grain size distribution curve (Figure 3.4) it can be concluded that the New York City fly ash sample obtained during our second visit to that facility is predominantly of silt size having a mean grain size of 0.09 mm. This is significantly finer than the first sample that was collected which has a mean grain size of 0.25 mm. Sand sized particles are dominant in the Westchester ash; the mean particle size is 0.6 mm. The largest particle size is represented by the two Huntington samples which compare very well. Huntington ash has the highest fraction of gravel sized particles and a mean particle size of slightly less than 2.0 mm.

Moisture Content and pH

Moisture content was determined in replicate ($n=10$) on 30 - 40 g samples of fresh residue ash following each collection event. Samples were dried to constant weight in an oven at about 90°C, Tables 3.3 - 3.5. Moisture contents were fairly uniform, despite the heterogeneity of the materials and the large solid inclusions. New York City fly ash and Westchester residue were significantly dryer than the Huntington ash which has a moisture content of approximately 24%.

The pH of the various residues was determined using an Orion Research Model 701A pH meter attached to a standard glass electrode. Table 3.6 presents the data.

Figure 3.1. Particle size fractions, New York City incineration ash.

Illustration	Sample Retained by Sieve Number
A	18 (1.00 mm)
B	40 (425 μm)
C	60 (250 μm)
D	150 (100 μm)
E	200 (75 μm)
F	Pan (<75 μm)

Figure 3.1

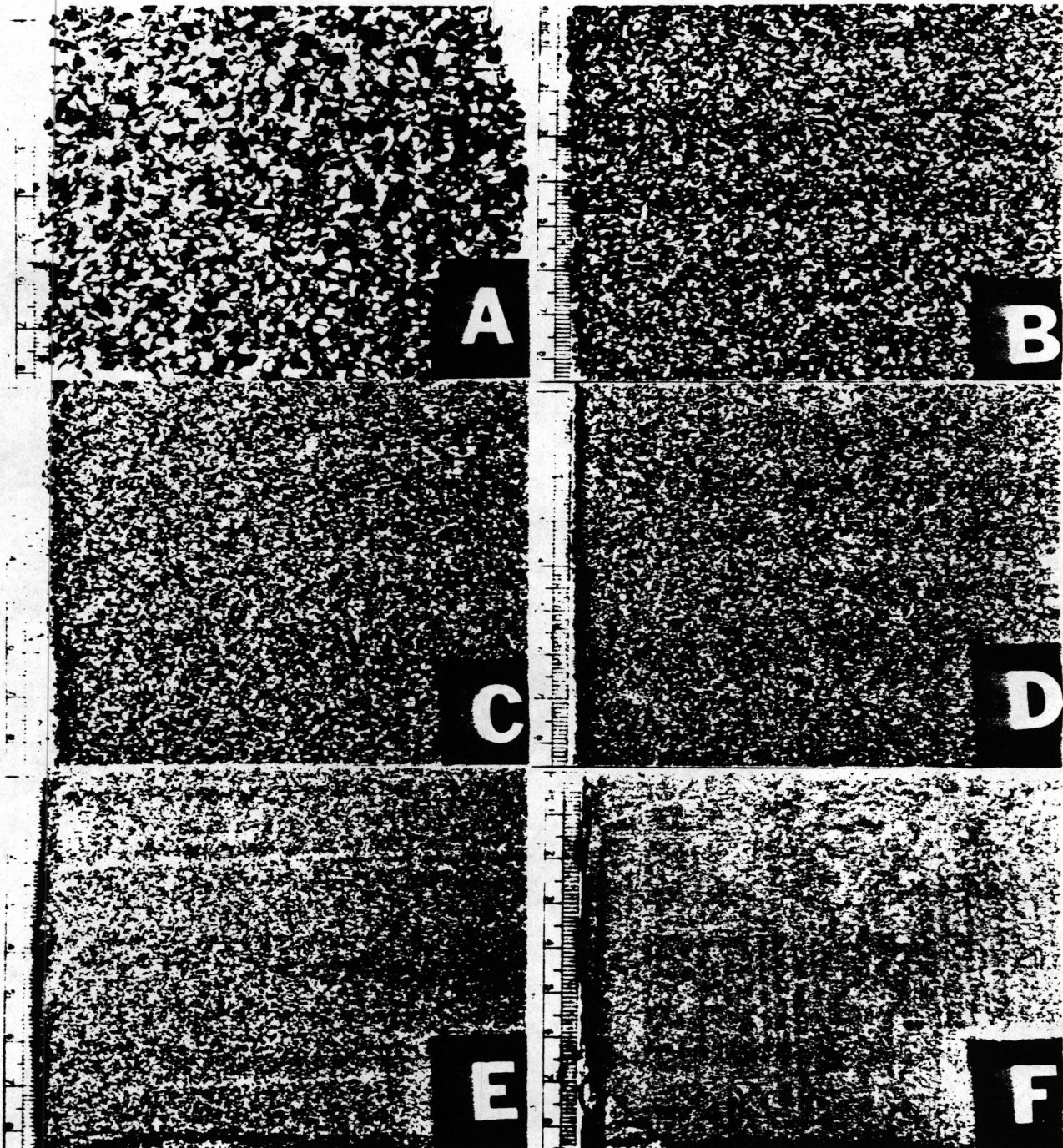


Figure 3.2. Particle size fractions, Huntington incineration residue.

Illustration	Sample Retained by Sieve Number
A	(3/4")
B	(1/2")
C	4 (4.75 mm)
D	18 (1.00 mm)
E	60 (250 μm)
F	Pan (<75 μm)

Figure 3.2



Figure 3.3. Particle size fractions, Westchester incineration residue.

Illustration	Sample Retained by Sieve Number
A	4 (4.75 mm)
B	10 (2.00 mm)
C	18 (1.00 mm)
D	60 (250 μm)
E	200 (75 μm)
F	Pan (<75 μm)

Figure 3.3

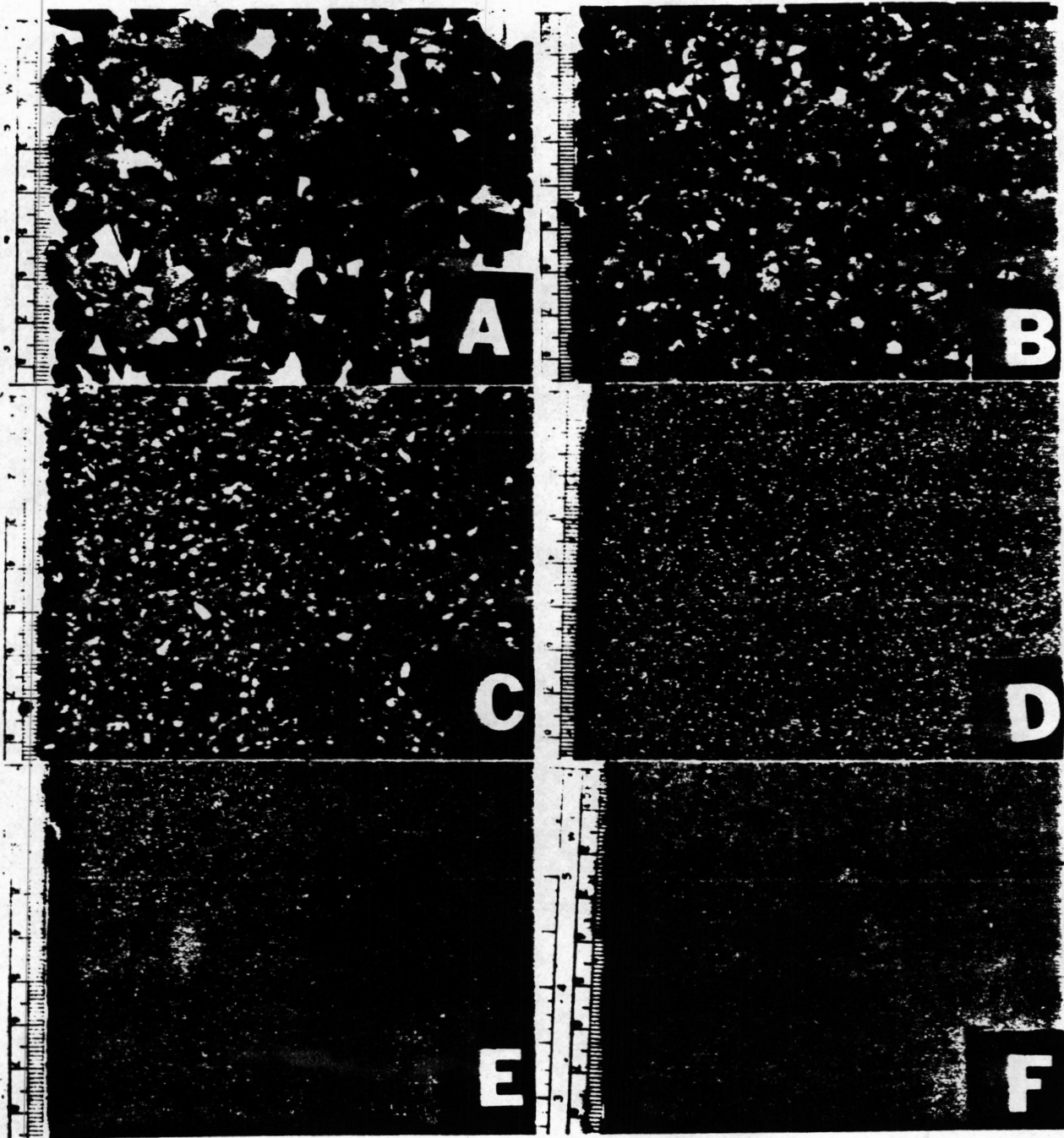


Table 3.2. Size fraction of residues.

PARTICLE SIZE ANALYSIS

SIEVE NUMBER	OPENING SIZE	<u>HUNTINGTON COMPOSITE ASH</u>		<u>NEW YORK CITY FLY ASH</u>		<u>WESTCHESTER COMPOSITE ASH</u>		<u>NEW YORK CITY FLY ASH*</u>		<u>HUNTINGTON FLY ASH*</u>	
		GRAMS RETAINED	% RETAINED	GRAMS RETAINED	% RETAINED	GRAMS RETAINED	% RETAINED	GRAMS RETAINED	% RETAINED	GRAMS RETAINED	% RETAINED
	.75"	239.1	4.08	0.0	0.00	0.0	0.00	0.0	0.00	88.3	4.76
	.50"	324.5	5.54	0.0	0.00	0.0	0.00	0.0	0.00	128.98	6.96
	.375"	451.5	7.70	0.0	0.00	47.2	4.47	0.0	0.00	139.08	7.50
4	4.75 mm	866.2	14.78	0.0	0.00	72.5	6.87	0.0	0.00	294.32	15.87
10	2.00 mm	844.6	14.41	0.6	0.11	111.4	10.56	4.0	0.69	254.77	13.74
18	1.00 mm	779.9	13.30	3.7	0.70	183.1	17.36	5.0	0.86	212.48	11.46
40	425 μ m	1108.8	18.91	74.2	14.12	310.8	29.46	16.3	2.80	315.01	16.99
60	250 μ m	487.6	8.32	174.0	33.13	136.3	12.92	29.8	5.10	162.73	8.78
100	150 μ m	262.8	4.48	149.0	28.37	73.0	6.92	78.4	13.45	106.46	5.74
200	75 μ m	186.9	3.19	84.3	16.04	54.6	5.18	185.6	31.84	75.04	4.05
	<75 μ m	310.3	5.29	39.5	7.52	66.1	6.27	263.8	45.25	77.13	4.16
TOTAL WEIGHT:		5862.1		525.3		1055.0		582.9		1854.3	

* Represents ash collected on a second visit to the facility.

Figure 3.4

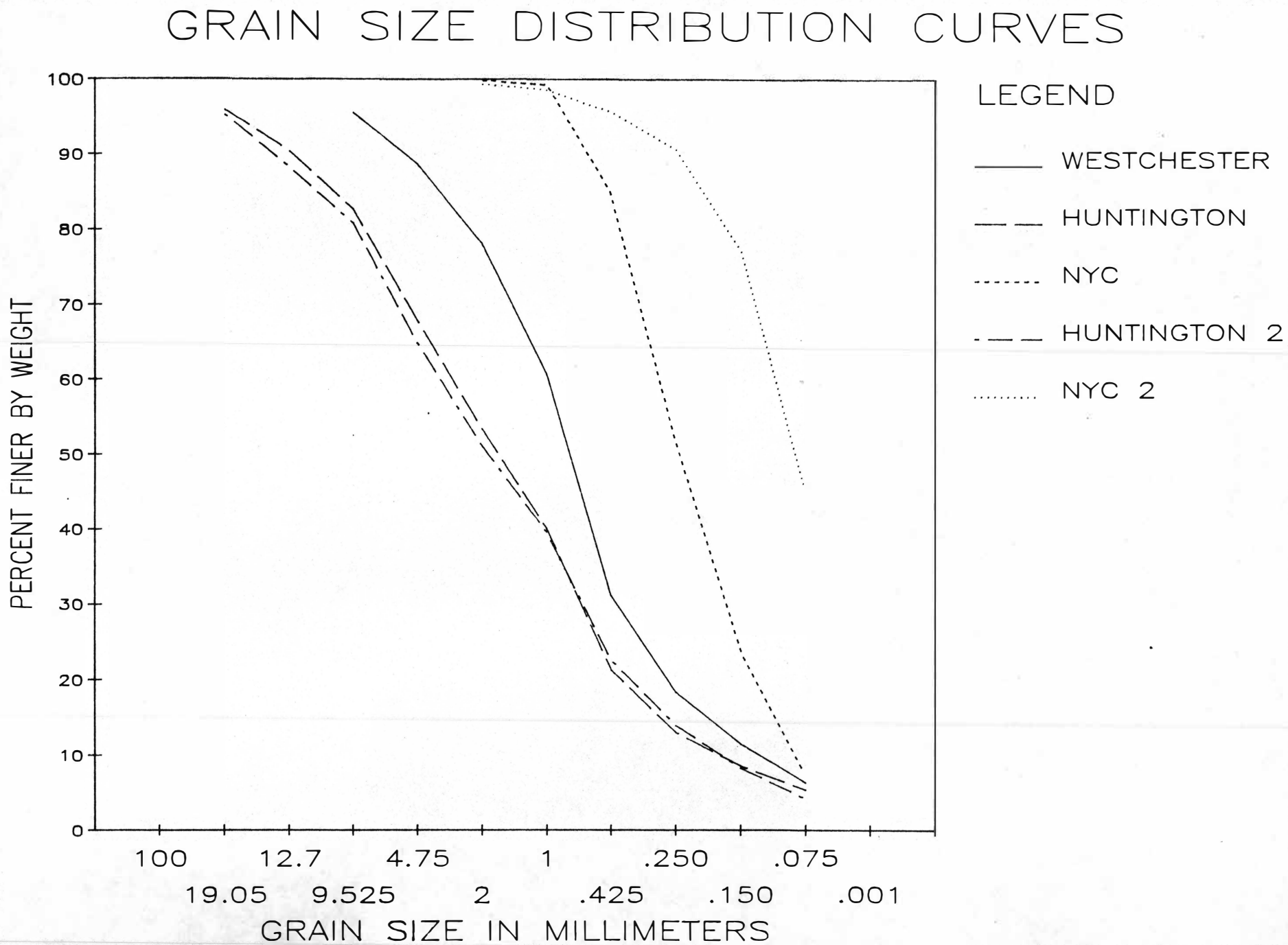


Table 3.3. Moisture content of Huntington incineration ashes.

WEIGHT	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
BEAKER	27.74	27.28	27.93	27.21	27.50	28.89	28.05	27.39	48.81	49.48
BEAKER + ASH	59.56	58.13	61.31	60.65	62.78	60.31	64.99	62.33	87.28	89.27
WET ASH	31.83	30.85	33.38	33.43	35.29	31.43	36.94	34.94	38.46	39.79
BEAKER + ASH (DRY)	51.62	50.15	52.41	52.15	54.11	52.70	56.37	53.49	77.63	79.17
DRY ASH	23.89	22.87	24.48	24.94	26.61	23.81	28.31	26.10	28.81	29.69
MOISTURE CONTENT	7.94	7.98	8.90	8.50	8.67	7.62	8.62	8.84	9.65	10.10
% MOISTURE	24.94	25.87	26.66	25.41	24.58	24.24	23.34	25.30	25.09	25.39
AVE. MOISTURE	25.08									
VARIANCE	0.74									
STD. DEV.	0.86									
WEIGHT	H1*	H2*	H3*	H4*	H5*	H6*	H7*	H8*	H9*	H10*
BEAKER	49.92	50.31	50.13	49.96	49.96	48.74	50.56	49.59	49.96	51.50
BEAKER + ASH	90.19	91.14	81.01	77.71	76.40	72.70	83.49	87.55	79.62	83.48
WET ASH	40.27	40.83	30.88	27.75	26.44	23.95	32.93	37.96	29.66	31.98
BEAKER + ASH (DRY)	81.08	80.98	74.42	71.34	69.84	67.23	75.63	79.77	72.61	77.02
DRY ASH	31.16	30.68	24.29	21.38	19.88	18.49	25.07	30.18	22.65	25.52
MOISTURE CONTENT	9.11	10.16	6.60	6.37	6.56	5.46	7.86	7.78	7.01	6.46
% MOISTURE	22.63	24.88	21.36	22.96	24.80	22.81	23.87	20.49	23.62	20.21
AVE. MOISTURE	22.76									
VARIANCE	2.43									
STD. DEV.	1.56									

* Represents ash collected on a second visit to the facility.

Table 3.4. Moisture content of New York City incineration ashes.

WEIGHT	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
BEAKER	30.08	27.10	27.32	28.01	29.48	30.00	28.05	29.00	51.50	49.56
BEAKER + ASH	46.82	46.40	47.00	45.52	48.43	50.37	45.92	48.45	76.11	76.56
WET ASH	16.74	19.30	19.68	17.51	18.94	20.37	17.87	19.45	24.61	27.00
BEAKER + ASH (DRY)	45.94	45.23	45.83	44.53	47.26	49.12	44.71	47.19	74.48	74.77
DRY ASH	15.86	18.13	18.51	16.52	17.78	19.12	16.66	18.19	22.98	25.20
MOISTURE CONTENT	0.88	1.17	1.17	0.99	1.16	1.25	1.21	1.26	1.63	1.79
% MOISTURE	5.25	6.07	5.96	5.64	6.13	6.14	6.75	6.49	6.63	6.64
AVE. MOISTURE	6.17									
VARIANCE	0.21									
STD. DEV.	0.45									
WEIGHT	C1*	C2*	C3*	C4*	C5*	C6*	C7*	C8*	C9*	C10*
BEAKER	50.04	51.60	48.29	49.57	48.82	51.30	49.46	50.85	48.75	48.99
BEAKER + ASH	67.67	67.17	68.31	66.70	70.21	69.54	66.88	69.60	66.90	66.36
WET ASH	17.63	15.57	20.02	17.14	21.39	18.23	17.41	18.75	18.15	17.37
BEAKER + ASH (DRY)	67.37	66.90	67.96	66.40	69.81	69.22	66.58	69.28	66.58	66.05
DRY ASH	17.33	15.30	19.66	16.83	20.99	17.91	17.12	18.43	17.83	17.06
MOISTURE CONTENT	0.30	0.27	0.35	0.30	0.40	0.32	0.30	0.32	0.32	0.31
% MOISTURE	1.70	1.76	1.77	1.78	1.87	1.75	1.72	1.70	1.75	1.79
AVE. MOISTURE	1.76									
VARIANCE	0.002									
STD. DEV.	0.048									

* Represents ash collected on a second visit to the facility.

Table 3.5. Moisture content of Westchester incineration ashes.

WEIGHT	W1	W2	W3	W4	W5
BEAKER	51.60	48.29	49.57	48.83	50.63
BEAKER + ASH	89.17	82.98	82.53	84.27	86.33
WET ASH	37.57	34.69	32.96	35.44	35.70
BEAKER + ASH (DRY)	88.38	82.18	81.82	83.43	85.47
DRY ASH	36.78	33.89	32.26	34.60	34.84
MOISTURE CONTENT	0.78	0.79	0.70	0.83	0.86
% MOISTURE	2.08	2.29	2.14	2.35	2.40
AVE. MOISTURE	2.25				
VARIANCE	0.01				
STD. DEV.	0.12				

Table 3.6. pH values for the various residues.

<u>Residues</u>	<u>pH</u>
New York City Fly Ash	10.89
New York City Fly Ash*	6.59
Huntington Composite Ash	7.72
Huntington Composite Ash*	7.71
Westchester Composite Ash	12.74

* represents ash collected on a second visit to the facility

Once again the two New York City samples differed considerably, the first sample was alkaline while the second sample collected was slightly acidic. The two Huntington samples were virtually identical and the most alkaline residue was obtained from the Westchester facility.

Loss on Ignition

The dried samples of residue used for determination of moisture content were used to measure loss on ignition (LOI). In this method the samples were ignited in a covered crucible in a muffle furnace at controlled temperature. Separate determinations were made for LOI at two temperatures, $500 \pm 50^{\circ}\text{C}$ and $900 \pm 50^{\circ}\text{C}$. LOI is frequently determined at temperatures of 900 to $1,000^{\circ}\text{C}$ but biogenic organics are burned off at 500°C and this was a materials group of interest for the present characterization.

Figure 3.5 and Tables 3.7 - 3.11 clearly illustrate that Huntington ash possessed the highest amount of uncombusted material, approximately 14% at 900°C . The second sample of New York City ash was significantly higher in organics when compared to the first sample and Westchester composite ash lost only 1.8% of its dry weight after being heated to 500°C .

Figure 3.5 Loss on ignition

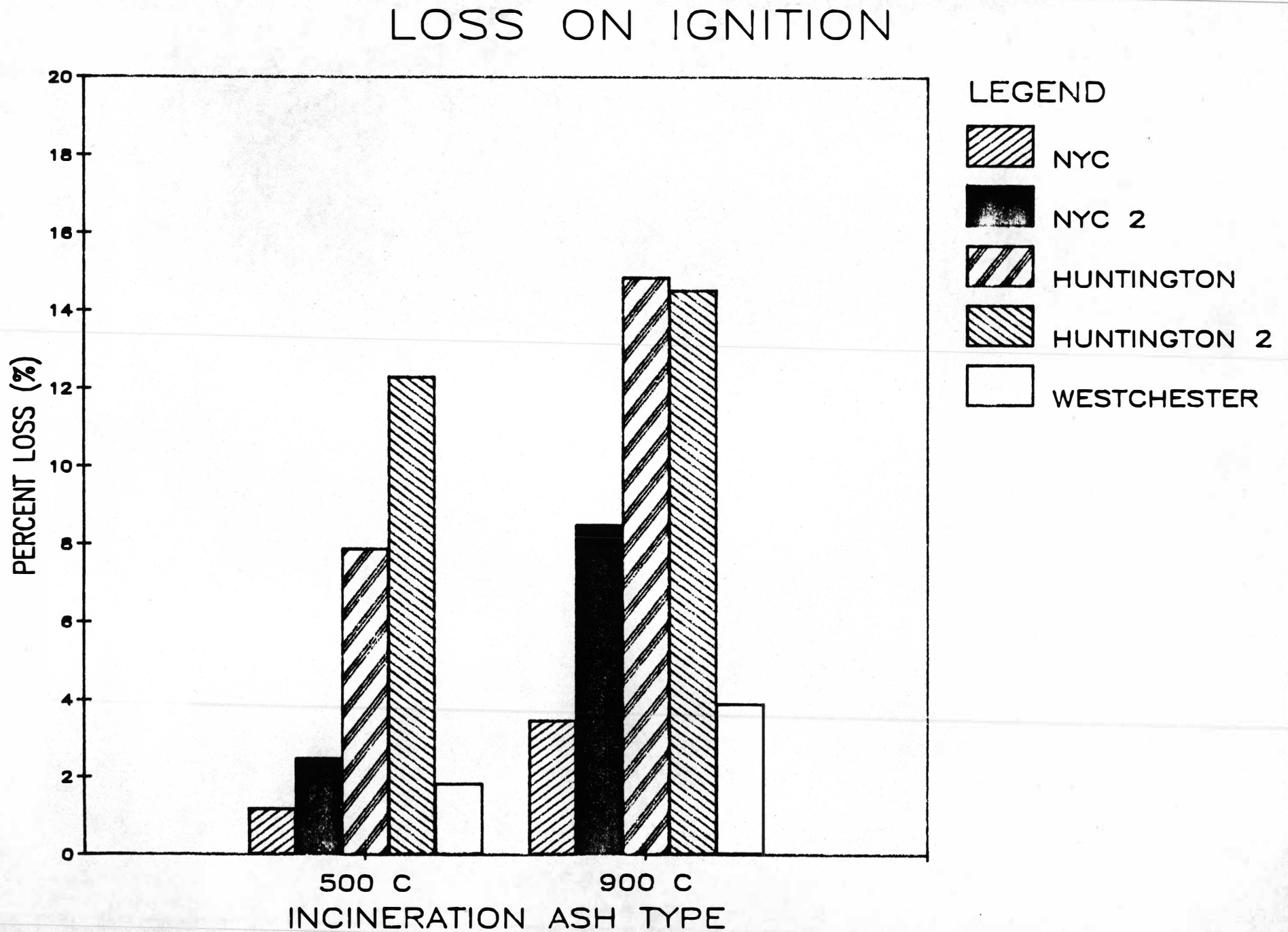


Table 3.7. New York City fly ash, loss on ignition 500°C, 900°C.

WEIGHT	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
CRUCIBLE + COVER	13.86	14.13	13.60	13.76	13.86	13.96	14.03	13.76	14.01	50.83
CRUCIBLE + ASH	20.38	19.49	19.30	18.67	18.52	18.04	19.06	19.03	19.22	68.57
ASH (PREIGN.)	6.52	5.36	5.70	4.91	4.67	4.08	5.03	5.27	5.20	17.74
CRUCIBLE + ASH (POST)	20.31	19.44	19.24	18.63	18.49	17.99	18.98	18.94	19.14	68.40
ASH (POSTIGN)	6.46	5.30	5.63	4.87	4.63	4.03	4.95	5.18	5.13	17.57
LOI (@500)	0.07	0.06	0.06	0.05	0.03	0.05	0.08	0.09	0.08	0.17
% LOI (@500)	1.01	1.09	1.09	0.94	0.75	1.28	1.62	1.78	1.48	0.96
AVG. % LOI (@500)	1.20									
VARIANCE	0.10									
STD. DEV	0.31									
CRUCIBLE + ASH (POST)	20.17	19.31	19.10	18.51	18.37	17.89	18.88	18.84	19.03	67.95
ASH (POSTIGN)	6.31	5.18	5.50	4.75	4.51	3.93	4.85	5.09	5.02	17.13
LOI (@900)	0.21	0.18	0.20	0.16	0.15	0.16	0.18	0.19	0.18	0.62
% LOI (@900)	3.23	3.42	3.42	3.35	3.32	3.83	3.64	3.55	3.56	3.47
AVG. % LOI (@900)	3.48									
VARIANCE	0.03									
STD. DEV.	0.17									

Table 3.8. New York City fly ash*, loss on ignition 500°C, 900°C.

WEIGHT	C1*	C2*	C3*	C4*	C5*	C6*	C7*	C8*	C9*	C10*
CRUCIBLE + COVER	13.6097	14.2302	13.8725	13.9815	13.759	13.89	13.9099	13.7816	14.0237	50.3976
CRUCIBLE + ASH	15.1298	15.5602	15.4956	15.7813	15.3532	15.2704	15.7026	15.2201	15.8605	55.4538
ASH (PREIGN.)	1.52	1.33	1.62	1.80	1.59	1.38	1.79	1.44	1.84	5.06
CRUCIBLE + ASH (POST)	15.09	15.5271	15.455	15.7343	15.3141	15.2342	15.6586	15.183	15.8207	55.3301
ASH (POSTIGN)	1.48	1.30	1.58	1.75	1.56	1.34	1.75	1.40	1.80	4.93
LOI (@500)	0.04	0.03	0.04	0.05	0.04	0.04	0.04	0.04	0.04	0.12
% LOI (@500)	2.62	2.49	2.50	2.61	2.45	2.62	2.45	2.58	2.17	2.45
AVG. % LOI (@500)	2.49									
VARIANCE	0.02									
STD. DEV	0.13									
CRUCIBLE + ASH (POST)	14.9945	15.4446	15.3506	15.6178	15.2695	15.1392	15.4961	15.0866	15.7357	55.0947
ASH (POSTIGN)	1.38	1.21	1.48	1.64	1.51	1.25	1.59	1.31	1.71	4.70
LOI (@900)	0.14	0.12	0.14	0.16	0.08	0.13	0.21	0.13	0.12	0.36
% LOI (@900)	8.90	8.69	8.93	9.08	5.25	9.50	11.52	9.28	6.79	7.10
AVG. % LOI (@900)	8.51									
VARIANCE	2.69									
STD. DEV.	1.64									

* Represents ash collected on a second visit to the facility.

Table 3.9. Town of Huntington composite ash, loss on ignition 500°C, 900°C.

WEIGHT	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
CRUCIBLE + COVER	50.23	23.76	24.47	87.27	88.82	49.34	24.65	23.64	24.47	85.57
CRUCIBLE + ASH	71.30	45.83	44.78	127.90	136.55	65.02	40.14	40.38	42.50	127.40
ASH (PREIGN.)	21.07	22.07	20.31	40.63	47.73	15.68	15.49	16.75	18.03	41.83
CRUCIBLE + ASH (POST)	70.05	44.40	43.43	125.18	133.66	63.75	38.47	38.68	40.45	124.65
ASH (POSTIGN)	19.82	20.64	18.97	37.91	44.84	14.41	13.82	15.04	15.98	39.07
LOI (@500)	1.25	1.43	1.35	2.72	2.89	1.27	1.67	1.71	2.05	2.75
% LOI (@500)	5.93	6.48	6.62	6.69	6.06	8.09	10.76	10.19	11.37	6.59
AVG. % LOI (@500)	7.88									
VARIANCE	3.96									
STD. DEV	1.99									
CRUCIBLE + ASH (POST)	68.41		42.08	121.92	130.16	62.68	37.58	37.76	39.60	120.89
ASH (POSTIGN)	18.18		17.61	34.65	41.34	13.34	12.94	14.12	15.13	35.32
LOI (@900)	2.89		2.70	5.98	6.39	2.34	2.56	2.63	2.90	6.51
% LOI (@900)	13.74		13.29	14.72	13.39	14.91	16.50	15.68	16.09	15.57
AVG. % LOI (@900)	14.88									
VARIANCE	1.25									
STD. DEV.	1.12									

Table 3.10. Town of Huntington composite ash*, loss on ignition 500°C, 900°C.

WEIGHT	H1*	H2*	H3*	H4*	H5*	H6*	H7*	H8*	H9*	H10*
CRUCIBLE + COVER	6.9482	7.0982	24.6426	23.6228	24.3341	23.7857	23.6358	24.47	23.8519	6.82
CRUCIBLE + ASH	12.2523	11.5105	40.3781	36.3578	40.803	43.304	43.0079	40.3944	37.7056	9.0541
ASH (PREIGN.)	5.30	4.41	15.74	12.73	16.47	19.52	19.37	15.92	13.85	2.23
CRUCIBLE + ASH (POST)	11.6332	11.1526	38.3832	34.7655	38.1904	41.3771	40.6259	38.1368	36.1448	8.7287
ASH (POSTIGN)	4.69	4.05	13.74	11.14	13.86	17.59	16.99	13.67	12.29	1.91
LOI (@500)	0.62	0.36	1.99	1.59	2.61	1.93	2.38	2.26	1.56	0.33
% LOI (@500)	11.67	8.11	12.68	12.50	15.86	9.87	12.30	14.18	11.27	14.57
AVG. % LOI (@500)	12.30									
VARIANCE	4.64									
STD. DEV	2.15									
CRUCIBLE + ASH (POST)	11.4773	11.0448	37.988	34.34	37.8947	40.9061	40.6232	37.8298	35.8675	8.6594
ASH (POSTIGN)	4.53	3.95	13.35	10.72	13.56	17.12	16.99	13.36	12.02	1.84
LOI (@900)	0.78	0.47	2.39	2.02	2.91	2.40	2.38	2.56	1.84	0.39
% LOI (@900)	14.61	10.55	15.19	15.84	17.66	12.29	12.31	16.10	13.27	17.67
AVG. % LOI (@900)	14.55									
VARIANCE	5.16									
STD. DEV.	2.27									

* Represents ash collected on a second visit to the facility.

Table 3.11. Westchester composite ash, loss on ignition 500°C, 900°C.

WEIGHT	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10
CRUCIBLE + COVER	14.1611	13.9618	13.7895	13.9748	13.6363	13.88	13.7186	13.882	14.0202	50.2386
CRUCIBLE + ASH	19.5761	18.5713	17.7568	18.481	18.7635	19.6731	18.8331	19.211	18.5563	64.32
ASH (PREIGN.)	5.42	4.61	3.97	4.51	5.13	5.79	5.11	5.33	4.54	14.08
CRUCIBLE + ASH (POST)	19.4894	18.4794	17.6902	18.3855	18.6658	19.5552	18.7476	19.1046	18.4778	64.0927
ASH (POSTIGN)	5.33	4.52	3.90	4.41	5.03	5.68	5.03	5.22	4.46	13.85
LOI (@500)	0.09	0.09	0.07	0.10	0.10	0.12	0.09	0.11	0.08	0.23
% LOI (@500)	1.60	1.99	1.68	2.12	1.91	2.04	1.67	2.00	1.73	1.61
AVG. % LOI (@500)	1.83									
VARIANCE	0.03									
STD. DEV	0.19									
CRUCIBLE + ASH (POST)	19.3654	18.3944	17.6114	18.2983	18.5707	19.4201	18.6532	19.01	18.3612	63.766
ASH (POSTIGN)	5.20	4.43	3.82	4.32	4.93	5.54	4.93	5.13	4.34	13.53
LOI (@900)	0.21	0.18	0.15	0.18	0.19	0.25	0.18	0.20	0.20	0.55
% LOI (@900)	3.89	3.84	3.66	4.05	3.76	4.37	3.52	3.77	4.30	3.93
AVG. % LOI (@900)	3.91									
VARIANCE	0.06									
STD. DEV.	0.25									

Section 4

PROCTOR FABRICATION

INTRODUCTION

The proctor fabrication stage of this project dealt with four major tasks:

- Initial research and development of proctor fabrication techniques.
- Determination of optimum water content for making proctors.
- Production of test proctors for all of the mix types studied.
- Comparison of proctor compressive strengths in order to select optimum mixes.

In order to accomplish these tasks the following types of equipment were used. Proctor compaction was done with a Soil Test, Inc. model CN-4230 Mechanical Compactor equipped with a 4 inch replacement mold, Soil Test model CN-4230-100. Mold dimensions were 4.6 inches height by 4.0 inches diameter for a volume of 1/30 cubic foot. The mechanical compactor permitted operator selection of either a 5.5 or 10 pound, 2 inch diameter circular face rammer as well as a 12 or 18 inch drop height. Hot Pack Corporation model 435300 Bench Top Steady-State Humidity Chambers were used for accelerated cures at different temperature and 98-100 % relative humidity. Compressive strength testing was performed using a Model FS 160 Riehle Universal Testing Machine which conformed with ANSI/ASTM C39-72 standards.

ADDITIVES

Additives such as sodium carbonate (Na_2CO_3), lime ($\text{Ca}(\text{OH})_2$), calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and Portland cement (type 1) were used in this study. These additives were obtained from Fisher Scientific, Inc. except Portland cement which was supplied from local supplier.

According to Fisher Scientific, Inc. 1983, Na_2CO_3 (Fisher CERTIFIED) used in this study contains only 0.01% insoluble matters and 0.005% silica (SiO_2), 0.003% sulfur compounds (SO_4), 0.01% calcium and magnesium ppt, and 0.5 ppm heavy metals (as Pb). For $\text{Ca}(\text{OH})_2$ (Fisher CERTIFIED), it shows 0.03% insoluble in hydrochloric acid and contains 0.1% sulfur compounds (SO_4), 1.0% magnesium and alkali salts, and 0.003% heavy metals (as Pb). Fisher CERTIFIED gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was used in this study. Portland cement (designated as type 1 by the ASTM) is the most important of the inorganic cementing materials by far. There are three predominant compounds in common portland cement, i.e., dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$), and Tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$).

FABRICATION TECHNIQUES

ASTM D698-78 provided guidelines for proctor fabrication techniques. These conditions in general require the compaction of the sample using:

- a 5.5 pound rammer falling a distance of 12 inches,
- 3 compactions of material per proctor,
- a total of 75 compactions per proctor.

The appropriate components of a test mixture were mixed on a weight basis and in the sequence: incineration wastes (first), calcium

hydroxide (lime), additives (cement, gypsum, sodium carbonate) and water (last). Hand mixing was used to distribute the materials as they were added. After thoroughly mixing the dry components, water was added to the mix and vigorously stirred to achieve a uniform distribution. In some cases additional water was added to the mix prior to final hand mixing. Subsamples of the wet mix were taken in order to determine the total moisture content prior to compaction and curing. Prior to mixing particles larger than 0.75 in were screened out.

The ASTM D698 method was used for proctor fabrication. Approximately 600 grams of mix were placed in a mold and a 5.5 pound rammer was dropped twenty five times from a height of 12 inches. Between each drop the mold was automatically rotated 36 in order to assure uniform compaction of the proctor surface. A second 600 gram portion of mix was added to the mold and the process repeated. After addition and compaction of a third 600 gram sample, the extension collar of the mold was removed. The proctors surface was trimmed and leveled prior to weighting. After extrusion from the mold, the proctor was ready for curing.

Three curing temperatures were studied. Ambient (approximately 23°C), 49°C and 71°C. Proctors cured at 23°C in air were wrapped in 1 ml thick plastic bags to prevent premature dehydration. These samples were air cured for intervals of 7, 14 and 21 days. The accelerated cures at 49°C and 71°C were performed in controlled humidity chambers for two time intervals, 24 and 72 hr.

After curing, proctors were permitted to cool to room temperature or were removed from the double wrapped plastic bags. Their weight, height, diameter and physical appearance were recorded prior to unconfined compressive strength testing.

Cured proctors were tested for unconfined compressive strength on a Model FS160 Riehle Universal Testing Machine. The FS160 was equipped with a 7 inch diameter self-aligning compressive head and spherical seat which conforms to the requirements of ANSI/ASTM C39-72, "Standard

Methods for Compressive Strength Testing of Cylindrical Concrete Specimens". The rate of loading was 3200 pounds per second. The total load withstood during testing was divided by the cross sectional area of the proctor to calculate unconfined compressive strength in pounds per square inch.

DETERMINATION OF THE OPTIMUM MIX

The first formulation of proctors were fabricated using lime portland cement and sodium carbonate, three additives that were shown in prior investigations to enhance stabilization. While holding relatively constant the concentrations of incinerator residue and additives, moisture content was altered between 13 and 25% for the three different residues. Following compaction, the proctors were subdivided into three groups and each group cured at different temperatures [49°C, 71°C, and air (23°C)]. The duration of the cure was also altered for each of the groups. For the proctors being cured at elevated temperatures, curing time was either 24 or 72 hours. For the air cured samples, the curing time was either 168, 336 or 504 hours (7, 14 or 21 days). The data in Tables 4.1 and Figures 4.1-4.3, in concert with the detailed fabrication information found in Appendixes A, B and C reveals the following information:

- a) Huntington residue produced proctor samples having the lowest compressive strength,
- b) in order to achieve a maximum compressive strength, as the particle size of the residue increased, moisture content also increased
- c) increased curing time resulted in improved structural integrity,
- d) proctors fabricated using Westchester residue yield the highest density, while New York City samples exhibited the best compressive strength.

The effects of increasing the lime concentration was examined by fabricating a series of proctor samples having a 9% lime content.

Table 4.1. Results of proctor fabrication using
6% lime, 3% cement, 0.5% Na₂CO₃.

NEW YORK CITY INCINERATION ASH			
PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
CA	17	18.6	438 - 875
CB	19	19.4	458 - 1134
CC	21	22.1	601 - 903
CD	23	22.2	430 - 688
CE	24	23.6	386 - 637

WESTCHESTER INCINERATION ASH			
PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
WA	17	17	251 - 446
WB	15	14.8	394 - 533
WC	13	13	161 - 521
WD	11	11.5	84 - 414
WE	19	19.5	139 - 398

HUNTINGTON INCINERATION ASH			
PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
HA	18	21.5	115 - 254
HB	22	23.7	96 - 217
HC	24	25.1	62 - 183
HL	20	21.6	203 - 386
HM	18	19.2	219 - 314
HN	16	18.8	219 - 330
HO	14.6	16.3	171 - 235

Figure 4.1

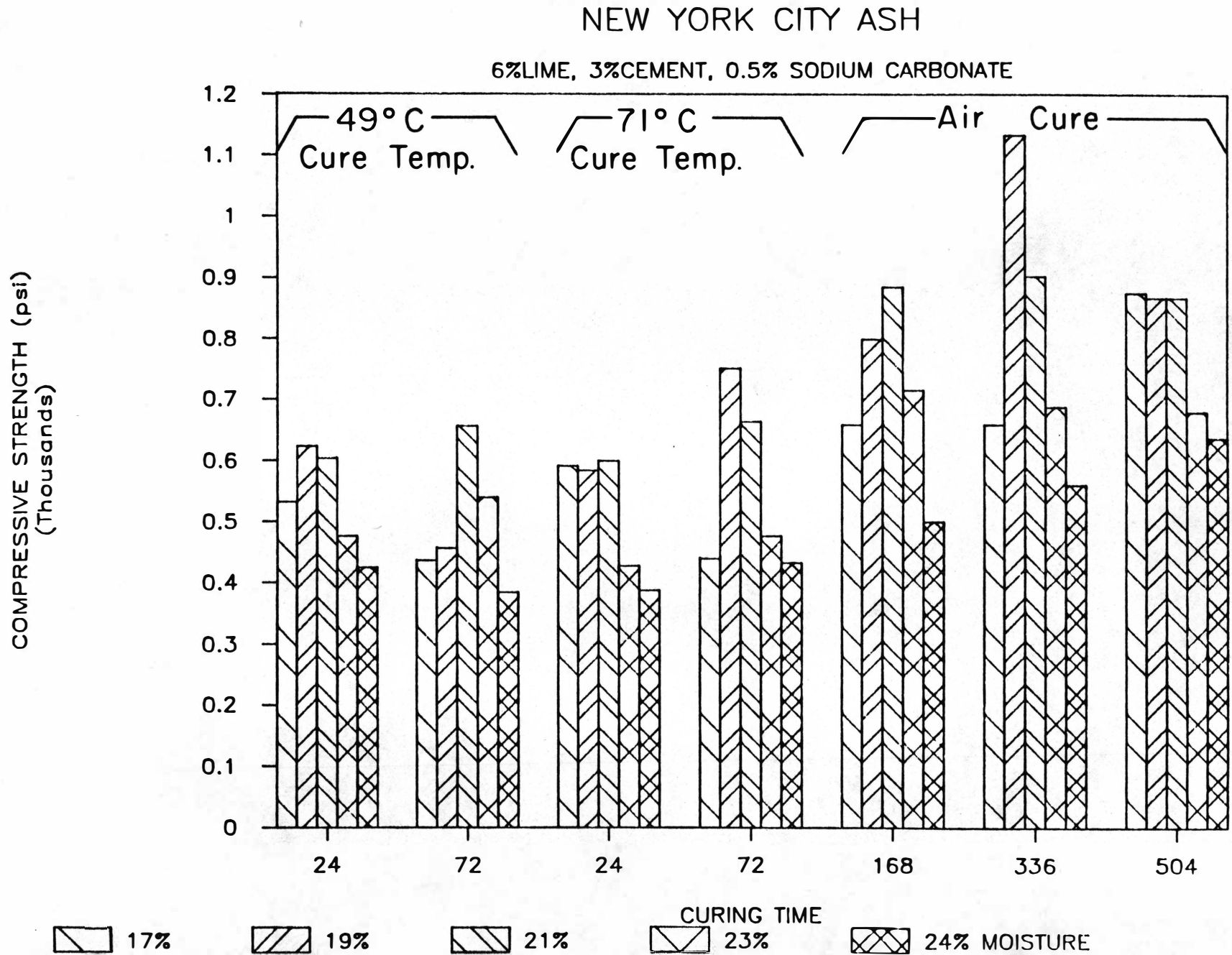


Figure 4.2

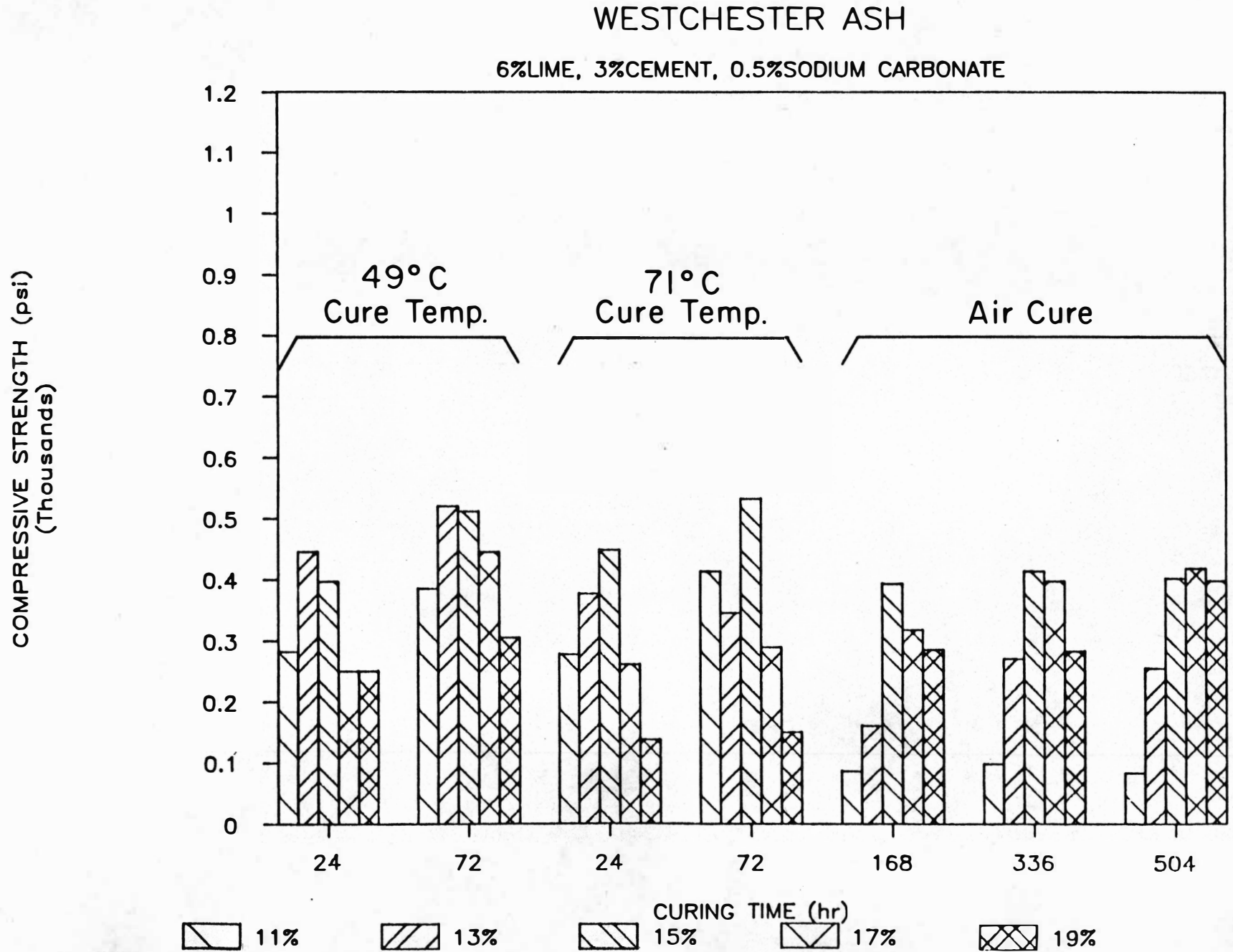


Figure 4.3

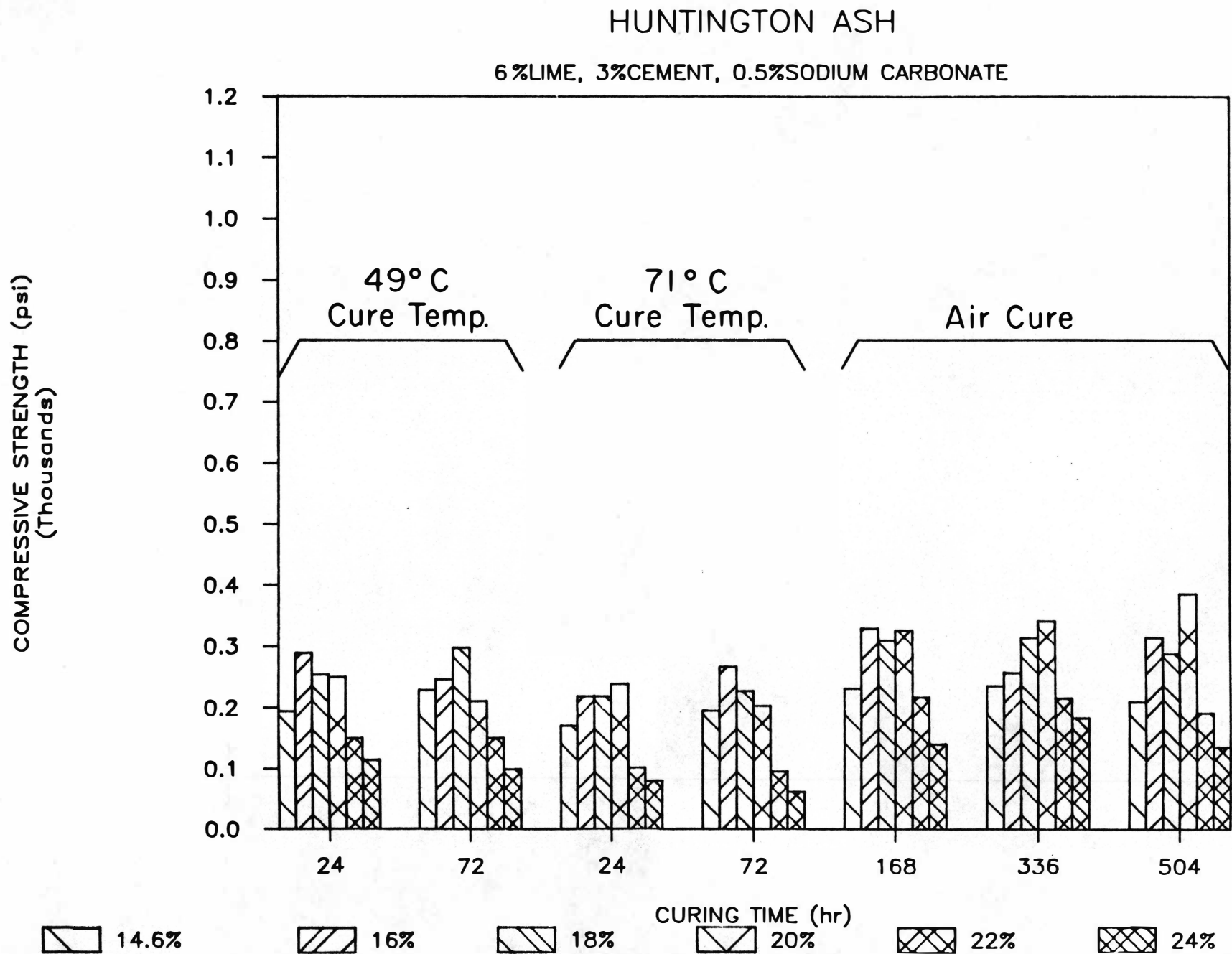


Table 4.2 and Figures 4.4 - 4.6 illustrates that little benefit with respect to the structural integrity is realized by increasing lime concentration. New York City and Huntington proctor samples exhibited a decline in compressive strength and only a slight increase in strength was noted for the Westchester samples. In all cases increasing the lime content did not alter the pH of the mix. It can be concluded that lime content in excess of 6% offers no significant structural improvement.

Sodium carbonate (Na_2CO_3), was used in this research for prior investigations by Harder et al., 1981, Vincent et al., 1961 and Roethel et al., 1985 has shown that this additive accelerates the strength gain of various coal ash mix designs. This investigation reveals that sodium carbonate has no effect on the compressive strength of stabilized incineration ash samples. Table 4.3 and Figures 4.7 - 4.9 indicates that New York City samples without sodium carbonate exhibit a slight increase in strength.

Portland cement (type 1) was added to the mix design and yielded proctor samples having the highest compressive strength. Samples fabricated using Westchester residue and 15% cement achieved a compressive strength of 1592 psi. Unfortunately by this time we were using the second batch of New York City fly ash which possessed properties that significantly reduced the structural integrity of the samples. Strengths measured for the New York City samples reached 400 psi, significantly lower than earlier samples though still acceptable for marine disposal. Data pertaining to this mix design is presented in Table 4.4 along with Figures 4.10 - 4.12.

One of the possible reasons the proctors fabricated using second batch of New York City fly ash failed to achieve a higher compressive strength was the significantly lower pH of the ash. In an attempt to improve the compressive strength a series of proctors were fabricated with 15% cement and 4% lime. While the lime did elevate the pH of these samples, no significant improvement in compressive strength was obtained. Table 4.5 and Figure 4.13 presents the data obtained from this investigation.

Table 4.2. Results of proctor fabrication using
9% lime, 3% cement, 0.5% Na₂CO₃.

NEW YORK CITY INCINERATION ASH			
PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
CF	17	15.9	386 - 625
CG	19	18.0	489 - 780
CH	21	20.3	637 - 949
CI	23	21.9	450 - 844

WESTCHESTER INCINERATION ASH			
PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
WF	17	17.9	183 - 454
WG	15	16.2	517 - 688
WH	13	14.7	269 - 645

HUNTINGTON INCINERATION ASH			
PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
HD	20	23.4	68 - 255
HE	22	27.4	80 - 147
HH	22	25.0	76 - 247
HJ	18	21.9	167 - 318
HK	16	20.2	171 - 285
HI	20	24.2	119 - 318

Figure 4.4

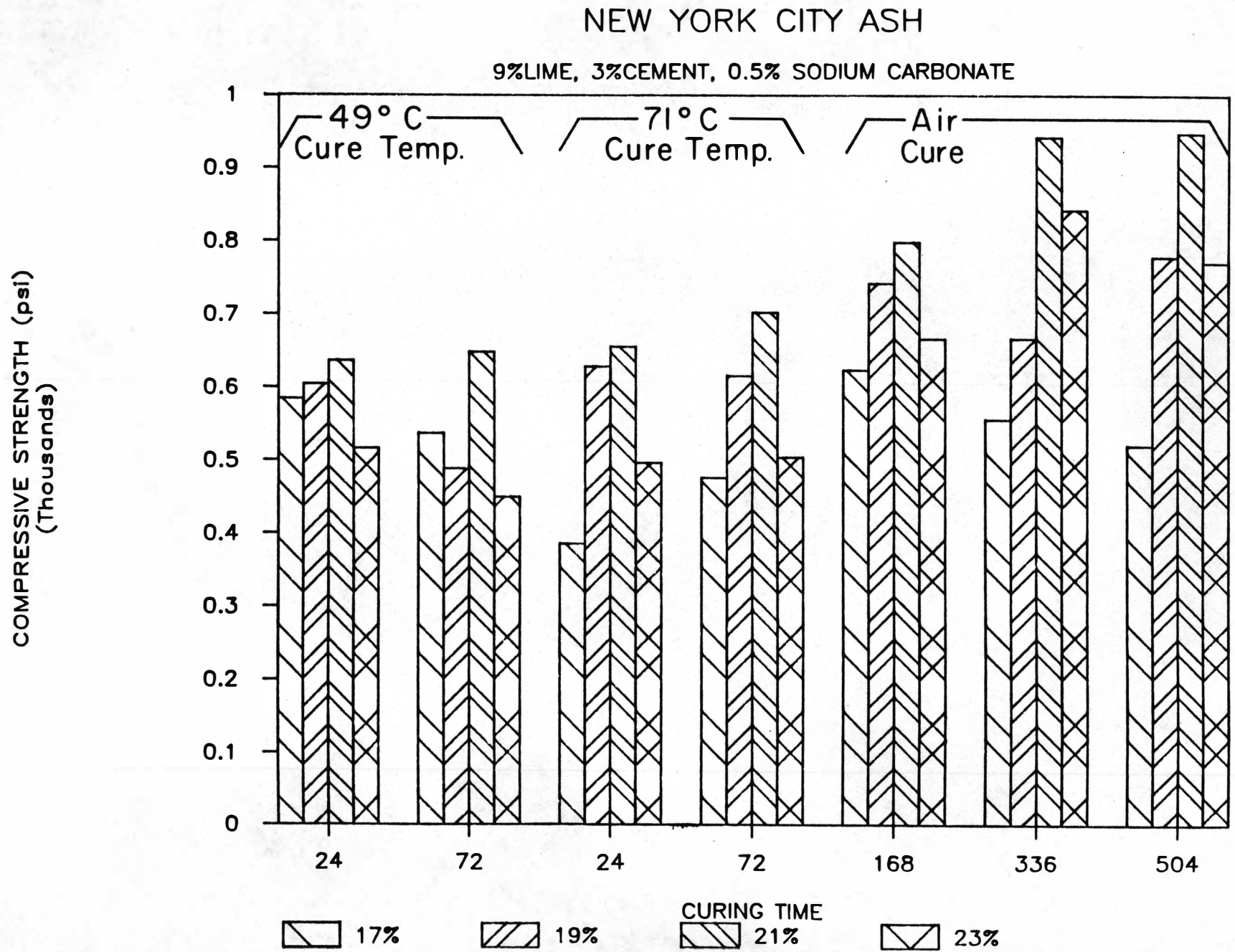


Figure 4.5

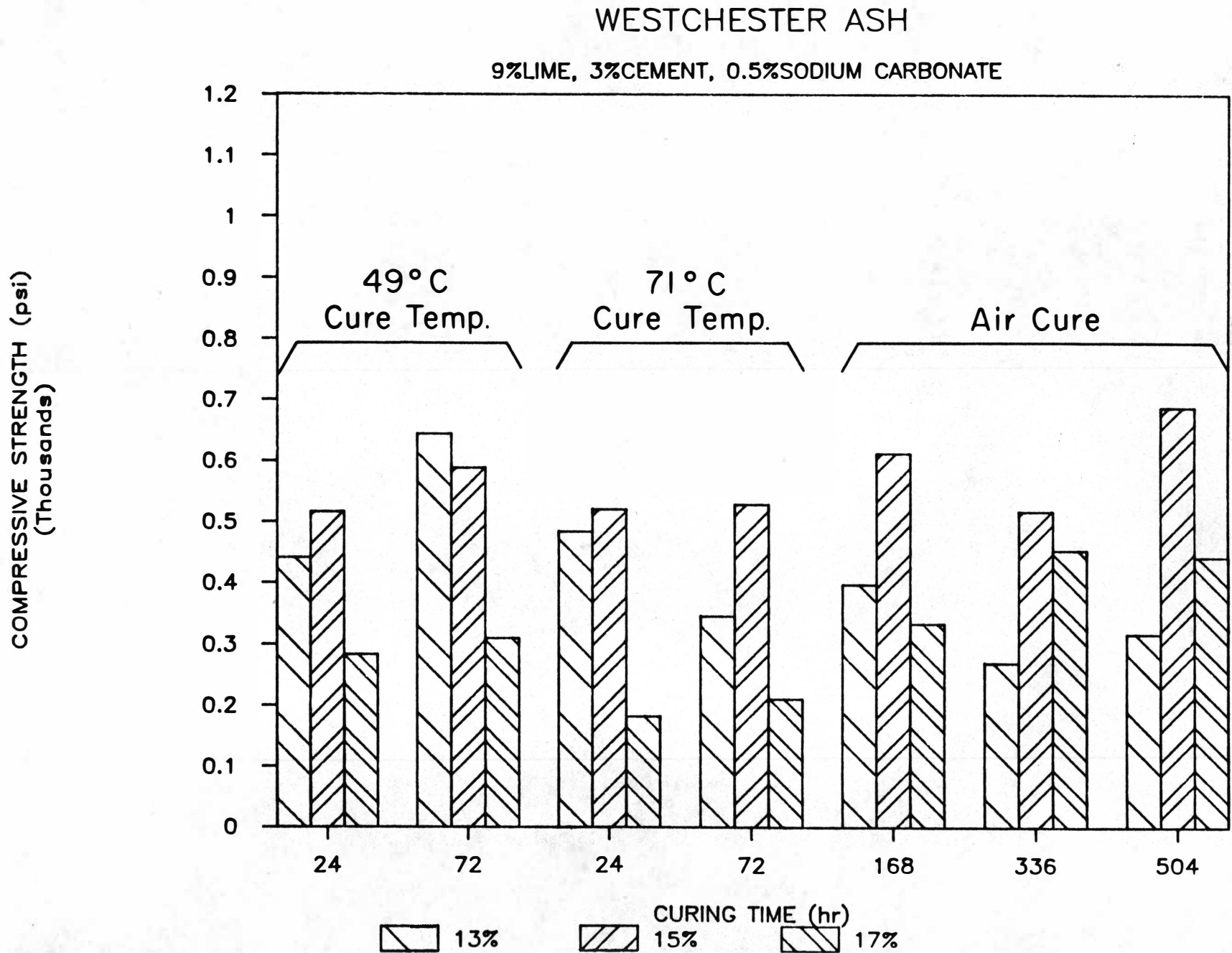


Figure 4.6

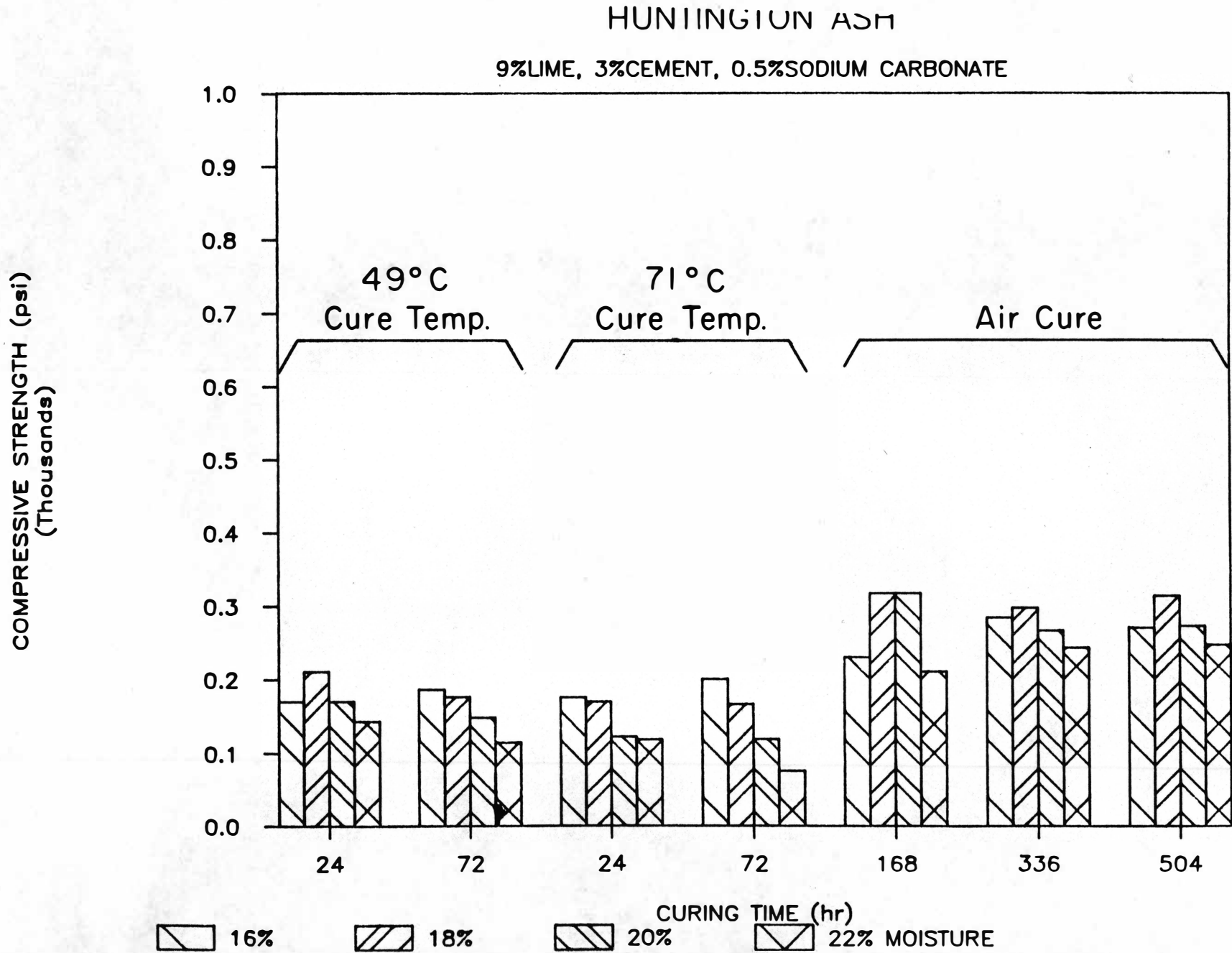


Table 4.3. Results of proctor fabrication using
6% lime, 3% cement.

NEW YORK CITY INCINERATION ASH

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
CJ	15	15.4	537 - 1122
CK	17	17.4	557 - 1194
CL	19	18.4	454 - 955
CM	21	20.5	312 - 891
CN	23	22.9	157 - 660

WESTCHESTER INCINERATION ASH

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
WI	17	16.3	199 - 450
WJ	15	14.9	217 - 410
WK	13	14.5	287 - 454
WR	11	10.5	101 - 398

HUNTINGTON INCINERATION ASH

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
HP	16	17.2	175 - 231
HQ	18	21.7	219 - 306
HR	20	22.0	163 - 314
HS	22	24.2	92 - 231

Figure 4.7

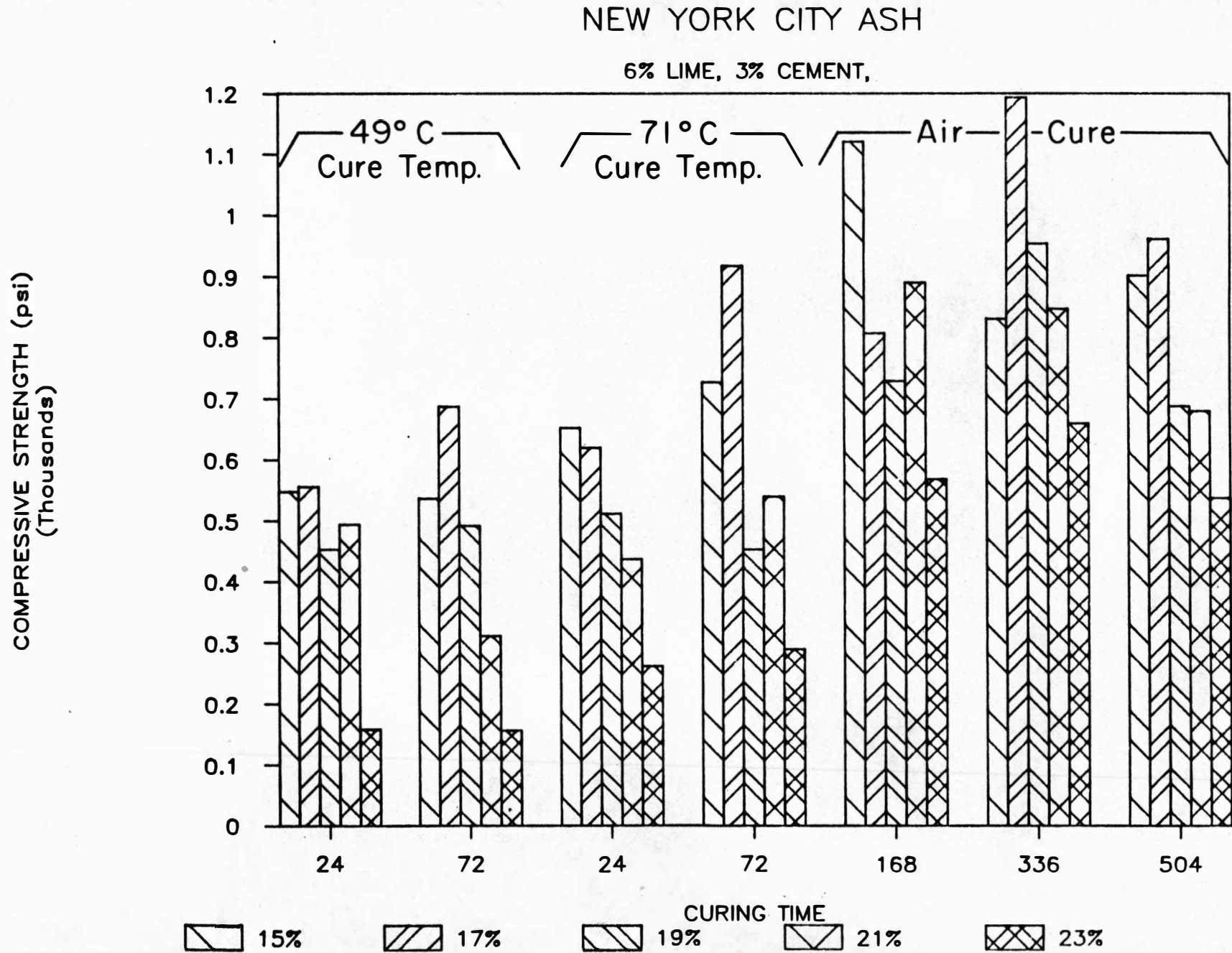


Figure 4.8

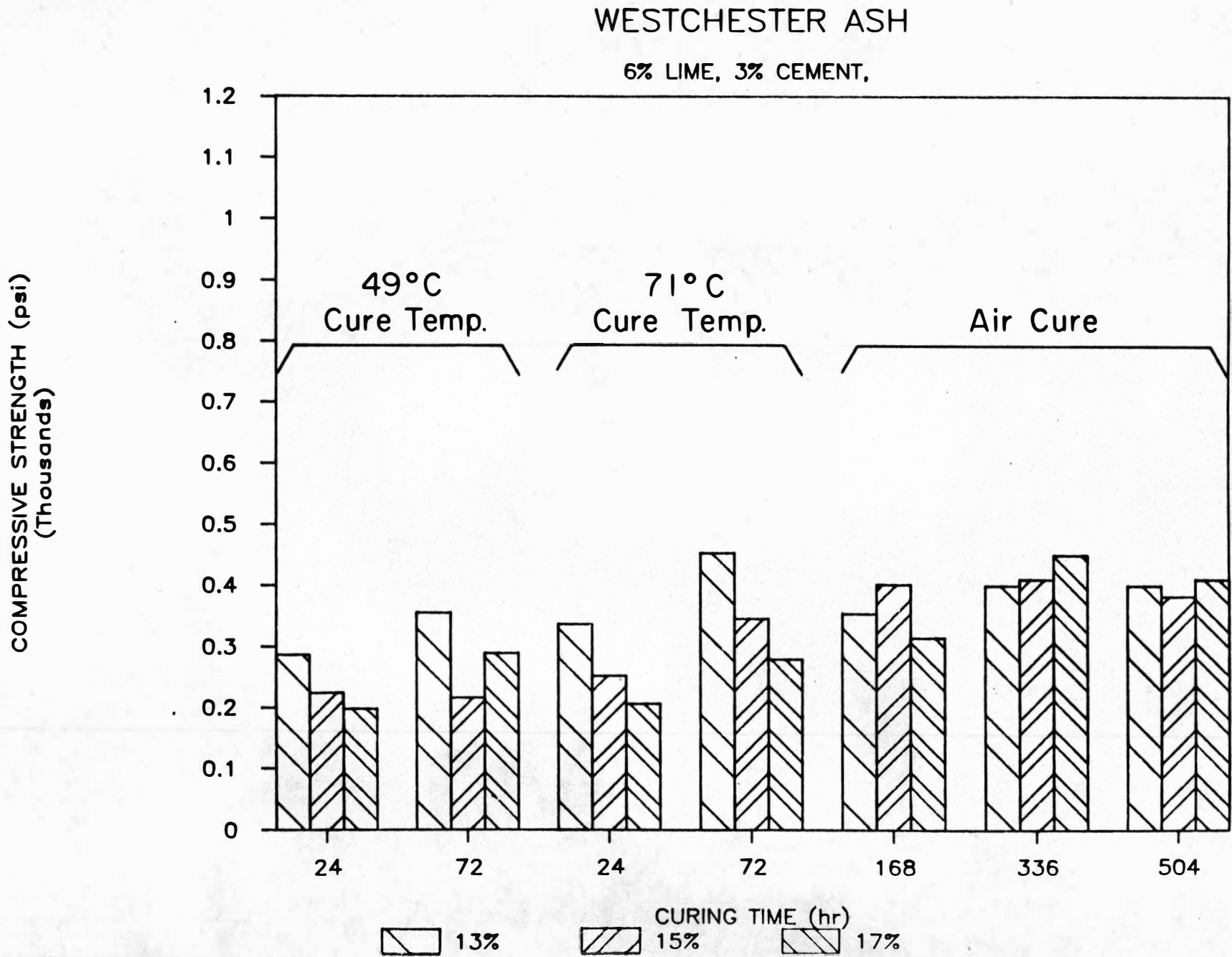


Figure 4.9

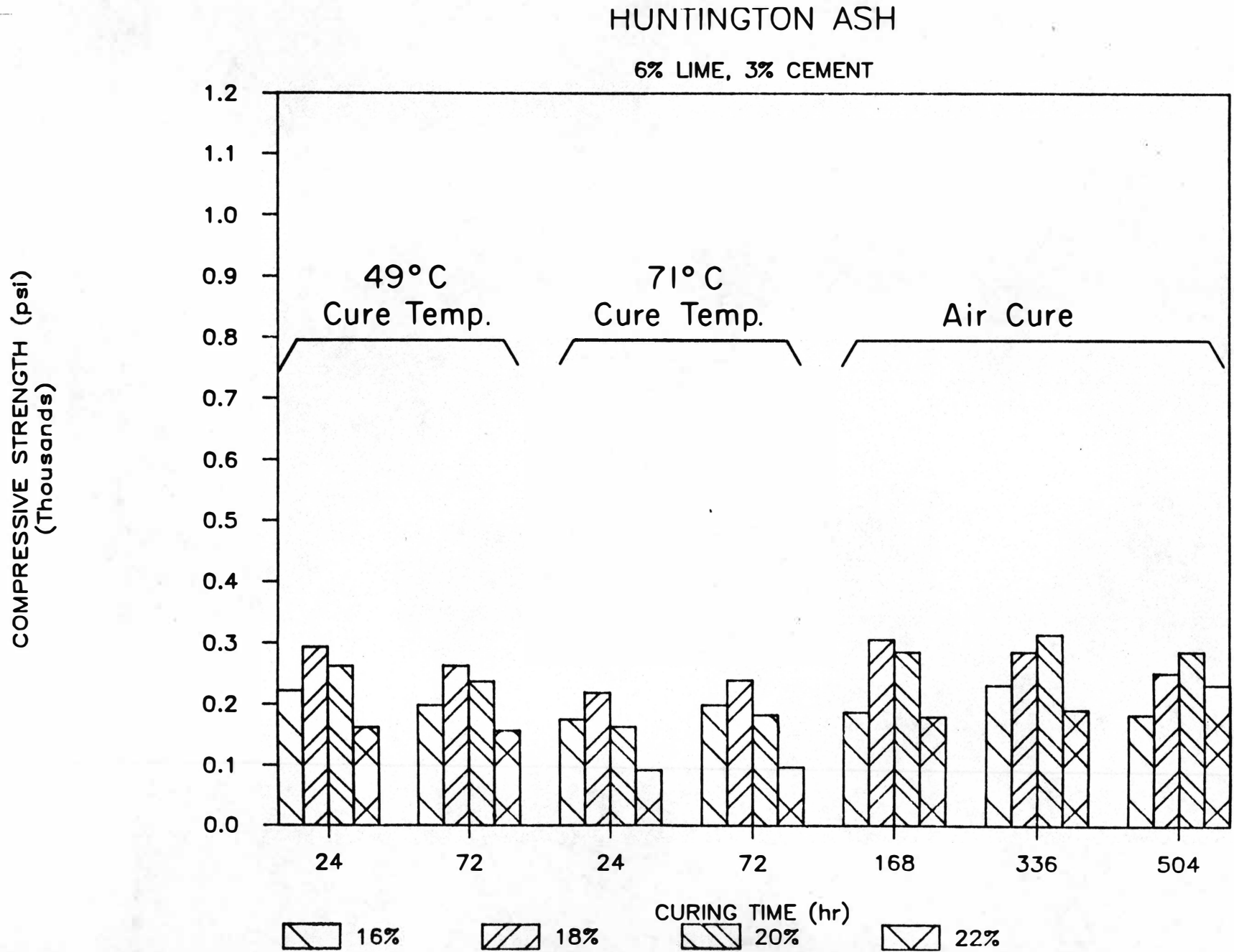


Table 4.4. Results of proctor fabrication using 15% cement.

NEW YORK CITY INCINERATION ASH*

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
CQ	15	14.4	251 - 398
CR	17	16.0	197 - 292
CS	19	18.2	119 - 247
CT	21	20.4	119 - 211
CY	23	22.4	88 - 390

HUNTINGTON INCINERATION ASH

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
HX	20	23.8	235 - 611
HY	18	22.1	330 - 569
HZ	16	19.1	322 - 466

WESTCHESTER INCINERATION ASH

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
WO	13	12.3	462 - 816
WP	15	14.1	513 - 1241
WQ	17	16.2	736 - 1377
WT	19	18.0	593 - 1592

* Represents ash collected on a second visit to the facility.

Figure 4.10

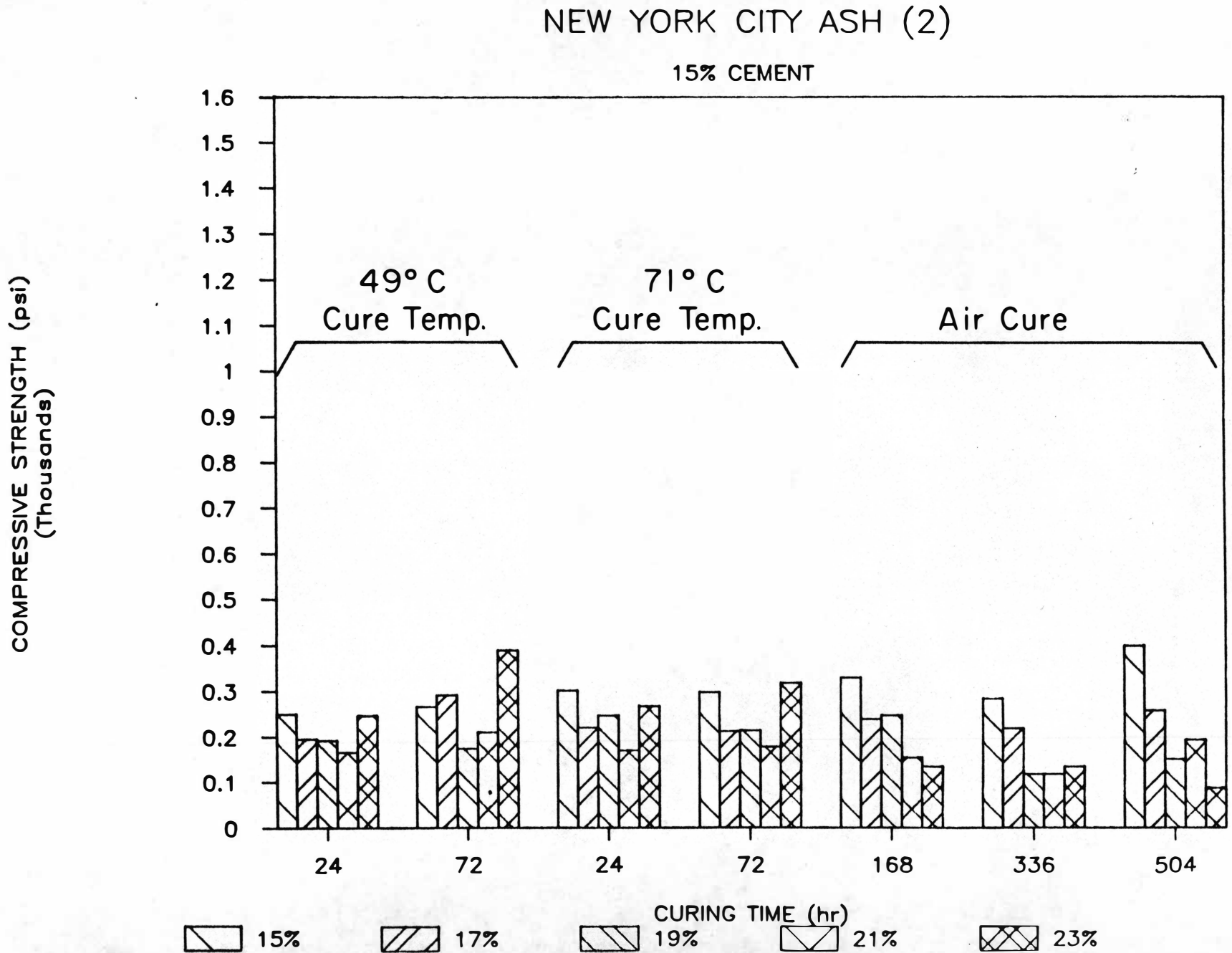


Figure 4.11

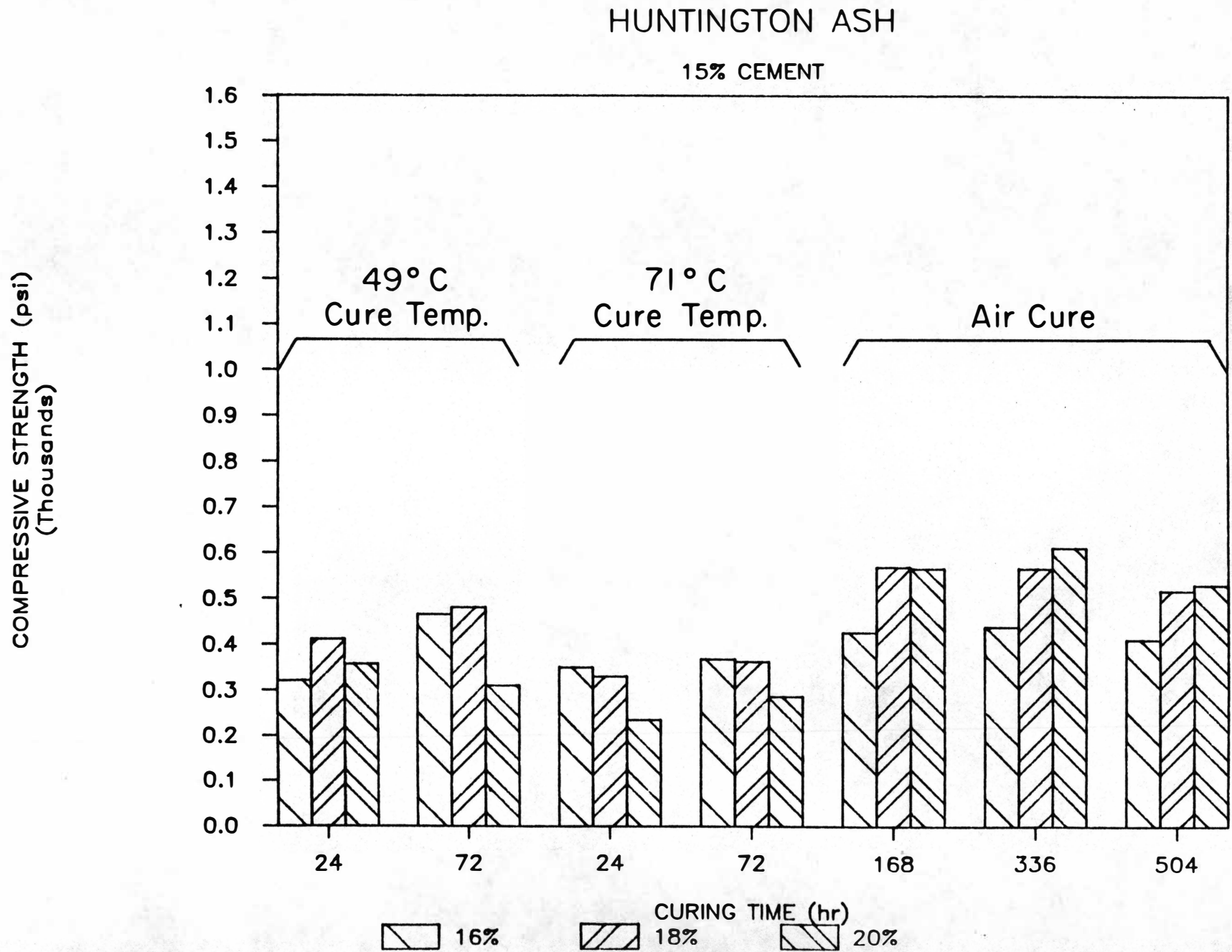


Figure 4.12

WESTCHESTER ASH

15% CEMENT

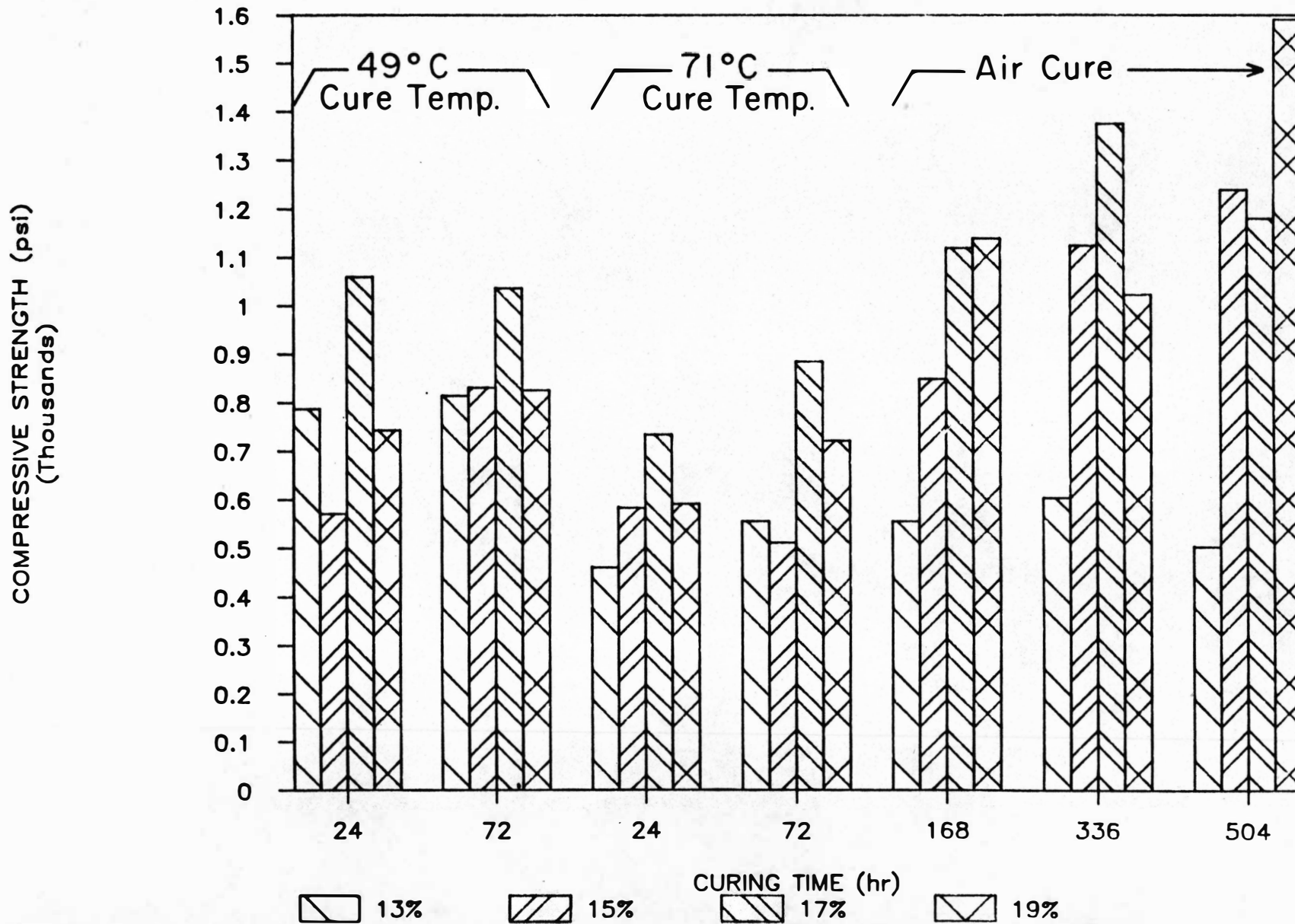


Table 4.5. Results of proctor fabrication using
4% lime, 15% cement.

NEW YORK CITY INCINERATION ASH*

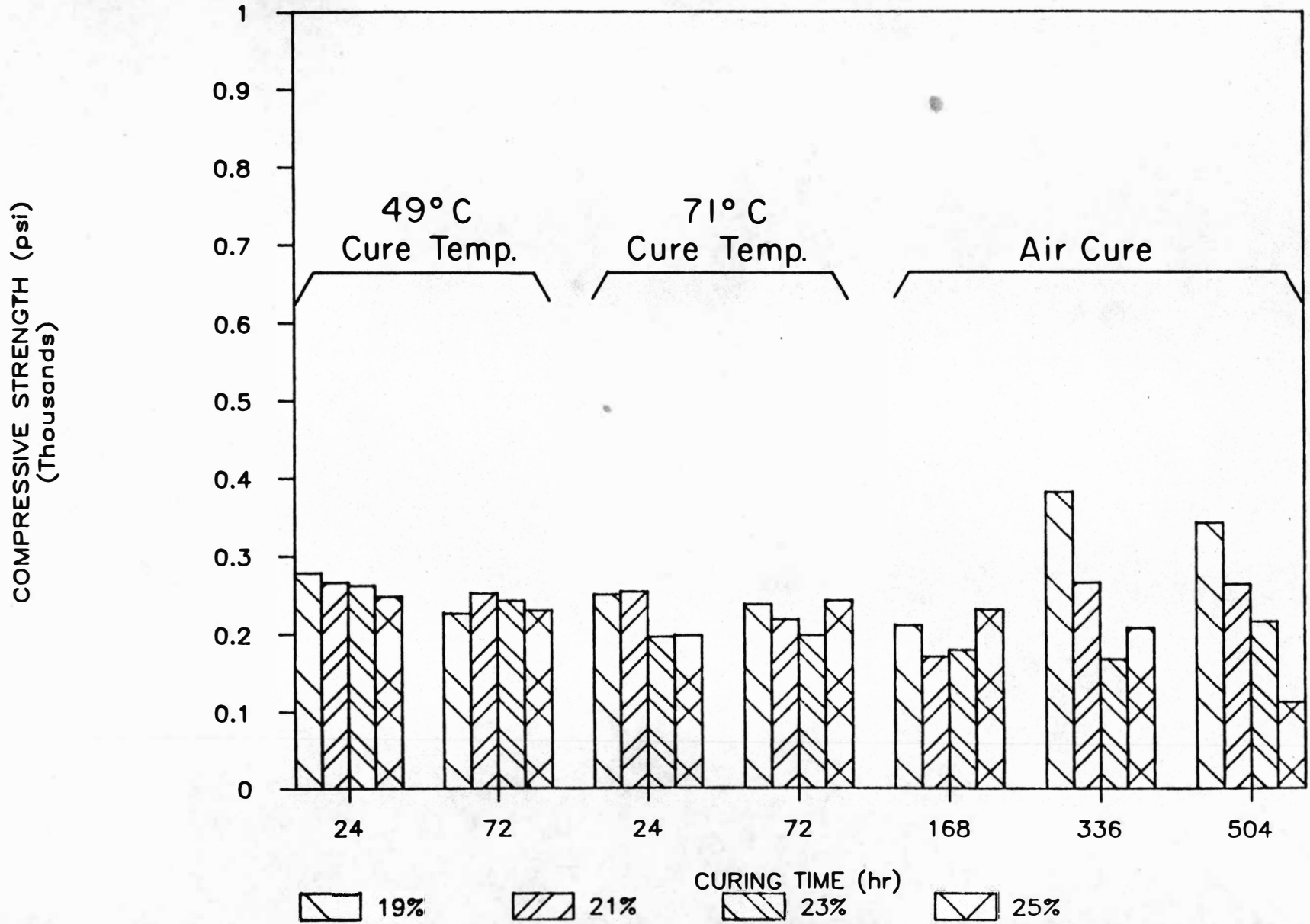
PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
CZ	19	17.9	211 - 382
CAA	21	19.1	171 - 267
CAB	23	21.3	167 - 263
CAC	25	23.5	111 - 249
CAD	29	27.2	80 - 207
CAE	31	29.8	24 - 195

* Represents ash collected on a second visit to the facility.

Figure 4.13

NEW YORK CITY ASH (2)

4% LIME, 15% CEMENT



Prior investigations with coal ash has shown that small amounts of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can significantly improve compressive strength. A series of proctor samples were fabricated using all three ashes and 6% lime, 6% gypsum and 3% cement. Significant deterioration in the structural integrity of the samples was observed. Table 4.6 and Figures 4.14 - 4.16 indicates that none of the samples achieved a strength of 300 psi, the minimum strength we accept for marine disposal.

GRAVEL ADDITIONS

The effects of adding small amounts of natural aggregates to the structural integrity of the proctor samples was examined. Two mix designs were fabricated; for both, Westchester residue and 15% Portland cement were added. For one mix design 15% of the total weight was represented by gravel sized aggregate. Proctor sized samples of both mix designs were fabricated following the same procedures described above. Once fabricated, the proctors were placed in constant temperature and humidity chambers for 24 h. They were then removed and allowed to air dry for a period of four days after which their compressive strength was tested.

Results are shown in Table 4.7. Strengths for the gravel addition proctors ranged from a 0% to 100% increase over blocks of the same ash and cure regime with no gravel addition. Optimum strength was achieved with 15% gravel and 11% water, a decrease from the 16% water used in optimum mixes without gravel.

Undoubtedly addition of gravel provides increased strength with lower optimum moisture content for the same mix and cure conditions. This would be expected since the stone that is added has a higher strength and nearly zero moisture content per unit volume. In addition, a greater percentage of the added cement is incorporated with the decreased ash fraction of the block as the relative volume of the added gravel increases. This results in better cementation of the ash which in part accounts for the enhanced structural integrity.

Table 4.6. Results of proctor fabrication using
6% lime, 3% cement, 6% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

NEW YORK CITY INCINERATION ASH

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
CU	17	16.5	115 - 199
CV	19	18.5	143 - 251
CW	21	20.9	135 - 219
CX	23	22.8	183 - 243

HUNTINGTON INCINERATION ASH

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
HT	20	21.0	199 - 294
HU	22	21.0	179 - 239
HV	24	25.6	147 - 199
HW	17	19.9	191 - 286
HAA	16	16.2	203 - 277
HAB	18	20.4	235 - 348
HAC	20	21.3	183 - 286

WESTCHESTER INCINERATION ASH

PROCTOR I.D.	CALC. MOISTURE	MEAS. MOISTURE	COMPRESSIVE STRENGTH
WL	13	12.8	0 - 231
WM	15	14.5	0 - 217
WN	17	16.1	0 - 255

Figure 4.14

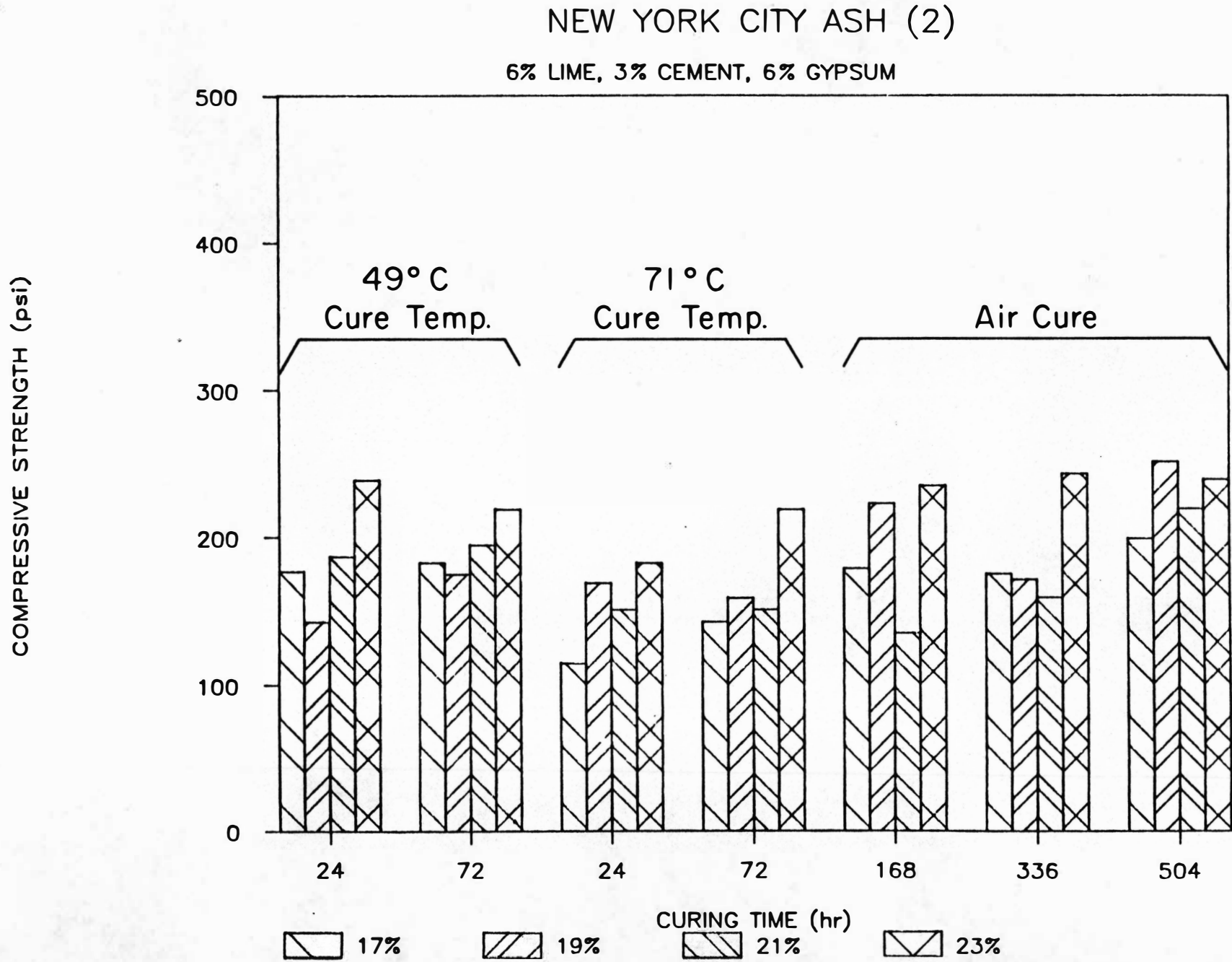


Figure 4.15

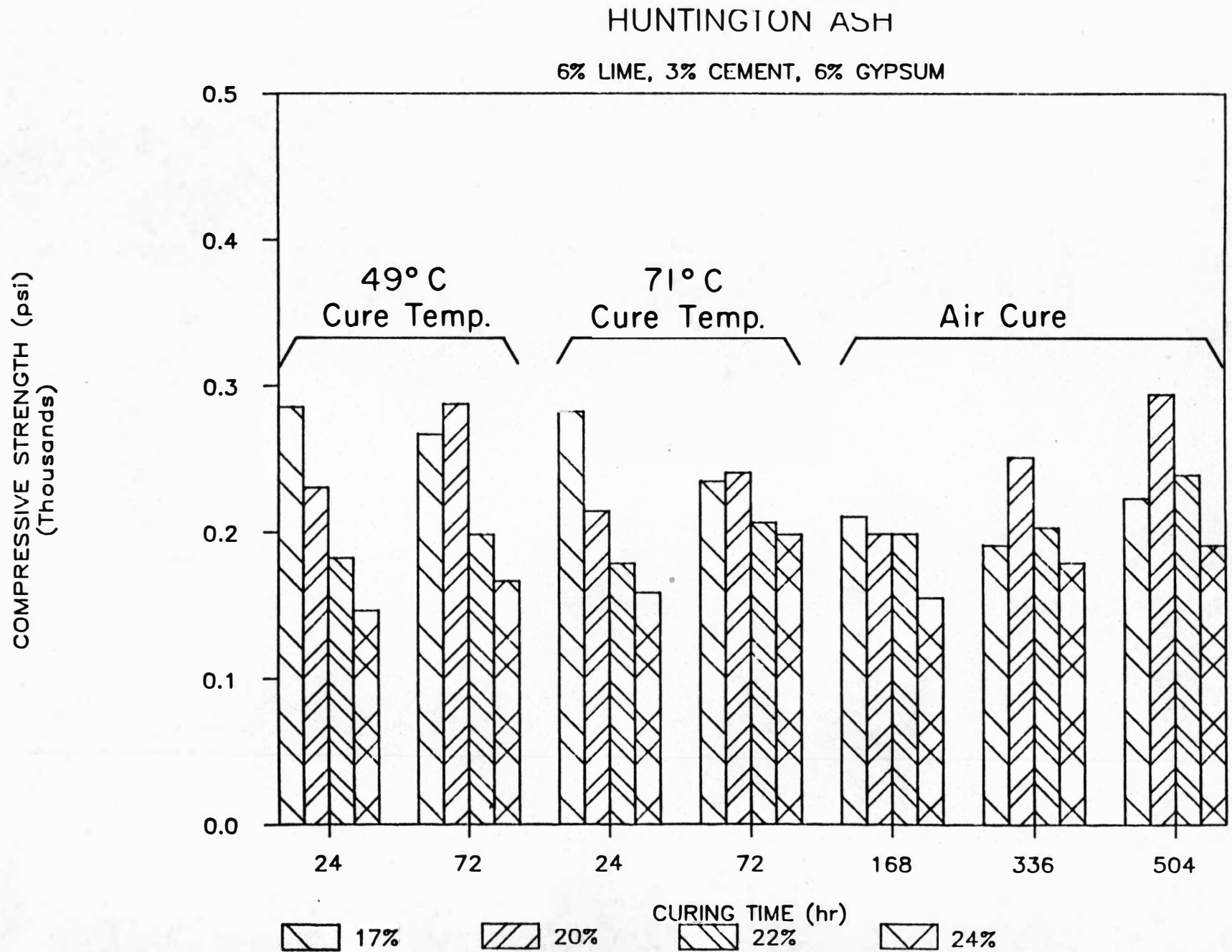


Figure 4.16

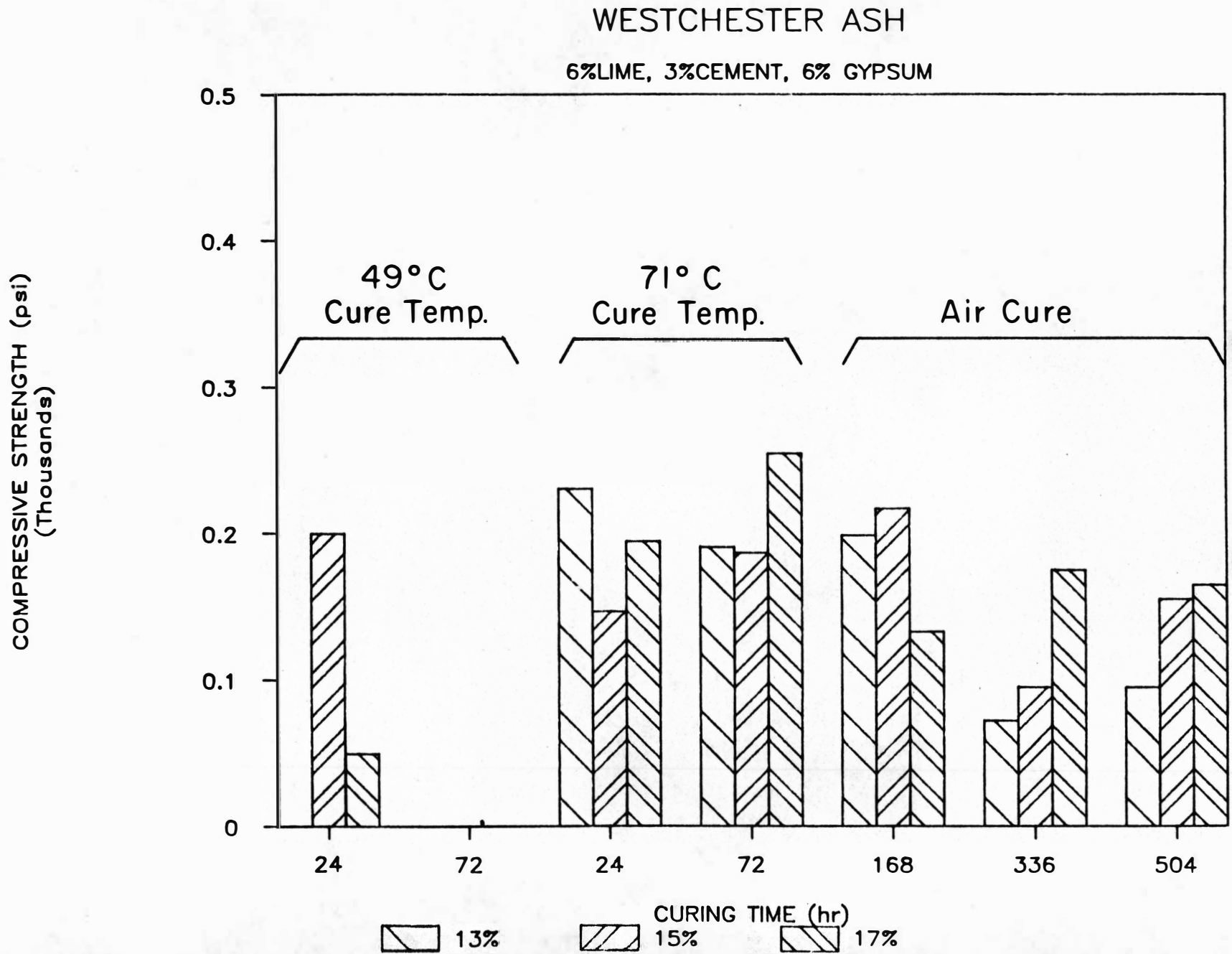


Table 4.7. Results of proctor fabrication using gravel additions.

<u>WESTCHESTER PROCTOR STRENGTHS WITHOUT GRAVEL</u>				
<u>PROCTOR I.D.</u>	<u>W03</u>	<u>WP3</u>	<u>WQ3</u>	<u>WT3</u>
INCINERATION RESIDUE (%)	72	70	68	66
CEMENT (%)	15	15	15	15
CALC. MOISTURE (%)	13	15	17	19
MEAS. MOISTURE (%)	13	14	16	19
GRAVEL (%)	0	0	0	0
COMPRESSIVE STRENGTH (psi)	462	585	736	593

<u>WESTCHESTER PROCTOR STRENGTHS WITH GRAVEL</u>				
<u>PROCTOR I.D.</u>	<u>WEG</u>	<u>WFG</u>	<u>WDG</u>	<u>WBG</u>
INCINERATION RESIDUE (%)	59	58	56	61
CEMENT (%)	15	15	15	15
CALC. MOISTURE (%)	11	13	15	17*
MEAS. MOISTURE (%)	11	14	16	9*
GRAVEL (%)	15	14	14	7
COMPRESSIVE STRENGTH (psi)	1029(±14)	752(±28)	736(±24)	511(±26)

* Value lower than calculated due to a large percentage of gravel in the moisture sample.

FULL SCALE PRODUCTION OF TEST PROCTORS

Having developed methods for fabricating proctors of acceptable quality, the next task was to begin full scale production of test proctors to be used in the second phase of this investigation. Thirty proctor sized cylinders of each residue were fixated with 15% Portland cement. Table 4.8 describes the mix design and proctor curing conditions for each residue examined and the resulting compressive strength measured for three randomly selected samples. All three solidified samples are presented in Figure 4.17.

These mixes will be subjected to additional physical and chemical tests including permeability, porosity, ASTM and EPA leachate tests, bulk chemical composition and x-ray diffraction.

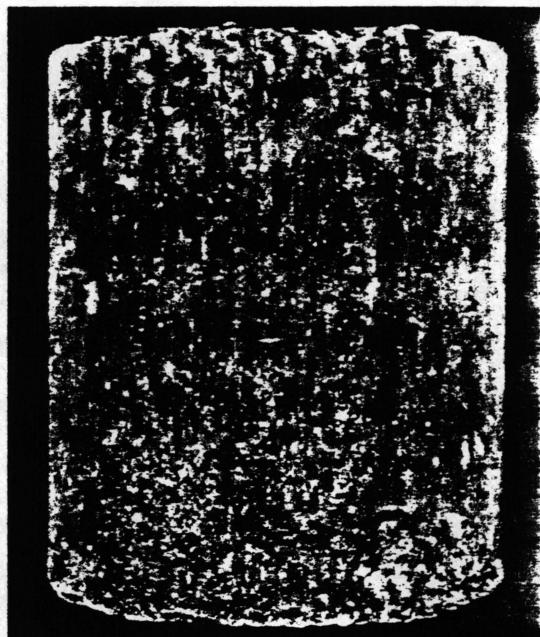
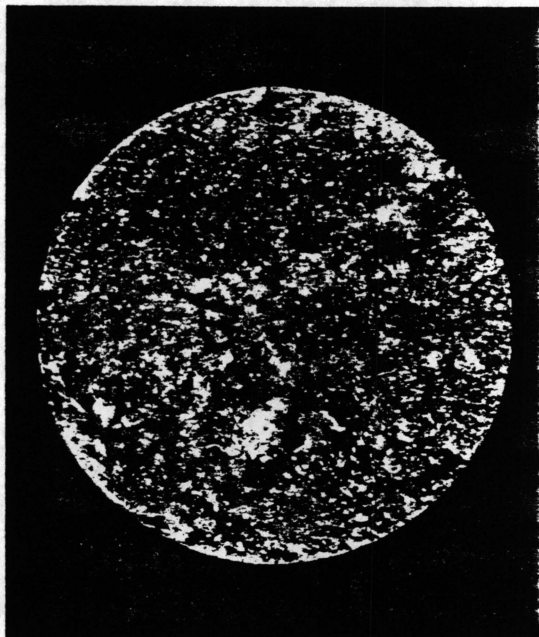
Table 4.8. Formulation of the optimum mixes.

RESIDUE	NEW YORK CITY*	HUNTINGTON	WESTCHESTER
INCINERATION RESIDUE (%)	62	67	68
CEMENT (%)	15	15	15
MOISTURE (%)	23	18	17
CURING TEMPERATURE ($^{\circ}$ C)	49	AIR (23)	49
CURING TIME (h)	72	168	24
COMPRESSIVE STRENGTH (psi)	228(\pm 43)	455(\pm 51)	1230(\pm 59)

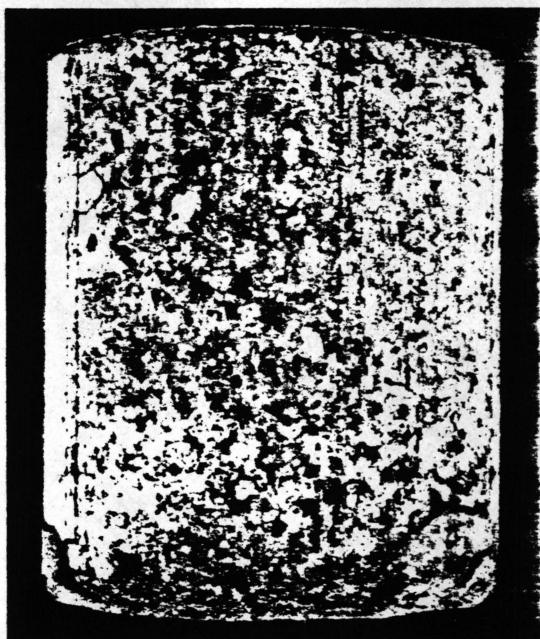
Figure 4.17. Solidified proctors of the three optimum mixes.

- a) Stabilized Huntington Incineration Residue
- b) Stabilized New York City Incineration Ash
- c) Stabilized Westchester Incineration Residue

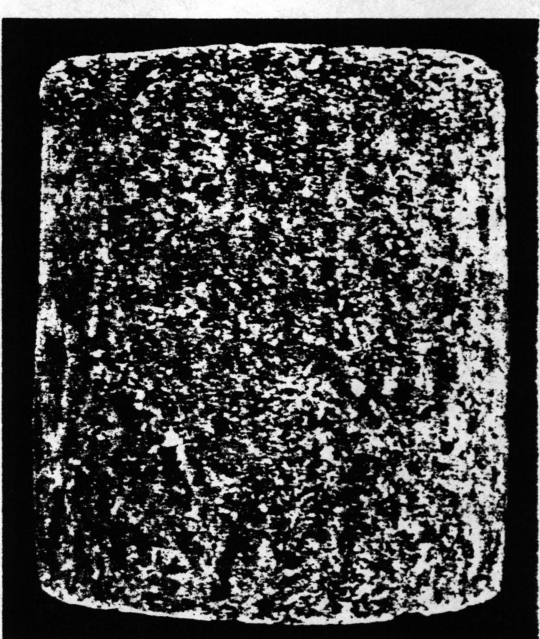
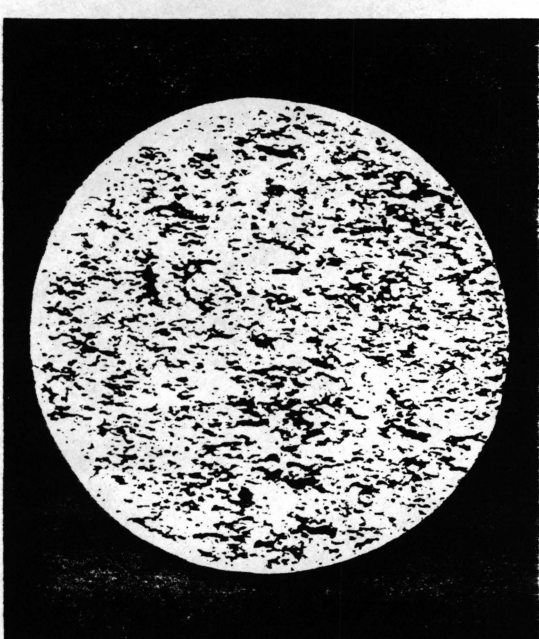
a)



b)



c)



Section 5

PHYSICAL CHARACTERIZATION OF THE STABILIZED RESIDUE

Porosity

Porosity of the optimum mixes was determined in accordance with ASTM C642-82 "Standard Test Method for Specific Gravity, Absorption and Voids in Hardened Concrete". Blocks were sectioned into three equal layers - top, middle, and bottom, with the middle layer reserved for the porosity study and the end sections used in the permeability investigation. Specific gravity, % absorption and % voids were calculated using the following equations:

$$\begin{aligned} \text{Absorption after immersion, \%} &= [(B-A)/A] * 100 \\ \text{Absorption after immersion and boiling, \%} &= [(C-A)/A] * 100 \\ \text{Bulk specific gravity, dry} &= A/(C-D) \\ \text{Bulk specific gravity after immersion} &= B/(C-D) \\ \text{Bulk specific gravity after immersion and boiling} &= C/(C-D) \\ \text{Apparent specific gravity} &= A/(A-D) \\ \text{Volume of permeable pore space (voids), \%} &= [(C-A)/(C-D)] * 100 \end{aligned}$$

Where:

- A = Weight (in air) of oven-dried sample; grams
- B = Weight (in air) of sample after immersion; grams
- C = Weight (in air) of sample after immersion and boiling; grams
- D = Weight (in water) of sample after immersion and boiling; grams

Samples were oven-dried at $100 \pm 5^\circ\text{C}$ for 24 h, then removed and allowed to cool to a room temperature of 20°C in a desiccating chamber, then weighed. This procedure was repeated until check weights were obtained, i.e. a difference less than .5% of the lesser weight exists between the two measurements; approximately 48 h. Saturated weight was obtained by placing the blocks into water at room temperature for 24 h increments. Blocks were then removed from the water and towel-dried to eliminate any surface moisture and weighed. This procedure was repeated until check weights were obtained showing an increase no greater than .5% of the heavier weight; approximately 72 h. Next the block was boiled in tap water for 5 h and allowed to cool for 24 h to room temperature. Surface moisture was removed with a towel and the sample weighed. Finally, the block was suspended from a monofilament line and weighed in water.

Results from ASTM C642-82 test can be found in Table 5.1 and the results of the calculations for specific gravity, absorption and voids can be found in Table 5.2. The volume of permeable pore space ranged from 35.77% to 47.92%. City block samples had the highest amount of pore space averaging 47.5%. This value was approximately 7.7% greater than Huntington blocks and 10.8% greater than Westchester blocks.

The percent pore space in the optimum mix blocks provides an indication of the extent to which cementitious crystals have permeated the void space between ash particles. These results parallel the compressive strength values of the optimum mix blocks. Westchester ash blocks have the highest compressive strength and lowest percent pore space while the City ash blocks have the lowest strength and highest percent pore space.

Permeability

Permeability of the optimum mixes was determined by the Darcy falling-head method (Harder *et al.*, 1981) shown in Figure 5.1. The proctors were cut into three equal sections approximately 1.5 inches in height with the top and bottom layers being used for the permeability study. The sections were ground with sand paper to reduce their diameter

Table 5.1. Measured values for ASTM C642-82: Test for specific gravity, % absorption and % voids of optimum mixes.

Proctor Number	Original Weight (g)	A	B	C	D
		Oven Dried Weight (g)	Saturated Wt. After Immersion (g)	Saturated Wt. After Boiling (g)	Immersed Weight (g)
COE5	395.75	370.50	497.54	511.00	214.45
COC5	385.37	364.53	508.19	511.90	204.35
HA5	494.93	475.93	573.04	593.80	287.85
HC3	456.84	439.60	535.27	556.70	265.81
WAB5	527.55	502.97	591.97	615.04	301.70
WAD1	498.23	474.83	564.13	586.55	285.92

- a. All proctors are middle portions.
- b. Total number of hours dried for Oven Dried Weight equal 48.
- c. Total number of hours soaked for Saturated Weight equal 72.
- d. Total number of hours boiled equal 5.

Table 5.2. A summary of specific gravity, % absorption and % voids for optimum mixes: ASTM C642-82.

Proctor Number	Absorption after Immersion (%)	Absorption after Immersion and Boiling (%)	Bulk Specific Gravity, Dry	Bulk Specific Gravity after Immersion	Bulk sp. Gravity after Immersion and Boiling	Apparent Specific Gravity	Vol. of Permeable Pore Space (Voids) (%)
COE5	34	38	1.25	1.68	1.72	2.37	47.38
COC5	39	40	1.19	1.65	1.66	2.28	47.92
HA5	20	25	1.56	1.87	1.94	2.53	38.53
HC3	22	27	1.51	1.84	1.91	2.53	40.26
WAB5	18	22	1.61	1.89	1.96	2.50	35.77
WAD1	19	24	1.58	1.88	1.95	2.51	37.16

to fit inside of a 4 inch i.d. PVC pipe. Each section was dusted with compressed air to remove any adhering dust particles resulting from the sanding and cutting of the proctors. Each specimen was then epoxied into the base of a 1 foot high translucent PVC pipe with PC-7 epoxy. A PVC threaded male collar was cemented to the bottom of the column and a PVC end cap fitted with a nylon hose nipple was threaded onto the male collar. Elutriates from the permeability column passed through the nylon nipple, through a length of Tygon tubing, and into a covered plastic beaker for collection. To begin the test, .45 μ m filtered seawater was added to the columns. A plastic bag was attached to the open end of the columns to prevent evaporation. Starting time and height of the water column were recorded. Water column heights for each column were next recorded when a measurable difference in height could be discerned. The coefficients of permeability of the optimum mixes in seawater were determined by the following equation:

$$K = [(Q*L)/(H_0*A*T)] * \ln(H_i/H_t)$$

where:

- K = coefficient of permeability, cm/sec
- Q = volume of elutriate, cm³
- L = height of proctors, cm
- A = area of proctor, cm²
- T = test time between readings, sec
- H_i = initial height of water column, cm
- H_t = height of water column at time t, cm
- H₀ = H_i - H_t, cm

The permeability of the top and bottom layers of optimum mix proctors from Westchester, Huntington and NY City incineration ash was determined in duplicate. Results are presented in Table 5.3 and in Figures 5.2 - 5.4. All samples show a decrease in permeability with time with the top sections always less permeable than the bottom sections for each ash type. Also, all bottom sections show higher standard deviation values than the top sections, indicating poor reproducibility in the bottom

Figure 5.1 Darcy falling head permeability apparatus.

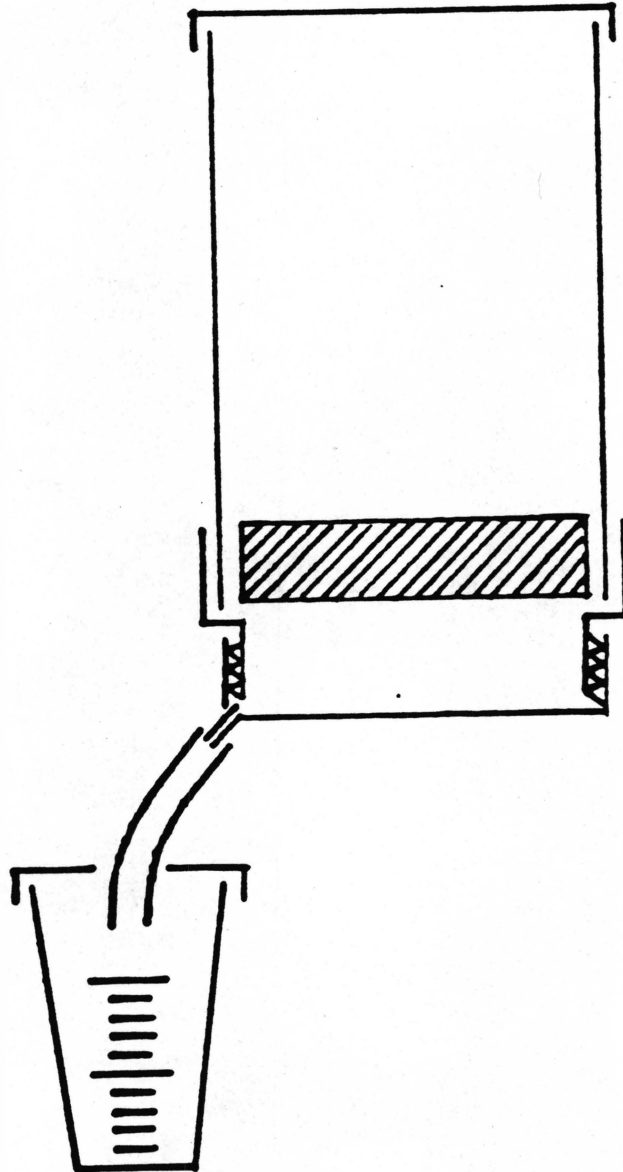


Table 5.3. Permeability coefficients^a for proctor sections.

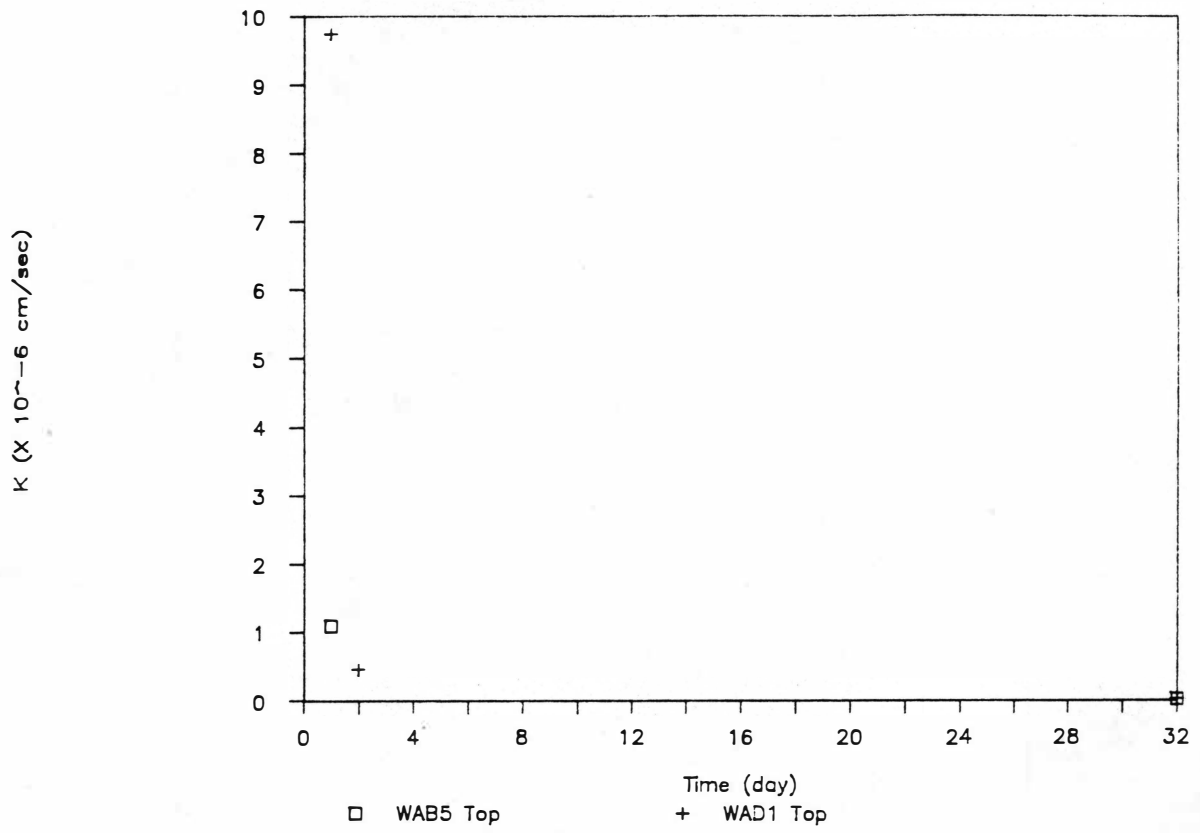
	<u>TOP</u>	<u>BOTTOM</u>
COC5	1.21×10^{-7}	1.35×10^{-5}
COE5	1.31×10^{-7}	7.65×10^{-6}
AVERAGE	$1.26(\pm 0.07) \times 10^{-7}$	$1.06(\pm 0.41) \times 10^{-5}$
HA5	5.96×10^{-8}	6.22×10^{-7}
HA3	1.51×10^{-7}	7.02×10^{-5}
AVERAGE	$1.05(\pm 0.65) \times 10^{-7}$	$3.54(\pm 4.92) \times 10^{-5}$
WAB5	2.05×10^{-8}	1.50×10^{-8}
WAD1	2.29×10^{-8}	3.56×10^{-8}
AVERAGE	$2.17(\pm 0.17) \times 10^{-8}$	$2.53(\pm 1.46) \times 10^{-8}$

a. Unit is cm/sec.

b. Numbers in parentheses denote standard deviations.

Figure 5.2 Permeability of Westchester optimum mix.

Coefficient of Permeability (K)



Coefficient of Permeability (K)

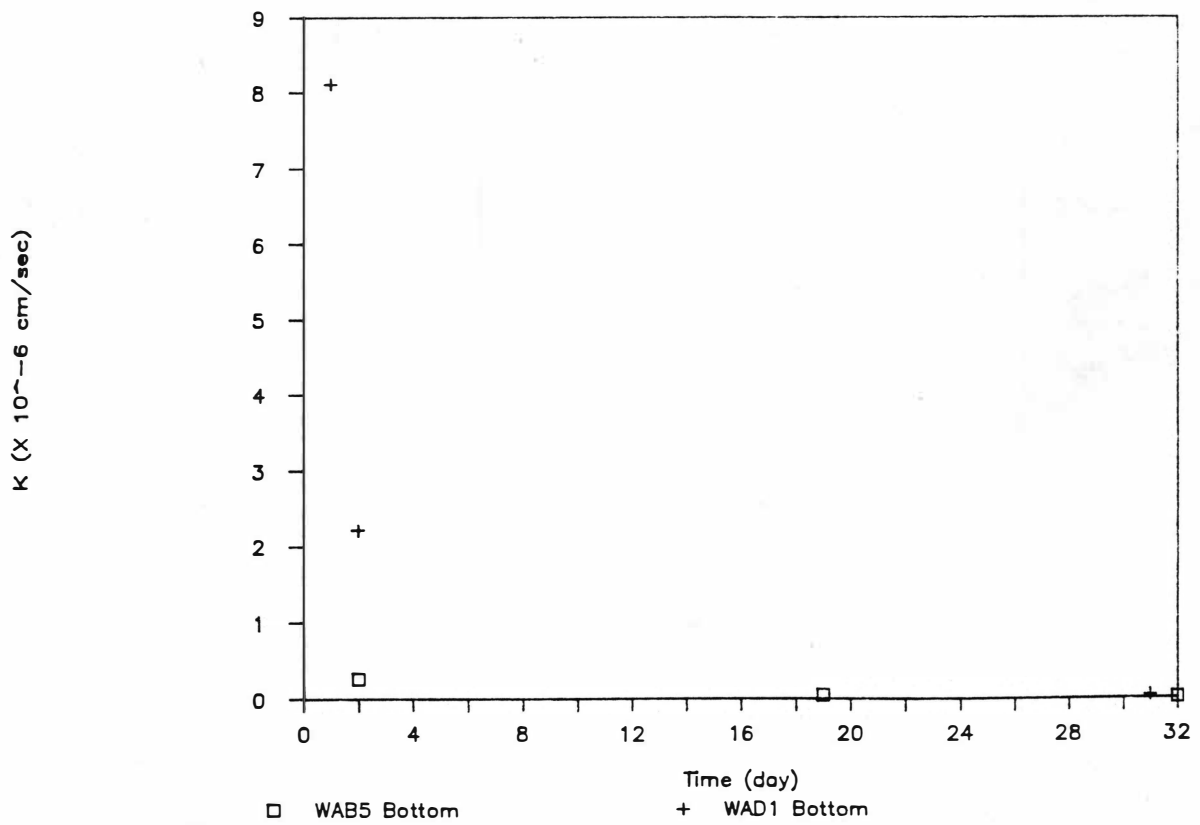
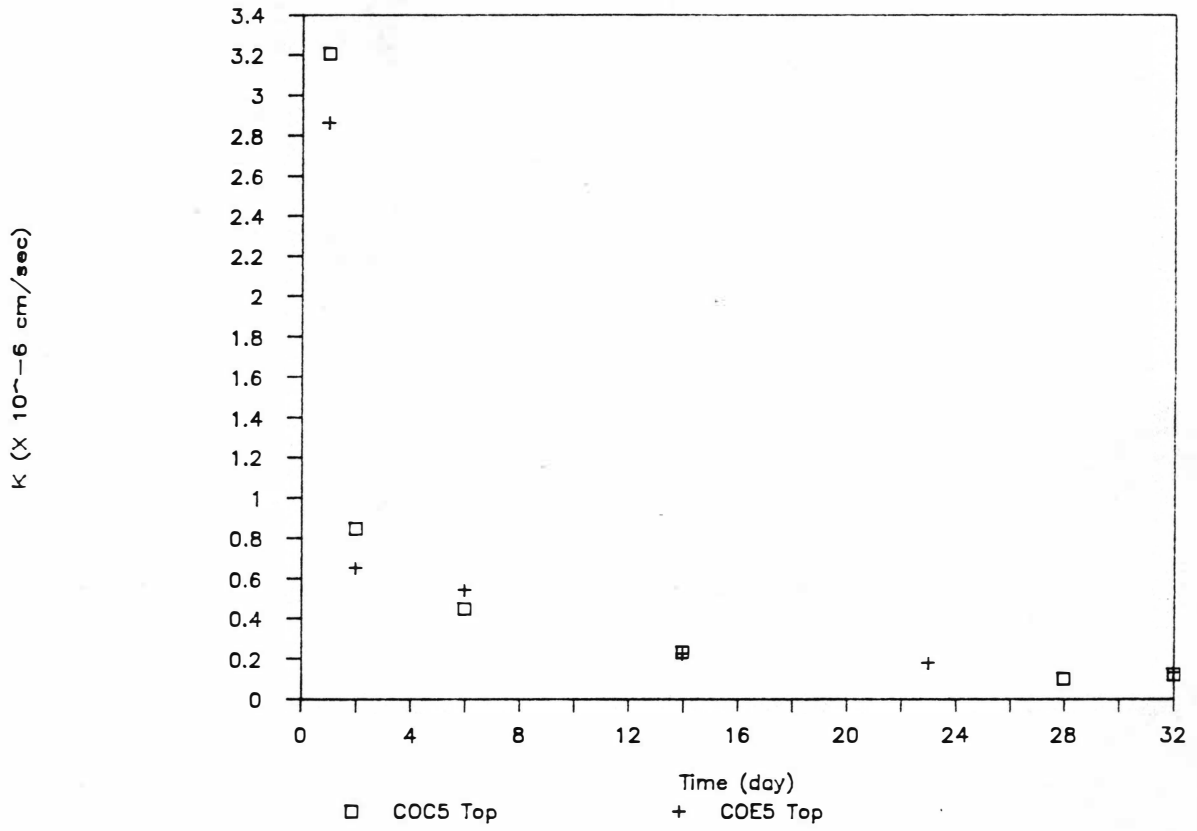


Figure 5.3 Permeability of New York City optimim mix.

Coefficient of Permeability (K)



Coefficient of Permeability (K)

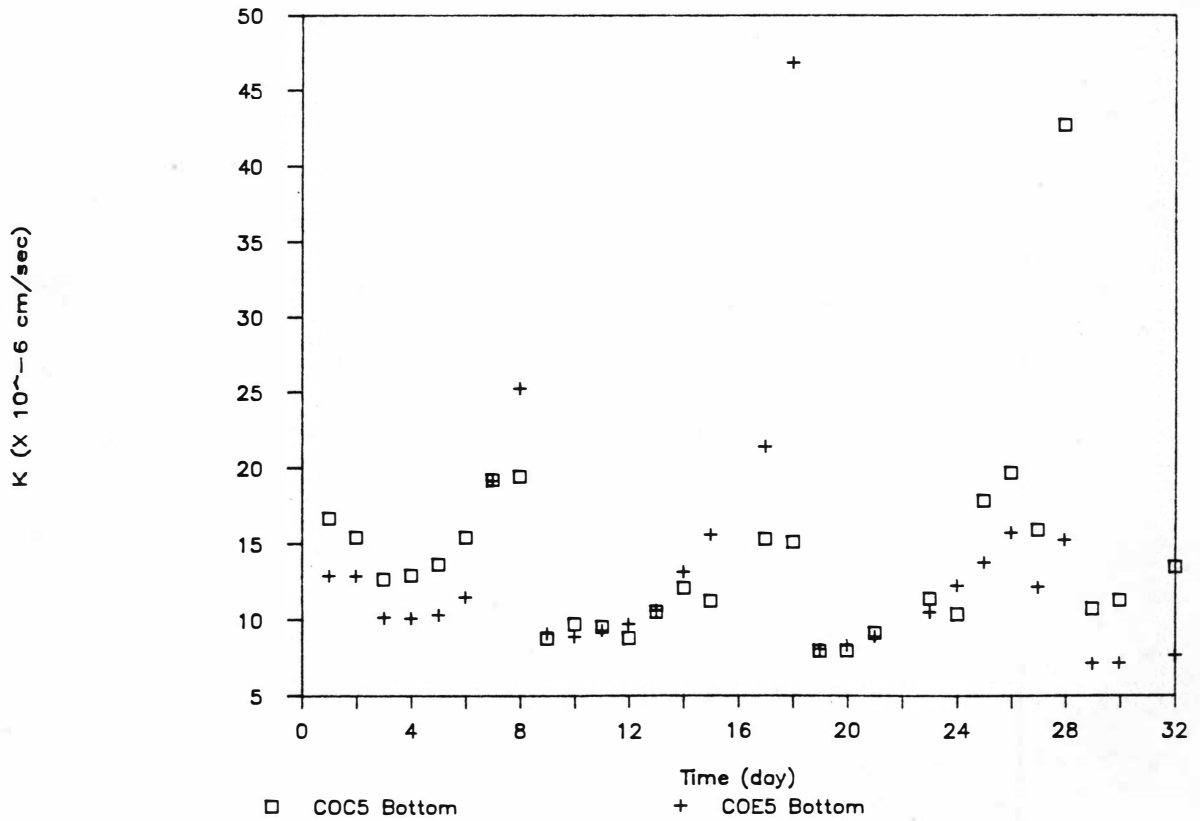
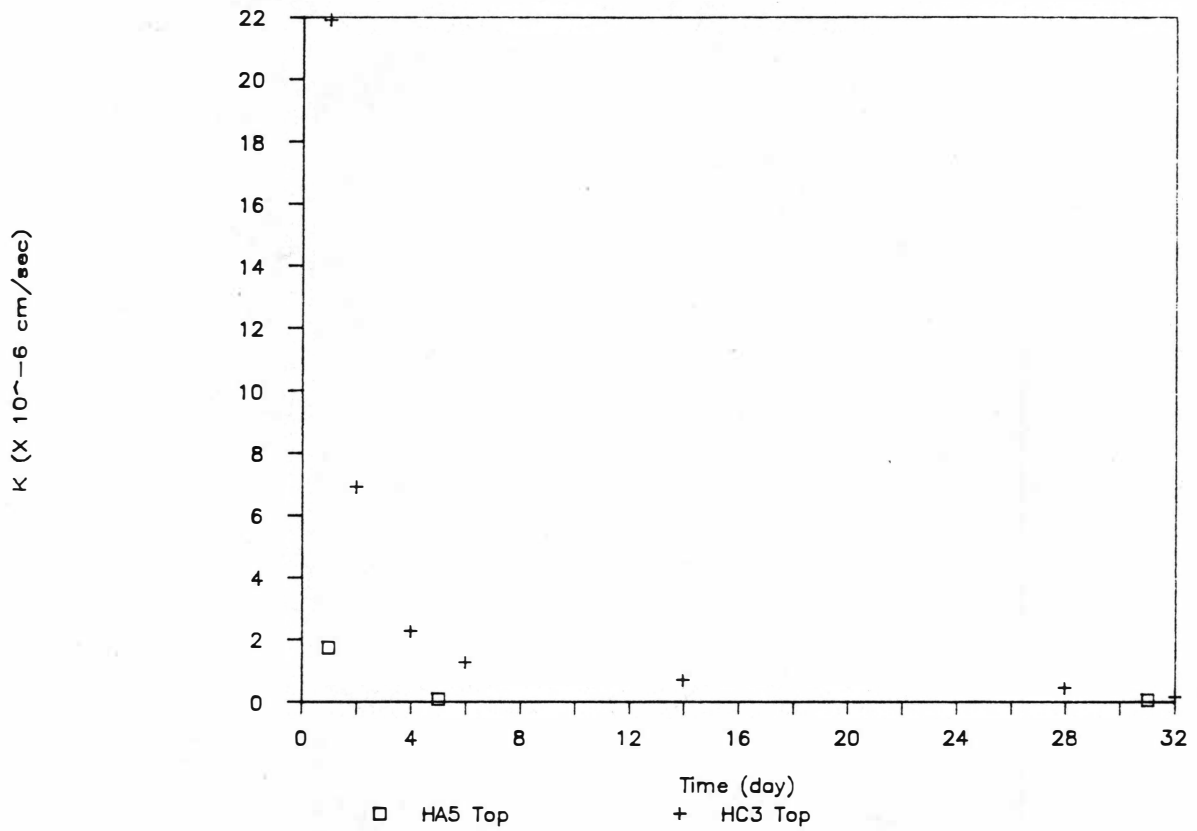
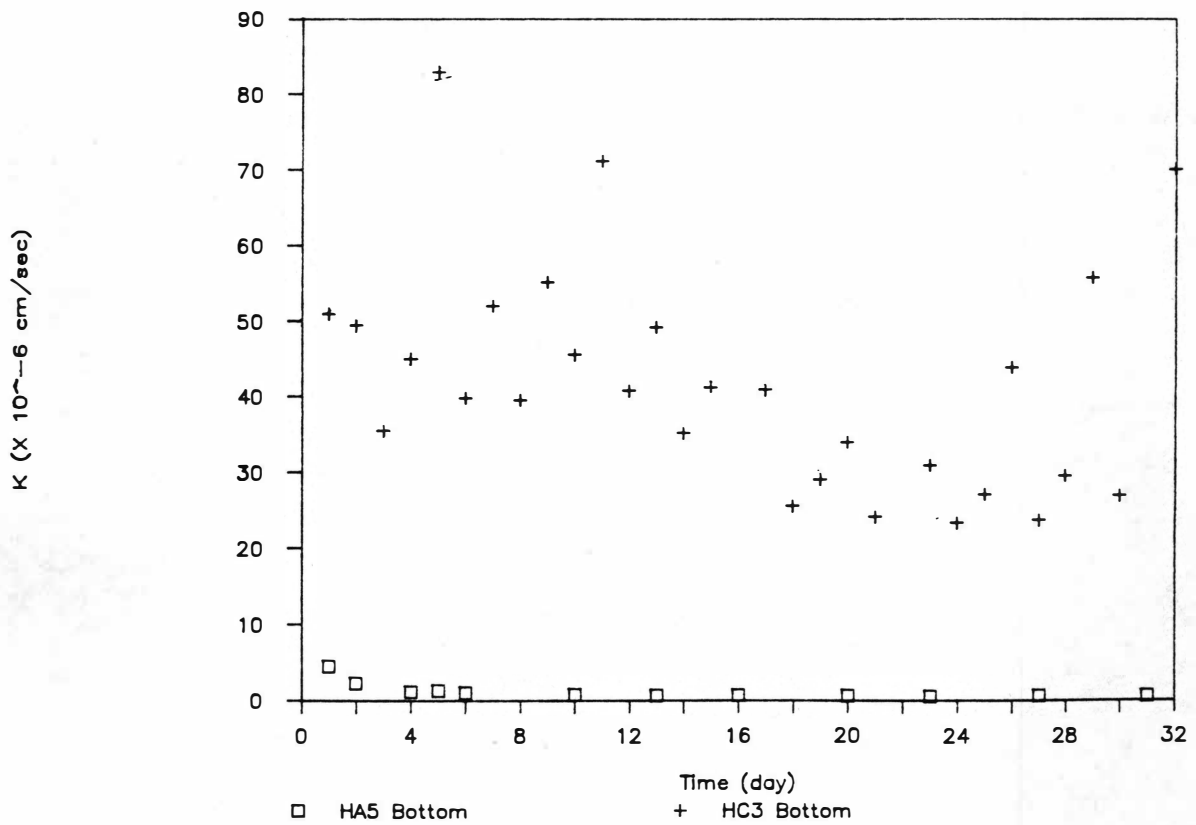


Figure 5.4 Permeability of Huntington optimum mix.

Coefficient of Permeability (K)



Coefficient of Permeability (K)



sections. The bottom sections of New York City and Huntington blocks have the highest average permeabilities of 1.06×10^{-5} and 3.45×10^{-5} cm/sec while the top sections of the Westchester blocks had the lowest average of 2.17×10^{-8} cm/sec.

A rapid initial decrease in permeability occurs in all samples as seawater fills the pore space of the blocks. When the block is fully saturated, the surface tension between the internal block surfaces and the seawater in the pore space slows the flow of fluid to the asymptotic value of the permeability coefficient. Seligman (1978) argues that the reduction of permeability may be due to the precipitation of calcium alumina-silicate in the cementation processes. Since seawater, which provides Ca^{2+} for the reaction, was used over the period of the test, Seligman's argument can also account for the decreasing permeability coefficient found in the study. The absorption of calcium from seawater by proctor sections was directly observed in our calcium-flux study (refer to Table 6.14 and 6.15).

One unexpected result of the permeability experiment is that the bottom sections of all proctors tested are more permeable than the corresponding top sections. This is surprising because our proctor fabrication technique follows ASTM D698-78 which results in the bottom layer receiving a total of 75 compactions during production and the top layer only 25. This should reduce the percentage of pore space in the bottom section below values for the top sections. However, this result has also been observed by Harder *et al.* (1981) where more compactions produced a higher porosity and permeability. Because our porosity experiment used only the middle section from the proctor, no comparison between compactions and porosity was available.

The most probable cause for this anomaly is that some damage results to the bottom portion of the proctor during extrusion from the mold. This may be difficult to detect and fully cover with epoxy when the section is mounted into the bottom of the PVC column. This effect could result in water channelling through small cracks between the exterior of the proctor and the PVC pipe. This could also explain the high standard deviation in the bottom sections due to the unreproducible manner in which

these cracks would occur.

Freeze-Thaw

To determine the behavior of the proctors to weathering, six blocks were exposed to a freeze-thaw regime following ASTM C666 protocol. Blocks were placed in a freezer at -5°C for 24 h, then removed and allowed to return to room temperature for 24 h and then returned to the freezer. This procedure, which was followed for forty-one (41) days, resulted in 20 freeze-thaw cycles after which the compressive strength of the blocks was tested following methods described earlier.

Results of the freeze-thaw procedure can be found in Table 5.4. No statistically significant change was observed in the average compressive strengths of New York City or Huntington blocks due to the procedure. This is observed from the overlap of the average values within the standard deviation of the averages. The Westchester blocks, however, exhibited a decrease of 16% in their strengths after the procedure.

Westchester blocks exhibited a 16% decrease in their strengths after the freeze-thaw procedure. They also showed the smallest percentage of pore space, the lowest permeability values and the smallest standard deviation in strength values. This indicates that the Westchester blocks are more uniform and more compact than the other two types of ash blocks. When the blocks are frozen, any moisture in the blocks will form ice crystals and, due to the lack of pore space, the formation of these crystals may disrupt the cementitious crystals of the block. This would result in lower compressive strength of the blocks. New York City blocks have the largest percentage of pore space and the greatest permeability thereby allowing ice crystals to form without causing much disruption of the cementitious bonds. In Table 5.4, it is observed that freeze-thaw cycled New York City block strengths fall within the standard deviation of the uncycled blocks indicating no major structural damage occurring during the weathering process. Huntington freeze-thaw blocks are slightly stronger than uncycled blocks. This could be explained by the variability of the blocks, as indicated by the large standard deviation values.

Table 5.4. Compressive strengths before and after freeze-thaw cycle.

		<u>Compressive Strength (psi)</u>
<u>New York City</u>		
Before		228 (± 73)
After	COB5	199
	COD5	247
	Average	224 (± 26)
<u>Huntington</u>		
Before		455 (± 63)
After	HB2	557
	HD2	374
	Average	466 (± 129)
<u>Westchester</u>		
Before		1231 (± 53.5)
After	WAA3	1031
	WAB3	1027
	Average	1029 (± 3)

a. Numbers in parentheses denote standard deviation.

EFFECTS OF SEAWATER EXPOSURE

Twelve proctor sized samples of the optimum mix for each ash were placed on a seatable at the Flax Pond facility. Filtered seawater was continuously circulated through the seatable to provide an indication of how the stabilized ash would behave in the sea. Two blocks were retrieved from the seatable at approximately 60 day intervals for compressive strength determinations. Results are shown in Table 5.5 and Figure 5.5. The results show that Westchester block average strength actually increases almost 19% above it's initial strength after the first 60 days of submersion then slowly decreases thereafter. The Huntington blocks initially lose less than 6% of their initial strength after 60 days of submersion then maintains a strength of approximately 385 psi which is still above our 300 psi minimum strength criteria after 185 days of submersion. The New York City blocks failed the submersion test. Total loss of structural integrity was observed after 122 days of submersion .

Fragments from the blocks broken after 60 days were then freeze-dried for 24 h, ground with mortar and pestle to pass through a 75 μ m opening sieve, and again freeze-dried. This sample was subsequently used for powder X-ray diffraction analysis (see Section 7).

HOLLOW UNIT MASONRY BLOCK MANUFACTURING

Using the facilities of Barrasso and Sons, Inc. at 160 Floral Park Road, Islip Terrace, New York, approximately 300 standard sized (8x8x16) hollow unit masonry blocks were fabricated substituting Westchester incineration residues sieved through a 3/4" flat mesh screen for aggregate. Three mix designs were examined:

Table 5.5. Effects of seawater submersion test on compressive strength.

Unsubmerged Optimum Mix Proctor Characteristics

	Westchester	Huntington	New York City
Moisture (%)	17	18	23
Cement (%)	15	15	15
Curing Temp (C)	49	Air	49
Curing Time (h)	24	168	72
Avg. Strength (psi)	1231 ± 54	455 ± 63	228 ± 74

Submerged Optimum Mix Proctor Characteristics

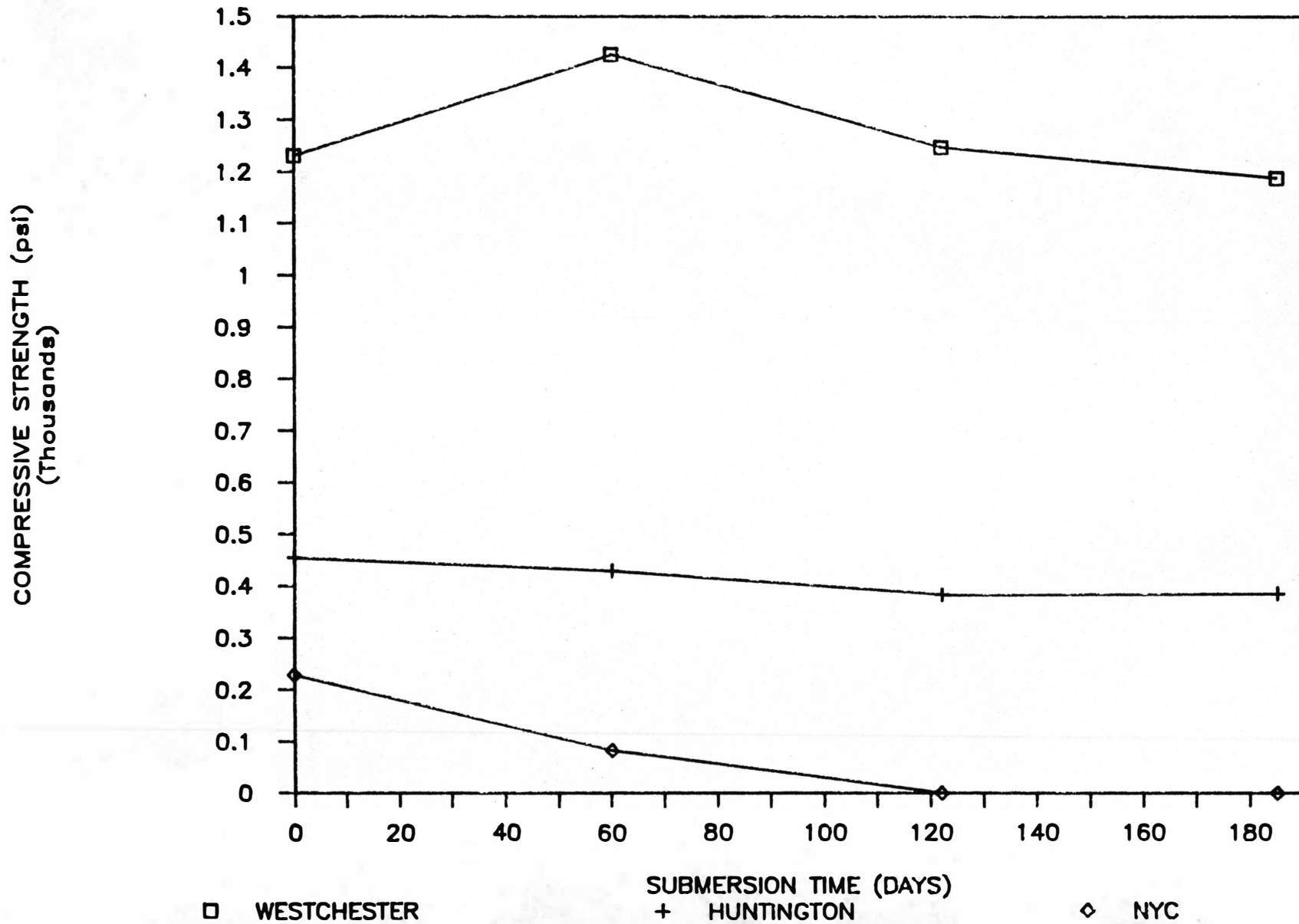
Date	Total submersed time : 60 days					
Proctor Code	WAB2	WAE2	HC4	HE1	COD7	COE7
Compressive Strength (psi)	1468	1456	458	402	72	95
Avg. Strength	1462 ± 6		430 ± 28		84 ± 12	
% Change	18.8		-5.5		-63.4	

Date	Total submersed time : 122 days					
Proctor Code	WAD2	WAE3	HA4	HE2	COA4	COC1
Compressive Strength (psi)	1110	1385	418	350	0	0
Avg. Strength	1248 ± 138		384 ± 34		0 ± 0	
% Change	1.3		-15.6		-100.0	

Date	Total submersed time : 185 days					
Proctor Code	WAD3	WAE5	HC2	HE4	COA1	COD3
Compressive Strength (psi)	1170	1206	414	358	0	0
Avg. Strength	1188 ± 18		386 ± 28		0 ± 0	
% Change	-3.5		-15.2		-100.0	

Figure 5.5

COMPRESSIVE STRENGTH vs SUBMERSION TIME



Mix Design	Materials	Volume (ft ³)	Weight (lbs)
1 (Red)	cement		251
	sand	15	1368
	residue	10	624
2 (yellow)	cement		250
	sand	10	900
	residue	15	900
3 (natural)	cement		250
	sand	0	0
	residue	25	1500

Each mix design was colored as noted above and cured for 18 hours at 134⁰F. One difficulty during the block manufacturing process was the inability to use the mixers moisture probe to determine the moisture content of the mix prior to compaction. This was due to the small sample size, and therefore only an estimate of the moisture content was established. Barrasso personnel were impressed by the ease of handling the incineration ash and moving the mix throughout the facility by conveyor belts prior to compaction. Overall it was their impression that this material behaved in a similar manner to the standard mixes they handle daily.

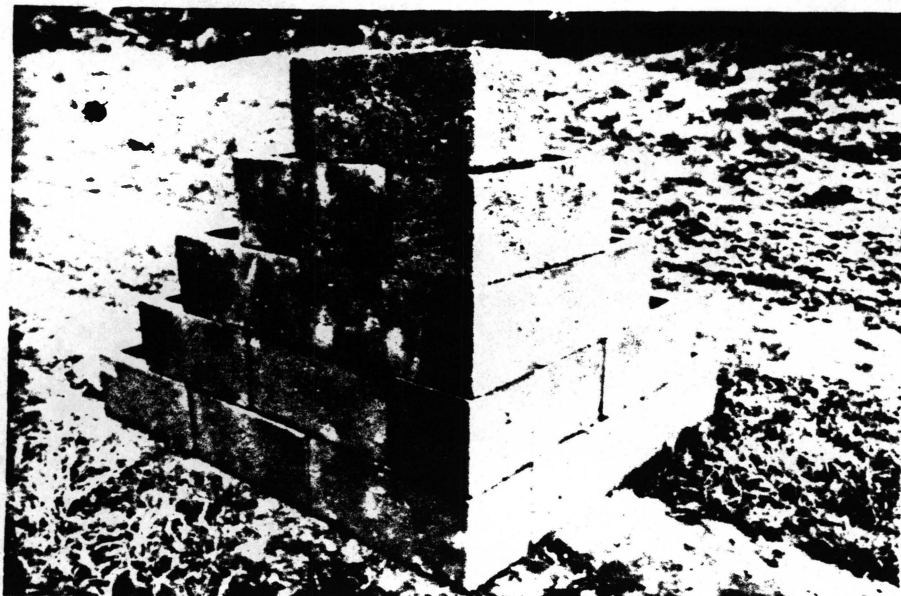
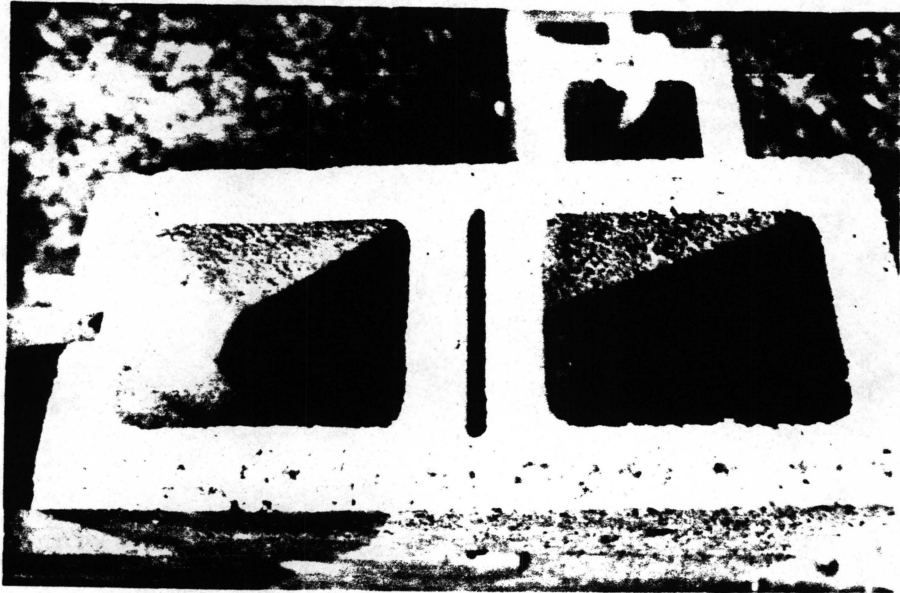
Following curing, the blocks were transported to MSRC where a number of blocks of each mix design were moistened and wrapped in plastic to determine whether additional moisture would result in a continuation of the curing process and therefore improve compressive strengths. Every seven days the structural integrity of the blocks was determined in replicate (n=3).

Table 5.6 indicates that the second mix design produced blocks possessing a mean compressive strength of approximately 90,000 lbs total load. The blocks manufactured using only incineration ash had a strength of 65,000 lbs. The data indicates that little, if any improvement in strength was accomplished by wetting the blocks and that compressive strength values fall short of the ASTM C-90 800 psi minimum strength.

Table 5.6. Compressive strengths of hollow masonry blocks.

Curing Time		Compressive Strength (total load) in pounds							
Time (day)	<u>RED MIX</u>		<u>YELLOW MIX</u>		<u>NATURAL</u>		<u>PUMICE</u>	<u>STANDARD</u>	
	DRY	WET	DRY	WET	DRY	WET			
7	46500	50000	65000	59000	72500	70500	138000	182500	
	47500	28000	63000	55500	48500	59000			
	63000	19000	61000	72000	72500	68000			
	AVE.	52333	32333	63000	62167	64500	65833		
	STD.	7554	13021	1633	7099	11314	4939		
14	48500	48500	84000	75500	94000	61500	101000	185000	
	59000	45000	75000	60500	53000	46500			
	47500	60500	105500	81500	65500	47000			
	AVE.	51667	51333	88167	72500	70833	51667		
	STD.	5201	6637	12795	8832	17158	6956		
% change	-1.27	58.76	39.95	16.62	9.82	-21.52			
21	66500	34000	105000	67500	71500	60500			
	54000	54000	114000	86000	68500	45000			
	53000	53500	60000	45000	68000	44000			
	AVE.	57833	47167	93000	66167	69333	49833		
	STD.	6142	9312	23622	16765	1546	7554		
% change	11.94	-8.12	5.48	-8.74	-2.12	-3.55			
28	66500	46500	70000	118000	57000	63000			
	86000	50000	104000	68000	39500	58000			
	60500	37500	97000	83000	90500	89500			
	AVE.	71000	44667	90333	89667	62333	70167		
	STD.	10886	5265	14659	20950	21159	13822		
% change	22.77	-5.30	-2.87	35.52	-10.10	40.80			

Figure 5.6 Hollow masonry blocks fabricated using Westchester incineration residue.



Section 6

CHEMICAL CHARACTERISTICS

Glass and Plasticware Preparation

All glass and plasticware used in this study were acid cleaned prior to use. Glassware was soaked in a bath of 10% HCl - 10% HNO₃ for at least 24 hours, rinsed with distilled-deionized water, soaked in 1% Ultrex HNO₃ for at least 24 hours, and again rinsed several times with distilled-deionized water; the plasticware was soaked in two solution baths of 10% HCl - 10% HNO₃ for at least 24 hours each and rinsed with distilled-deionized water between each bath. Acid cleaned glass and plasticware were then air dried in a laminar flow hood and stored in plastic bags until they were used, with the mouth of volumetric flasks wrapped in parafilm to prevent contamination.

BLOCK DIGESTIONS FOR ELEMENTAL ANALYSIS

Analysis of hydrofluoric/boric acid digests by atomic absorption spectrophotometry was used to determine the elemental composition of the optimum blocks and the starting materials (Westchester composite ash, New York City fly ash and Huntington composite ash). The method was a modification of the procedure reported by Silberman and Fisher (1979). The method utilizes the ability of hydrofluoric acid (HF) to breakdown silicious materials: boric acid (H₃BO₃) is used to complex remaining fluoride ions and to dissolve insoluble metal fluorides formed during digestion.

Sample Preparation

About 500 g of the stabilized blocks, starting materials and a cement block was freeze dried and ground using a mortar and pestle. Table 6.1 shows the particle size ranges digested and used in both the EPA and ASTM leachate analyses.

Table 6.1. Particle size for digest study and leaching tests.

<u>Sample</u>	<u>Particle Size</u>
Cement Block	< 9.5 mm
Westchester	
WAE6	< 9.5 mm
W1	2.00 mm - 4.75 mm
W2	425 μm - 1.00 mm
W3	< 200 μm
New York City	
COA2	< 9.5 mm
C1	250 μm - 4.75 mm
C2	150 μm - 250 μm
C3	< 75 μm
Huntington	
HA3	< 9.5 mm
H1	2.00 mm - 4.75 mm
H2	425 μm - 1.00 mm
H3	< 150 μm

- a. Optimum Blocks : WAE6, COA2 and HA3.
- b. Westchester Composite Ash : W1, W2 and W3.
- c. New York City Fly Ash : C1, C2 and C3.
- d. Huntington Composite Ash : H1, H2 and H3.

Approximately 0.5 g samples of each of the dry materials were weighed to 0.1 mg and then placed into 125 ml Nalgene plastic bottles followed by the addition of 10 ml of distilled-deionized water and 10 ml of concentrated HF. The mixtures were then shaken mechanically for 24 hours. Seventy milliliters of saturated boric acid solution made at $45 \pm 1^{\circ}\text{C}$ was added, and the samples were again agitated for 24 hours followed by ultrasonication for one hour. The digests were filtered through $0.45 \mu\text{m}$ millipore filter paper and then transferred to 100 ml glass volumetric flasks and brought to volume with saturated (at 25°C) boric acid. The digests were kept in 100 ml Nalgene plastic bottles and stored in refrigerator at 5°C prior to analysis.

Elemental Analysis by Atomic Absorption Spectroscopy

Three replicate samples for each of the starting materials, stabilized blocks and the cement block, which was used for comparison, were analyzed for Ca, Al, Fe, Mg, Si, As, Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn by atomic absorption spectrophotometer (AAS), using either flame or flameless graphite furnace. Mercury was analyzed using the MHS-10 hydride generation system. Six replicates of National Bureau of Standards (NBS) 1633a fly ash were analyzed by the same procedures to determine the completeness of digestion and the accuracy of the analytical methods. For each metal, standards were run and the regression coefficients for all metals were better than 0.999.

Calcium Determination

All calcium analyses were performed with acetylene/air flame on the Perkin Elmer 5000 AAS without background correction. Samples were diluted into the linear range with 1% (w/v) La^{+3} , added as $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, to increase the sensitivity of the analysis by suppressing interferences caused by the presence of other ions. Standards were serial dilutions of Fisher Scientific atomic absorption standards made up in 1% La^{+3} .

Determination of Al, Fe, Mg, Si, As, Cd, Cr, Co, Cu, Pb, Mn, Ni, Zn and Hg

All standards were serial dilutions of Fisher Scientific atomic absorption standards and were made up in the same HF/H₃BO₃ matrix present in the samples to be analyzed except Si, Pb, As and Hg. Since the hydrofluoric acid leached silicon from the glass pipet and glass volumetric flasks which were used for making standards, and the HF/H₃BO₃ matrix contained a considerable amount of lead, 0.1% Ultrex nitric acid matrix was used when analyzing Si and Pb. When determining As concentration, percent recovery of NBS samples was improved by using 0.1% Ultrex HNO₃ matrix compared to that of HF/H₃BO₃ matrix. Mercury standard solutions were stabilized by an addition of 0.1% potassium iodide (KI) solution in order to reduce the adsorption of Hg on the walls of glass volumetric flasks used for making standard solutions. Matrix modifiers, 0.5% (w/v) La₂O₃ and 1% (w/v) (NH₄)₂HPO₄, were used for the Mg and Cd analyses respectively to reduce interferences, and a solution containing 0.1% Ultrex HNO₃ and 1000 ppm Ni as Ni(NO₃)₂ (1:1) for the As analysis in order to increase the charring temperature.

Fe, Mg, Cu, Mn, Ni and Zn were determined with acetylene/air flame without background correction. Al and Si were determined with nitrous oxide/acetylene flame without background correction. As, Cd, Cr, Co and Pb were determined using the HGA 500 flameless graphite furnace with background correction.

Mercury was analyzed by the method of additions using the Perkin Elmer MHS-10 hydride generation system. Using the MHS-10, Hg is converted in dilute acid solution to its hydride by the addition of excess sodium borohydride (NaBH₄, 3% w/v) and sodium hydroxide (NaOH, 1% w/v). Argon and nitrogen gas was used to flush the vaporous hydride into a heated quartz tube through which the AAS beams are focused.

Results and Discussion

The elemental concentration of the stabilized blocks and cement block, and the concentration of some elements in the starting materials used in the fabrication of the blocks are presented in this section. For

the purpose of classification, major constituents are those present in concentration > 1 mg/g; minor constituents are those elements in the range $100 \mu\text{g/g} - 1$ mg/g; and trace elements are those present in concentrations $< 100 \mu\text{g/g}$.

Table 6.2 gives the NBS values for the fifteen metals in NBS 1633a fly ash, along with the measured values and percent recovery. The HF/H₃BO₃/atomic absorption method yields 100% recoveries for Ca, Al, Mg, Si, As, Cd and Zn. The elements, Fe, Cr, Cu, Pb and Mn, have recoveries lower than 100% but higher than 88%, which may be due to insufficient digestion or matrix interferences during analysis. Ni and Co show recoveries higher than 100%. Considering the variations between six replicates and also between three absorbances of one replicate, 108.2% recovery of Co can be acceptable. For Ni, the NBS samples were analyzed with acetylene/air flame, graphite furnace and then by the method of standard additions, giving the same results (about 130% recovery). Thus 130% recovery is assumed to be due to the contamination of NBS samples with respect to Ni rather than analytical error.

The elemental concentrations of the starting materials, that is New York City fly ash (NYCFA), Huntington composite ash (HCA) and Westchester composite ash (WCA) used to fabricate the optimum blocks are presented in Table 6.3. Table 6.3 displays the following trends. Samples of finer particles (W3, C3 and H3, refer to Table 6.1), in general result in higher concentration than coarser ones, and coarser particles (W1, C1 and H1) generally show higher variations between three replicate samples. This is probably due to volatile metals (Cd, Pb....) absorbing onto fly ash particles downstream of the combustion area as the flue gas temperature decreases. A few exceptions however were observed in NYCFA; larger particles tend to contain higher concentration of Ca, Al, Mg, Si and Hg than smaller particles. Figure 6.1 displays the data in graphical form, showing highest, lowest, average values and standard deviation of the three replicates.

Table 6.2. Elemental concentrations of NBS Standard 1633a fly ash and % recovery, HF-H₃BO₃ acid digest.

<u>Element</u>	<u>NBS</u>	<u>Measured</u>	<u>% Recovery</u> ^b
Ca (%)	1.11(±0.01) ^a	1.11(±0.08)	100
Al (%)	12.7 (±0.5)	12.98(±0.22)	100
Fe (%)	9.4 (±0.1)	8.74(±0.20)	93.0
Mg (%)	0.45(±0.01)	0.44(±0.02)	100
Si (%)	23 (±1)	22.3 (±0.6)	100
As (ppm)	145 (±15)	143.1 (±6.8)	100
Cd (ppm)	1.00(±0.15)	0.92(±0.05)	100
Cr (ppm)	196 (±6)	172.5 (±2.4)	88.0
Co (ppm)	46 (n.c.)	49.75(±1.41)	108.2
Cu (ppm)	118 (±3)	110.1 (±1.2)	93.3
Pb (ppm)	70 (±4)	63.8 (±1.8)	91.1
Mn (ppm)	190 (±7)	173.8 (±3.7)	91.5
Hg (ppm)	n.c. ^c	< 0.001	
Ni (ppm)	127 (±4)	163.8 (±3.5)	129.0
Zn (ppm)	210 (±10)	194.5 (±5.1)	100

- a. Values in parentheses denote standard deviation.
- b. Percent recovery considered to be 100% if standard deviations overlapped. Where < or > 100%, calculation was based on mean values.
- c. Not certified by NBS.

Table 6.3. Metal concentrations in starting materials.

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash			
	W1 ^a	W2	W3	C1	C2	C3	H1	H2	H3	
Ca (%)	8.77	7.19	16.0	6.04	5.45	7.48	6.70	5.12	6.62	
	6.73	6.52	16.0	5.98	4.38	5.94	4.91	4.68	6.57	
	4.12	6.39	14.7	5.93	4.22	3.81	4.75	4.02	6.43	
	AVERAGE	6.54	6.70	15.6	5.98	4.69	5.75	5.45	4.61	6.54
	STD.DEV	1.91	0.35	0.6	0.05	0.55	1.50	0.88	0.45	0.08
Al (%)	4.49	6.26	5.68	10.17	9.53	7.43	5.78	4.95	6.20	
	3.92	5.93	5.61	10.08	9.25	6.18	3.87	4.84	6.09	
	1.80	5.48	5.46	9.27	9.15	5.22	3.65	3.36	6.03	
	AVERAGE	3.40	5.89	5.58	9.84	9.31	6.27	4.43	4.38	6.11
	STD.DEV	1.16	0.32	0.09	0.40	0.16	0.91	0.96	0.73	0.07
Fe (%)	25.0	7.91	1.99	1.90	1.45	1.57	13.8	9.57	6.13	
	7.3	7.59	1.94	1.87	1.42	1.56	11.0	9.39	6.11	
	2.5	6.07	1.94	1.51	1.39	1.52	7.9	8.25	5.83	
	AVERAGE	11.6	7.19	1.96	1.76	1.42	1.55	10.9	9.07	6.02
	STD.DEV	9.7	0.80	0.02	0.18	0.03	0.02	2.4	0.59	0.14
Mg (%)	2.00	1.15	1.80	1.08	0.91	1.51	1.26	0.82	0.96	
	0.78	1.15	1.80	1.05	0.71	0.84	0.87	0.78	0.95	
	0.76	1.25	1.80	1.05	0.64	0.49	0.63	0.61	0.75	
	AVERAGE	1.18	1.18	1.80	1.06	0.76	0.95	0.92	0.74	0.89
	STD.DEV	0.58	0.04	0.00	0.01	0.12	0.42	0.26	0.09	0.10
Si (%)	23.6	23.0	9.77	12.3	21.8	22.1	20.9	21.4	12.3	
	15.6	21.3	9.55	11.1	21.7	13.1	14.8	20.9	12.2	
	11.4	20.8	9.51	10.7	17.4	9.9	12.0	16.7	11.8	
	AVERAGE	16.9	21.7	9.61	11.4	20.3	15.1	15.9	19.7	12.1
	STD.DEV	5.1	0.9	0.11	0.7	2.1	5.2	3.7	2.1	0.2

Table 6.3 Continued

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash			
	W1	W2	W3	C1	C2	C3	H1	H2	H3	
As (ppm)	11.21	28.7	23.1	65.0	74.7	125	15.8	17.8	28.2	
	6.80	26.9	20.4	60.4	74.4	124	10.4	16.0	26.5	
	4.40	26.3	19.6	54.9	66.8	120	6.2	14.3	25.0	
	AVERAGE	7.47	27.3	21.0	60.1	71.9	123	10.8	16.0	26.6
	STD.DEV	2.82	1.0	1.5	4.1	3.7	2	3.9	1.4	1.3
Cd (ppm)	14.3	42.2	91.5	823	660	1306	13.64	13.5	25.2	
	13.3	23.1	91.3	767	655	1245	7.13	10.9	25.0	
	2.5	21.1	71.1	755	654	1235	5.68	10.6	24.7	
	AVERAGE	10.0	28.8	84.6	781	656	1262	8.81	11.7	24.9
	STD.DEV	5.3	9.5	9.6	30	3	31	3.46	1.3	0.2
Cr (ppm)	286	195	131	185	158	189	160	159.7	91.0	
	151	148	129	159	157	181	187	74.5	88.0	
	83	129	129	154	145	174	96	58.9	87.6	
	AVERAGE	173	158	130	166	154	181	148	97.7	88.8
	STD.DEV	84	28	1	13	6	6	38	44.3	1.5
Co (ppm)	16.1	22.6	22.3	20.8	38.7	26.9	14.0	20.2	21.5	
	15.1	21.3	22.3	18.6	38.6	25.8	12.3	16.5	19.9	
	8.0	19.3	21.3	18.6	36.3	24.3	11.5	14.5	19.1	
	AVERAGE	13.1	21.1	22.0	19.3	37.9	25.7	12.6	17.1	20.2
	STD.DEV	3.6	1.3	0.5	1.0	1.1	1.1	1.0	2.4	1.0
Cu (ppm)	32941	3195	1992	667	643	871	712	6958	2031	
	7384	849	1913	599	521	718	439	1053	1766	
	341	836	1804	585	521	603	281	948	1766	
	AVERAGE	13555	1626	1903	617	561	730	477	2986	1854
	STD.DEV	14006	1109	77	36	58	110	178	2809	125
Pb (ppm)	2735	4355	3266	8660	8658	9513	966	2119	1516	
	1015	3817	3191	7526	7117	9363	616	1971	1479	
	391	2309	2775	6934	6726	7280	271	1949	1275	
	AVERAGE	1380	3494	3077	7707	7500	8719	618	2013	1423
	STD.DEV	991	866	216	716	834	1019	284	76	106

Table 6.3. Continued.

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash			
	W1	W2	W3	C1	C2	C3	H1	H2	H3	
Mn (ppm)	1450	1818	1758	842	795	1610	1494	1519	1238	
	1309	914	1751	837	776	1487	840	1183	1231	
	814	883	1735	781	719	1467	714	979	1223	
	AVERAGE	1191	1205	1748	820	763	1521	1016	1227	1231
	STD.DEV	273	434	9	27	33	63	342	223	6
Hg (ppm)	9.15	5.39	1.40	1.42		2.53				
	8.65	0.18	0.88	1.34		0.50				
	8.52	0.00	0.68	0.00		0.00				
	AVERAGE	8.78	1.74	0.99	0.24	b.d.l. ^b	0.13	b.d.l.	b.d.l.	b.d.l.
	STD.DEV	0.27	2.59	0.30	1.61		2.13			
Ni (ppm)	191	243	136	129	122	155	82.6	171	170	
	101	123	131	122	121	151	73.1	115	169	
	57	117	130	121	120	149	65.1	107	169	
	AVERAGE	116	161	133	124	121	152	73.6	131	170
	STD.DEV	56	58	3	3	1	3	7.2	28	1
Zn (ppm)	19966	4388	7674	55353	19146	28884	1793	3749	4537	
	1193	4125	7442	34774	18961	24580	1314	2932	4414	
	1144	3138	7394	22972	18702	20762	831	2868	4265	
	AVERAGE	7434	3884	7503	37700	18937	24742	1313	3183	4405
	STD.DEV	8861	538	122	13380	182	3318	393	401	111

a. Particle size ranges are listed in Table 6.1.

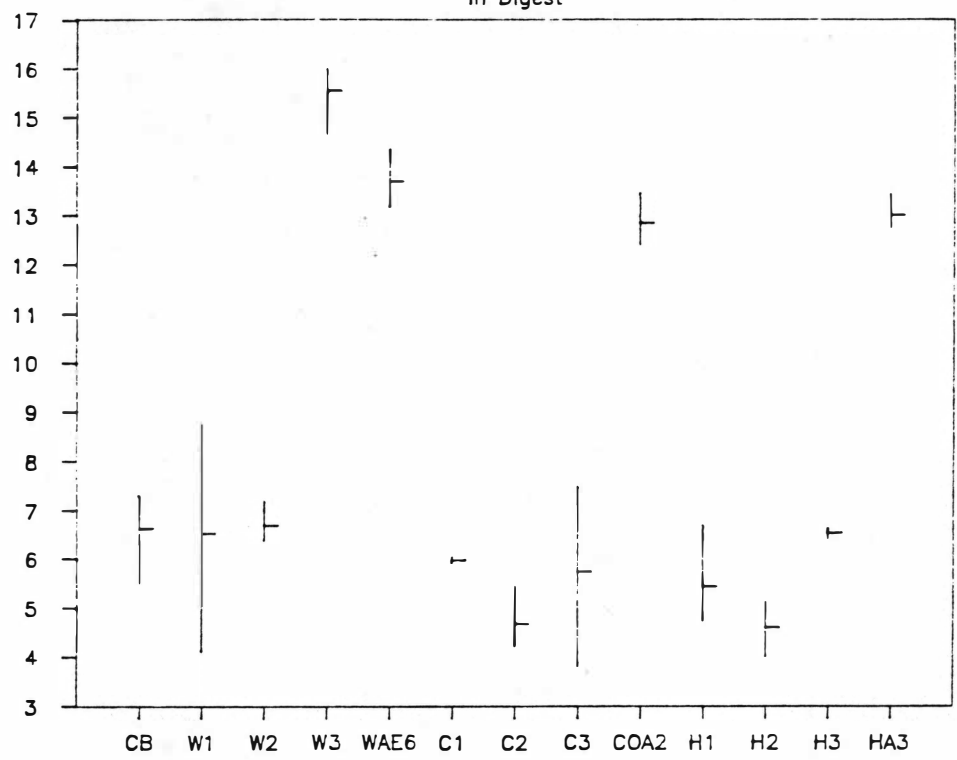
b. Below detection limits.

Figure 6.1 Metal concentrations in HF-H₃BO₃ digest

Ca Concentration

in Digest

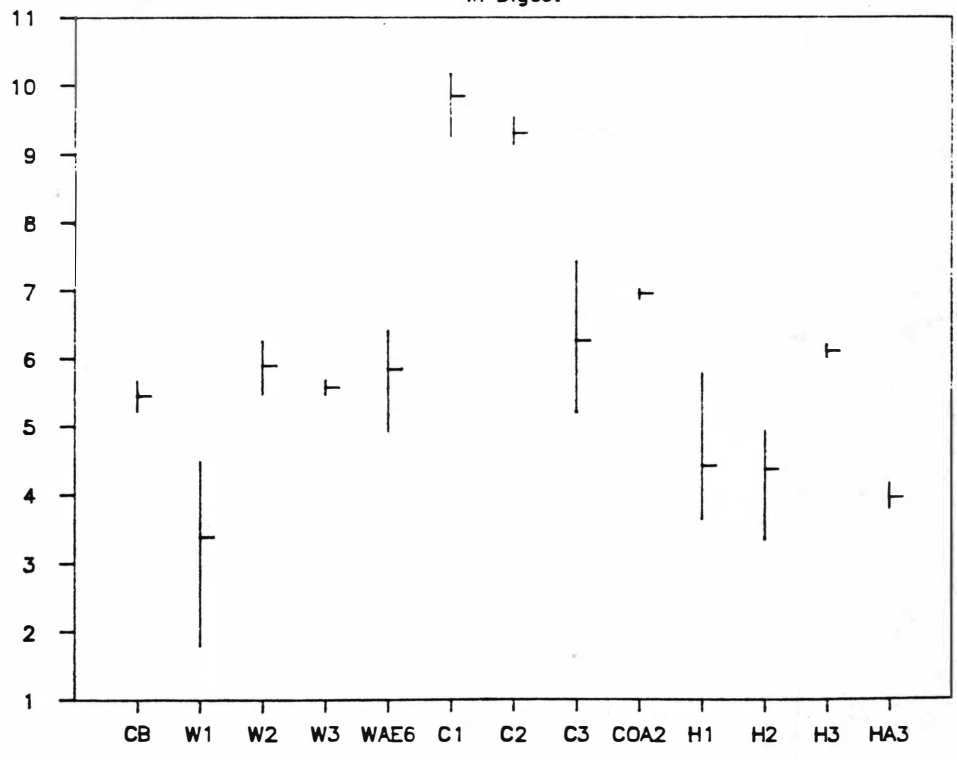
Ca Conc. (%)



Al Concentration

in Digest

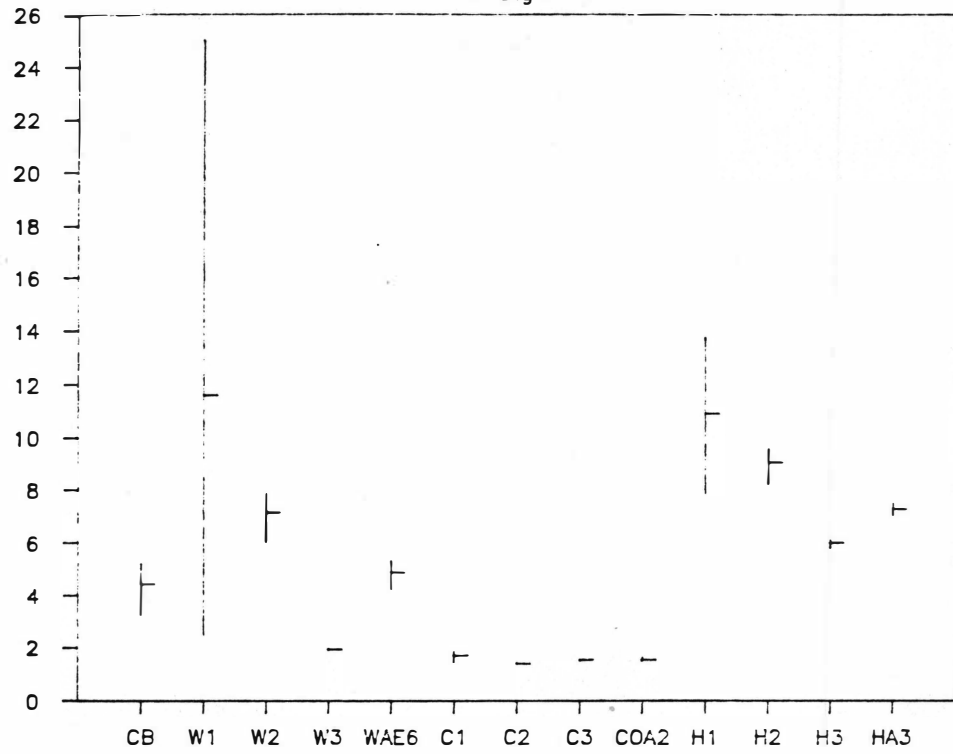
Al Conc. (%)



Fe Concentration

in Digest

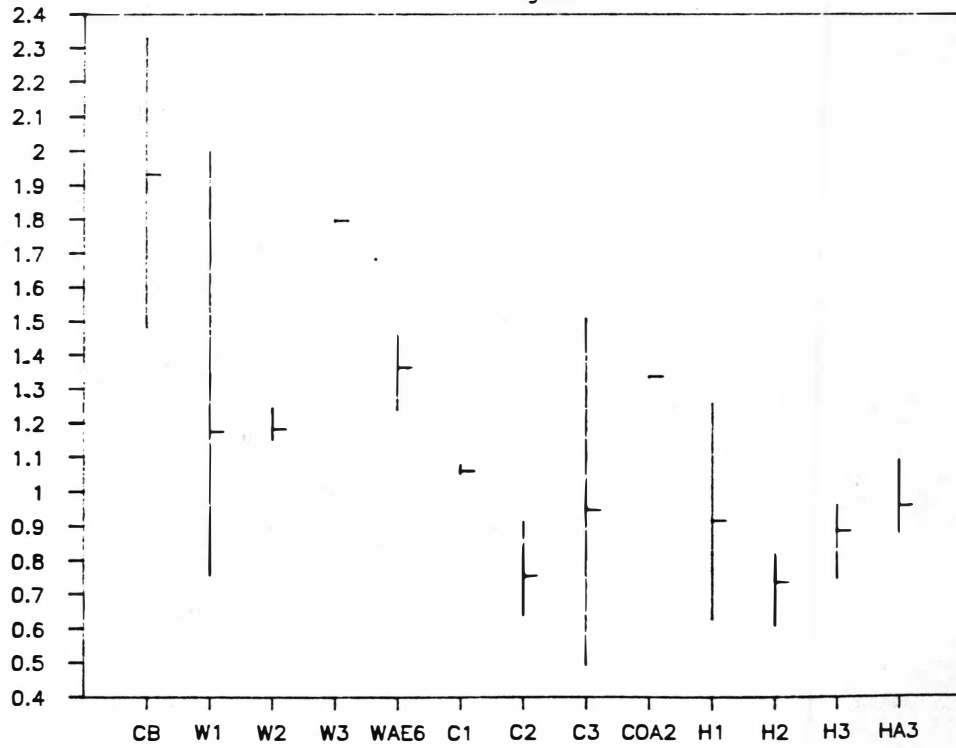
Fe Conc. (%)



Mg Concentration

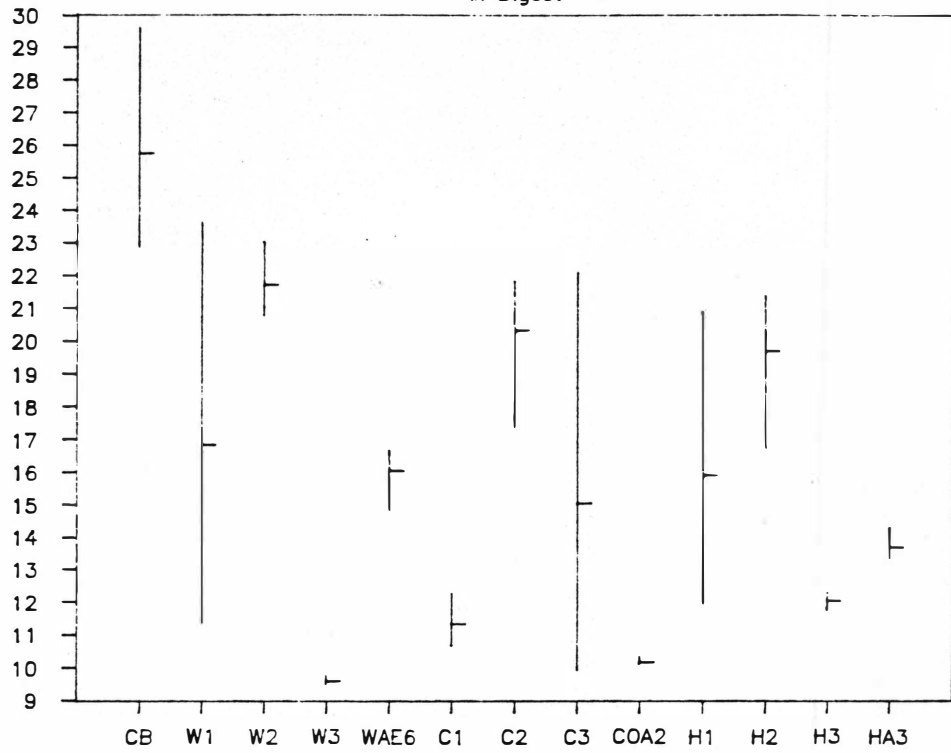
in Digest

Mg Conc. (%)



in Digest

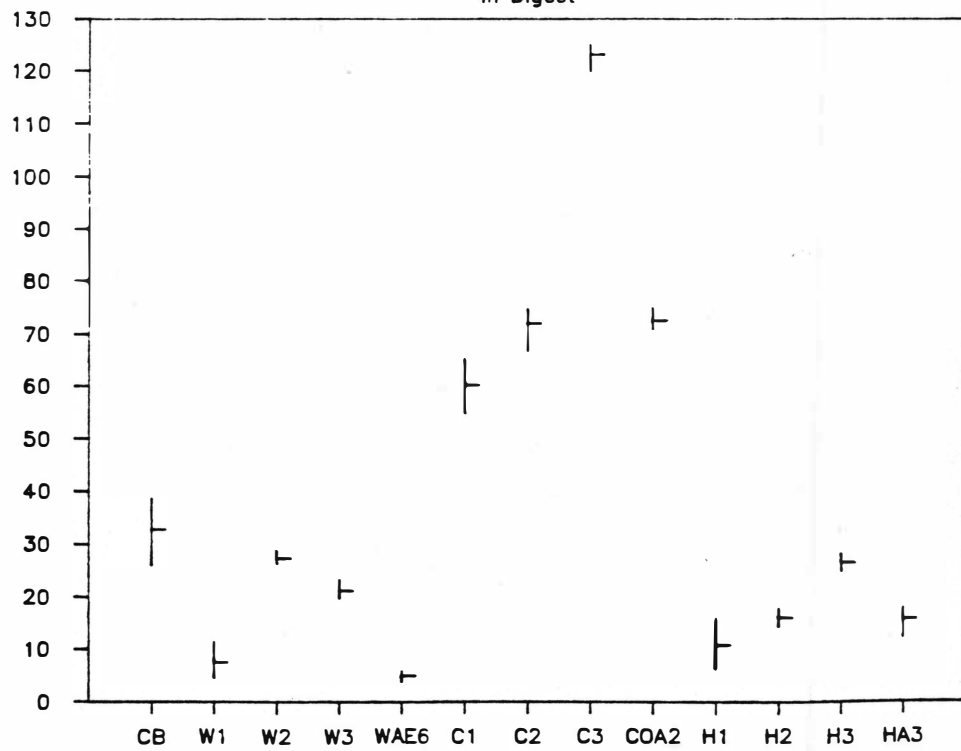
Si Conc. (%)



As Concentration

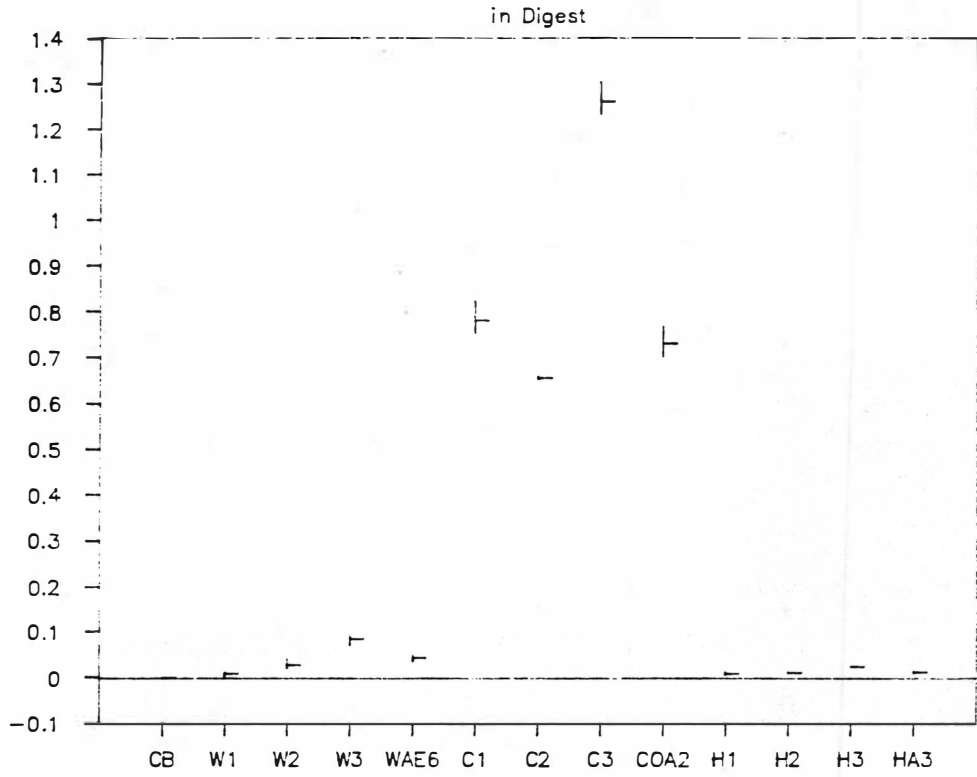
in Digest

As Conc. (ppm)



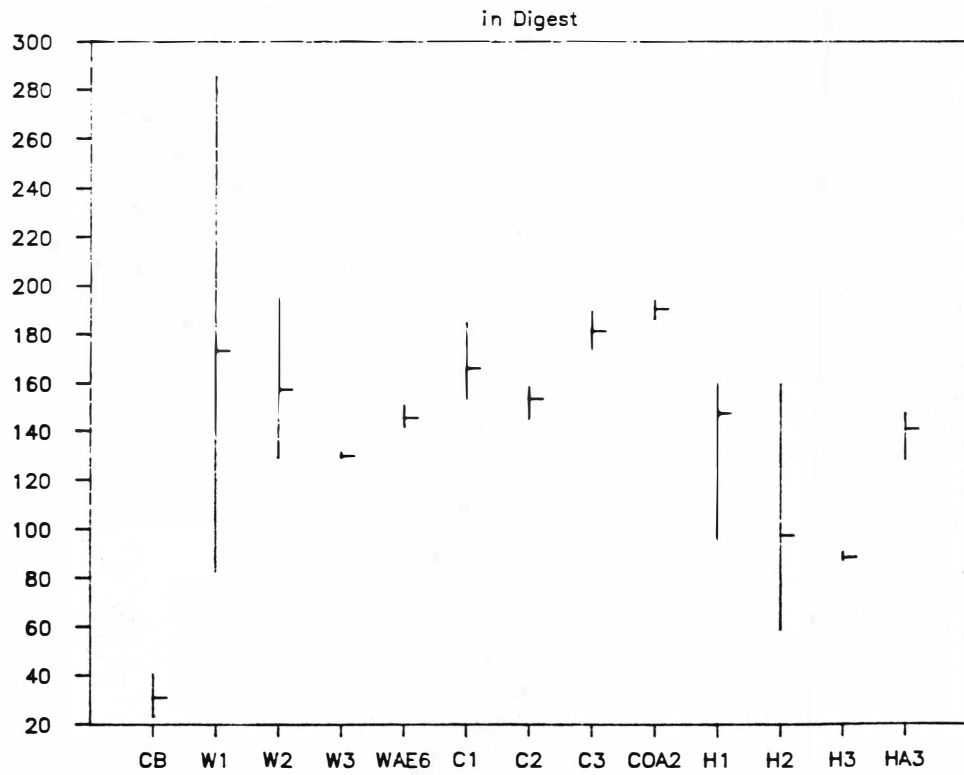
Cd Concentration

Cd Conc. (ppm)
(Thousands)



Cr Concentration

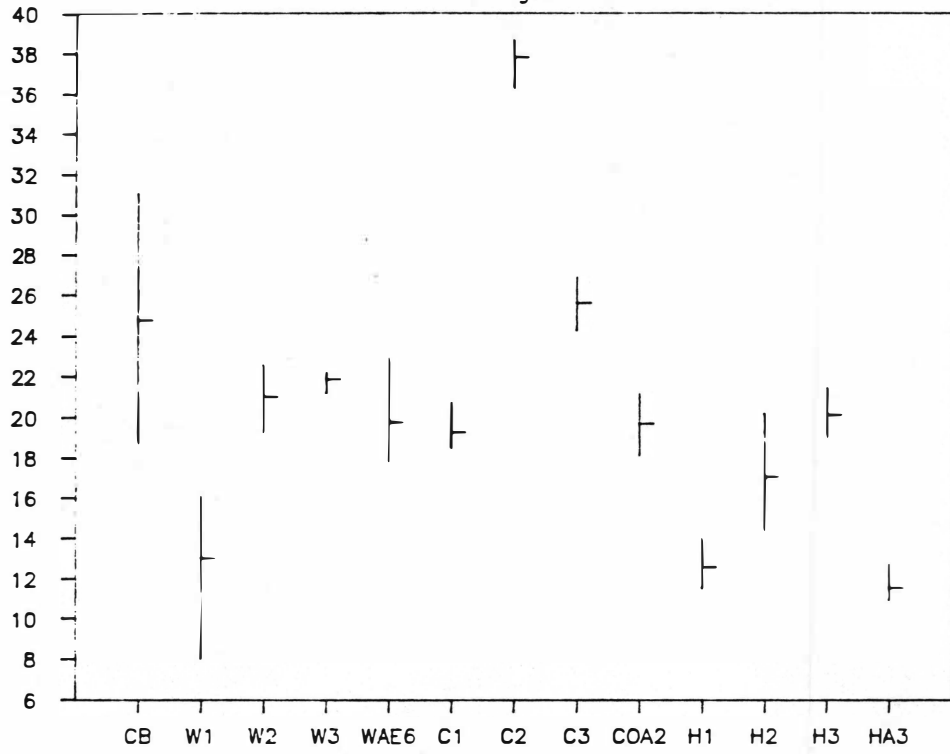
Cr Conc. (ppm)



Co Concentration

in Digest

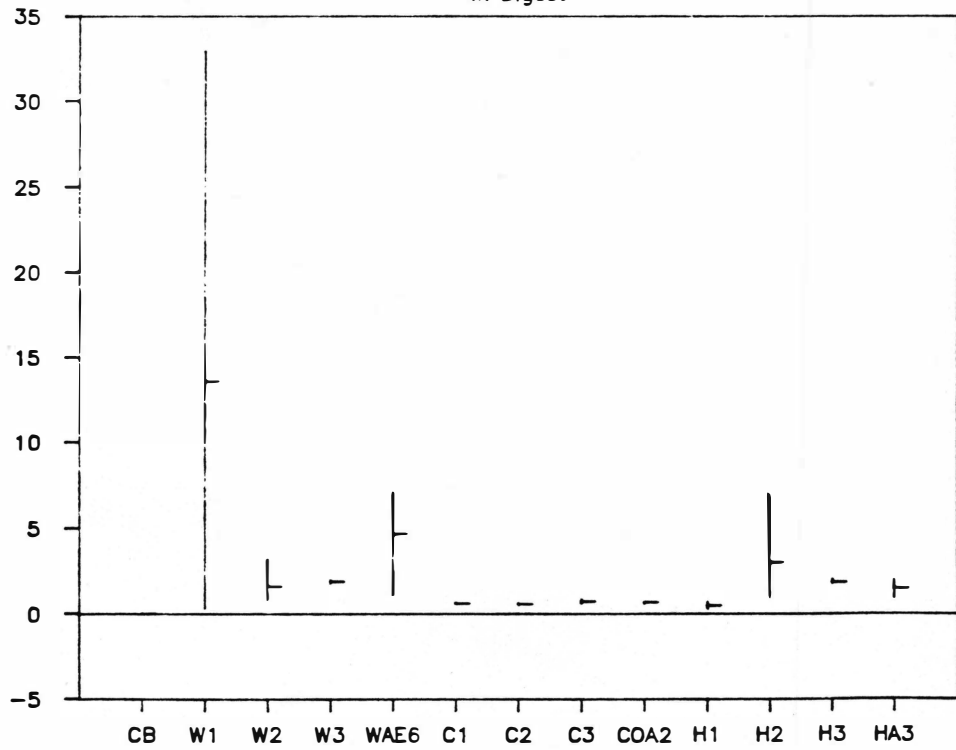
Co Conc. (ppm)



Cu Concentration

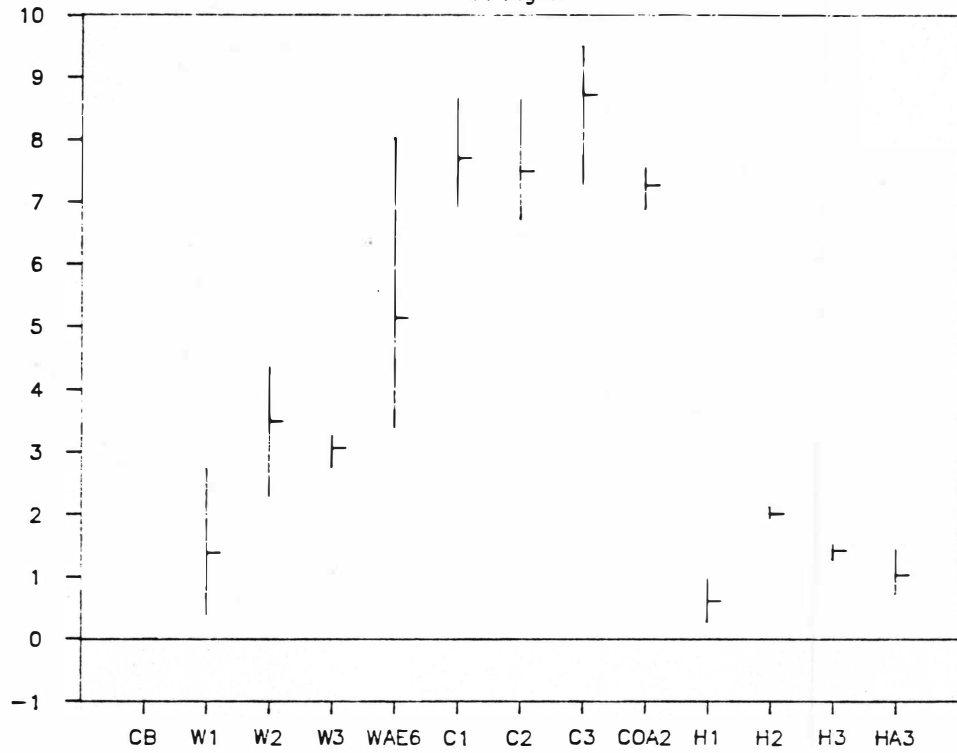
in Digest

Cu Conc. (ppm)
(Thousands)



in Digest

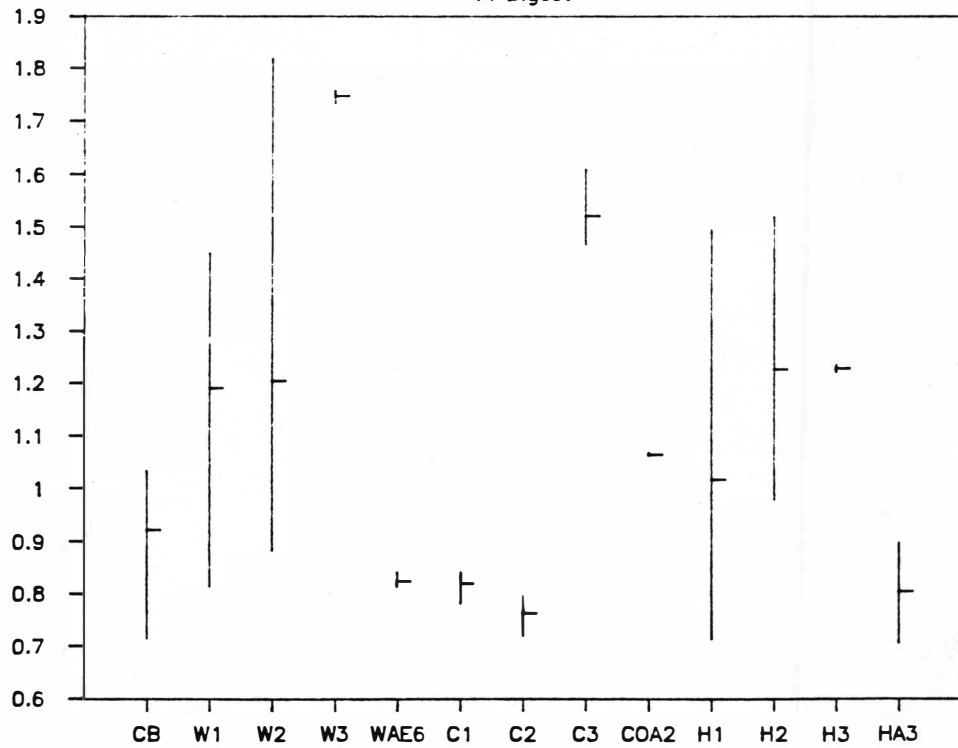
Pb Conc. (ppm)
(Thousands)



Mn Concentration

in Digest

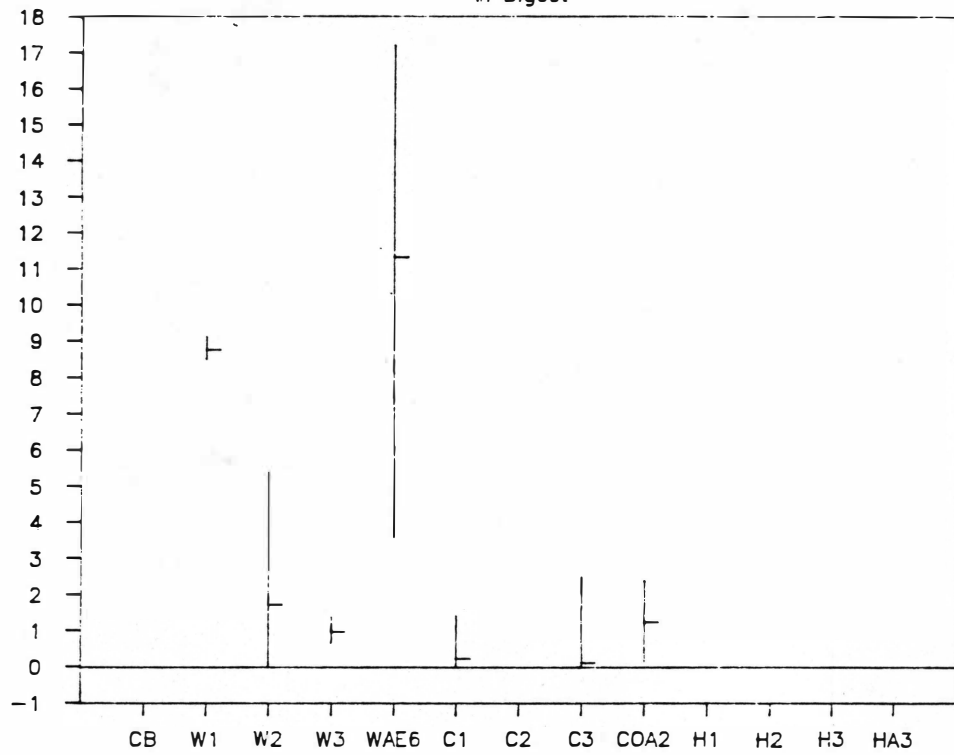
Mn Conc. (ppm)
(Thousands)



Hg Concentration

in Digest

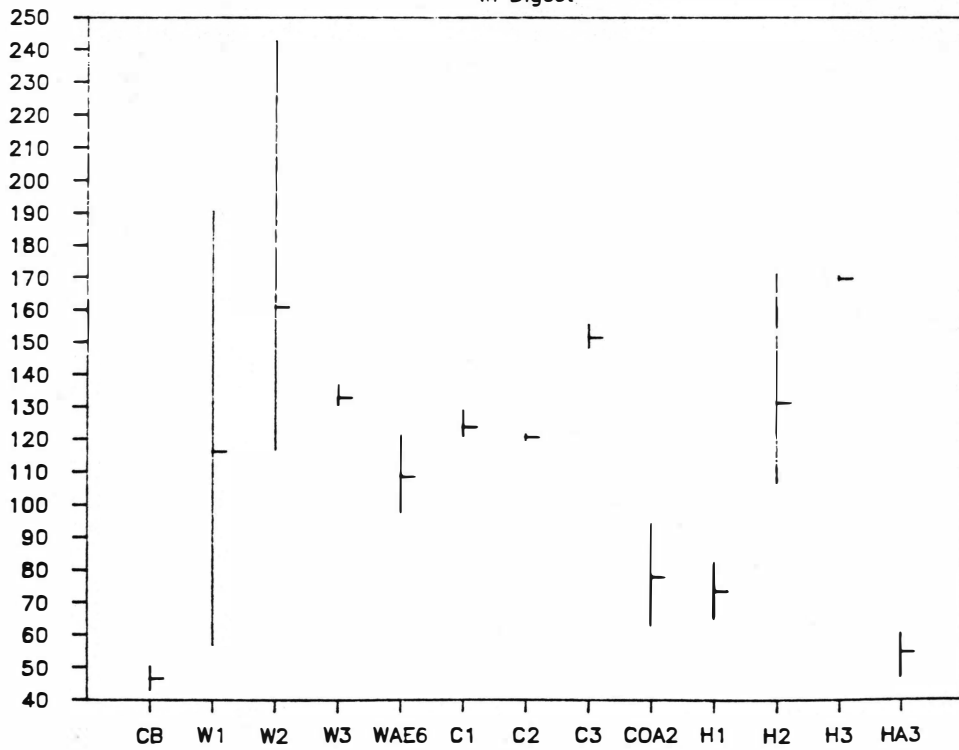
Hg Conc. (ppm)



Ni Concentration

in Digest

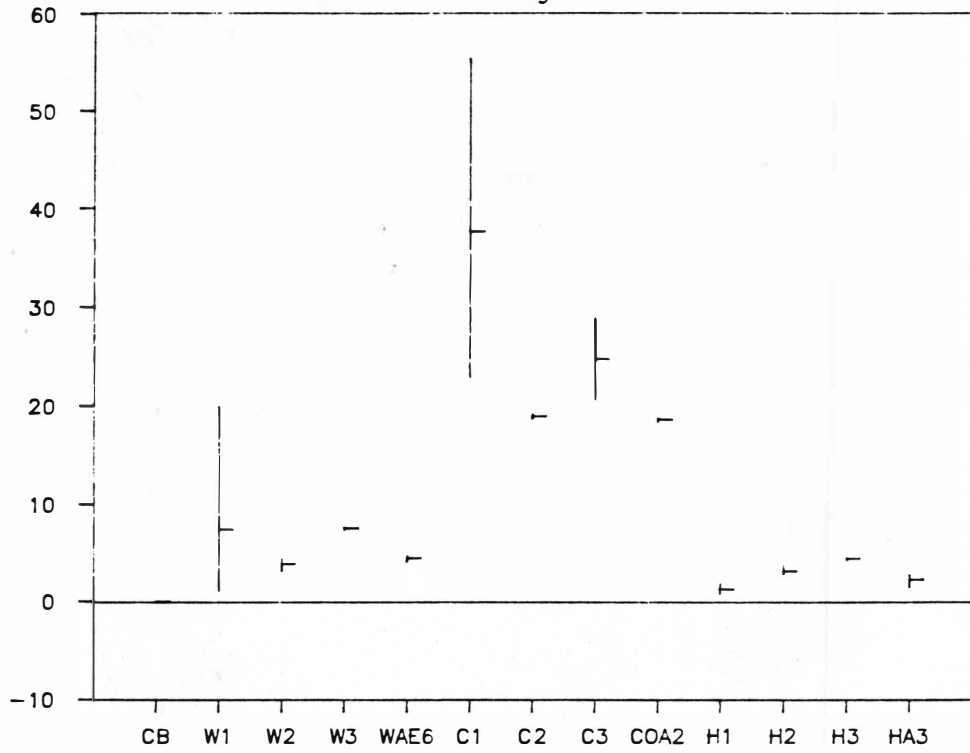
Ni Conc. (ppm)



Zn Concentration

in Digest

Zn Conc. (ppm)
(Thousands)



The major elements (> 1 mg/g) found in the starting materials were Ca, Al, Fe, Mg and Si. High concentration of Al and Si, elements necessary for the formation of cementitious crystals in the stabilized blocks, were found in WCA, NYCFA and HCA. Zinc was found in major amounts in NYCFA and minor amounts in WCA and HCA. The minor elements ($100 \mu\text{g/g} - 1$ mg/g) common to all three ashes were Cu, Pb and Mn. The elements, Cr and Ni, were present in high enough concentration in the WCA and NYCFA to be included as minor elements but slightly less abundant in one or two samples of HCA. Arsenic and cadmium were trace elements in WCA and HCA, while more abundant in NYCFA. Trace elements ($< 100 \mu\text{g/g}$) were Co and Hg. Huntington composite ash had virtually no mercury, less than 1 ppb. For comparison purposes, the published elemental concentration of portland cement (Duedall et al., 1981) is listed in Table 6.4, which shows that portland cement contained less amount of metals than the starting materials except calcium.

Table 6.5 and Figure 6.1 represent the results of individual chemical analyses performed on the optimum blocks and the cement block. Major elements in all three stabilized blocks include Ca, Al, Fe, Mg and Si. Zinc was found in major amounts in New York City block (COA2) and minor amounts in Westchester block (WAE6) and Huntington block (HA3). Minor elements of the three stabilized blocks were Cr, Cu, Pb and Mn, whereas As, Co, Ni and Hg were trace elements. Cadmium is present in trace amounts in WAE6 and HA3, although high enough concentration in COA2 to be included as minor element. Mercury concentration in HA3 was below the detection limit, i.e., less than 1 ppb.

For most metals, the blocks showed concentrations lower than or at least equal to the corresponding ashes except Ca. Even though three different particle sizes were used when analyzing elemental concentration of the ashes, particles larger than 4.75 mm were not analyzed (Table 6.1). These particles were however included in proctor fabrication, which is partly responsible for the lower concentrations in the stabilized blocks than those of ashes. The high concentration of Ca is due to the portland cement added to stabilize the raw ash. It is interesting to compare the cement block and the stabilized blocks, especially Westchester optimum

Table 6.4. Metal concentrations in portland cement^a

<u>Element</u>	<u>Portland Cement</u>
Ca (%)	39 (± 2) ^b
Al (%)	2.3 (± 0.1)
Fe (%)	1.7 (± 0.1)
Mg (%)	0.71 (± 0.01)
Si (%)	9.9 (± 0.3)
As (ppm)	2 (± 1)
Cd (ppm)	< 0.04
Cr (ppm)	38 (± 3)
Co (ppm)	5 (± 1)
Cu (ppm)	9 (± 1)
Pb (ppm)	< 1
Mn (ppm)	435 (± 15)
Hg (ppm)	n.d. ^c
Ni (ppm)	18 (± 2)
Zn (ppm)	29 (± 2)

a. From Duedall et al. (1981)

b. Values in parentheses denote standard deviations.

c. Not determined.

block (WAE6) which showed very strong structural integrity; compressive strength of 1231 ± 53.5 psi. Westchester block contained more Ca, Cd, Cr, Cu, Pb, Ni and Zn, less Si and As, and nearly same amount of Al, Fe, Mg, Co and Mn as cement block.

The concentration of selected major and acid leachable minor components were analyzed in replicates. The chemical composition of the raw ash will depend largely on the sociological and industrial factors related to the area, the combustion conditions and the removal efficiency of the air pollution control devices. There is no consistent tendency in metal concentrations between three different ashes. The differences between the three ashes in elemental concentrations can be attributed to, as mentioned above, differences in waste sources, plant design and combustion conditions.

Since the stabilized blocks were composed of raw ashes and 15% of portland cement and the blocks contained a greater proportion of raw ash, one would expect the elemental concentrations of the blocks closer to but slightly less than those of raw ash. Calcium is the only one of which blocks showed higher concentration than the corresponding raw ash, and this is due to the portland cement added to stabilize the raw ash. This is expected because the major compounds found in the portland cement are dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) and tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$).

EPA AND ASTM LEACHING TESTS

Leachate samples prepared using EPA and ASTM procedures were tested for fifteen metals by AAS. The particle size ranges listed in Table 6.1 were also used for these procedures.

Table 6.5. Metal concentrations^a in optimum blocks and cement block.

<u>Element</u>	<u>Cement Block</u>	<u>WAE6^b</u>	<u>COA2</u>	<u>HA3</u>
Ca (%)	7.30	14.4	13.5	13.4
	7.07	13.6	12.7	12.8
	5.53	13.2	12.4	12.8
	AVERAGE 6.63	13.7	12.8	13.0
	STD.DEV 0.78	0.5	0.4	0.3
Al (%)	5.66	6.41	7.03	4.16
	5.45	6.18	6.99	3.91
	5.22	4.93	6.87	3.80
	AVERAGE 5.44	5.84	6.96	3.96
	STD.DEV 0.18	0.65	0.07	0.15
Fe (%)	5.27	5.33	1.66	7.55
	4.90	5.06	1.51	7.25
	3.28	4.30	1.51	7.08
	AVERAGE 4.48	4.90	1.56	7.30
	STD.DEV 0.86	0.44	0.07	0.20
Mg (%)	2.33	1.46	1.34	1.09
	1.98	1.40	1.34	0.90
	1.48	1.24	1.34	0.88
	AVERAGE 1.93	1.37	1.34	0.96
	STD.DEV 0.35	0.09	0.00	0.10
Si (%)	29.6	16.7	10.3	14.3
	24.7	16.7	10.1	13.5
	22.9	14.9	10.1	13.4
	AVERAGE 25.7	16.1	10.2	13.7
	STD.DEV 2.8	0.9	0.1	0.4
As (ppm)	38.7	5.58	74.8	17.7
	34.0	5.14	71.7	17.2
	26.1	3.62	70.8	12.1
	AVERAGE 33.0	4.78	72.5	15.7
	STD.DEV 5.2	0.84	1.7	2.5

Table 6.5. Continued.

<u>Element</u>	<u>Cement Block</u>	<u>WAE6</u>	<u>COA2</u>	<u>HA3</u>	
Cd (ppm)	0.38	49.1	768	15.3	
	0.26	46.2	723	12.1	
	0.14	36.4	702	10.2	
	AVERAGE	0.26	43.9	731	12.6
	STD.DEV	0.10	5.4	28	2.1
Cr (ppm)	41.1	151	194	148	
	29.1	144	191	147	
	23.2	142	186	128	
	AVERAGE	31.1	146	190	141
	STD.DEV	7.5	4	3	9
Co (ppm)	31.1	23.0	21.2	12.7	
	24.5	18.5	19.9	11.0	
	18.8	17.9	18.2	11.0	
	AVERAGE	24.8	19.8	19.7	11.6
	STD.DEV	5.0	2.3	1.2	0.8
Cu (ppm)	13.1	7069	613	1956	
	12.8	5877	605	1486	
	12.8	1058	599	896	
	AVERAGE	12.9	4668	606	1446
	STD.DEV	0.1	2598	6	434
Pb (ppm)	5.53	8023	7557	1450	
	5.45	3982	7387	938	
	1.90	3404	6889	733	
	AVERAGE	4.30	5137	7278	1040
	STD.DEV	1.69	2055	283	301
Mn (ppm)	1033	841	1069	898	
	1017	818	1064	815	
	716	814	1062	707	
	AVERAGE	922	825	1065	806
	STD.DEV	146	12	3	78

Table 6.5. Continued.

<u>Element</u>	<u>Cement Block</u>	<u>WAE6</u>	<u>COA2</u>	<u>HA3</u>	
Hg (ppm)		17.2	2.40		
		13.2	1.18		
		3.6	0.16		
	AVERAGE	b.d.l. ^c	11.3	1.25	b.d.l.
	STD.DEV		5.7	0.92	
Ni (ppm)	50.6	121	94.3	60.0	
	46.4	107	77.0	57.0	
	43.1	98	63.0	46.8	
	AVERAGE	46.7	109	78.1	54.6
	STD.DEV	3.1	10	12.8	5.6
Zn (ppm)	56.1	4699	18729	2726	
	54.2	4642	18718	2664	
	49.9	4105	18407	1492	
	AVERAGE	53.4	4482	18618	2294
	STD.DEV	2.6	268	149	567

- a. Values are the highest, medium, lowest, average and standard deviation of the three replicates.
- b. WAE6 : Westchester composite ash with 15% portland cement and 17% moisture content, cured at 49°C for 1 day.
 COA2 : New York City fly ash with 15% portland cement and 23% moisture content, cured at 49°C for 3 days.
 HA3 : Huntington composite ash with 15% portland cement and 18% moisture content, cured at 23°C (air) for 7 days.
- c. Below detection limit.

EPA Extraction Procedure

The methods described in the Federal Register (1980) were used to test leaching characteristics of the stabilized blocks and the starting materials. Fifty grams of each material was added for each of the three replicates to a Nalgene plastic bottle containing 800 ml of distilled-deionized water. Acetic acid (0.5 N) was added to each bottle at the interval of 15, 30 and 60 minutes to achieve a pH of approximately 5 ± 0.02 . The EPA test procedure calls for the addition of not more than 4 ml of acid for every gram of solid. After adding not more than 200 ml of acid, pH was measured followed by 24 h shaking and then pH was measured again. More acid, up to 200 ml per bottle, was added when necessary. Table 6.6 lists the final pH and the total amount of acetic acid added to samples.

The tendency of increasing pH with time is probably due to the mineral phases, such as calcite (CaCO_3) and anhydrite (CaSO_4), present in the raw ash and calcium silicates ($2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$) present in the portland cement. Alkalinity produced by hydration reactions in the form of calcium hydroxide ($\text{Ca}(\text{OH})_2$) can neutralize the added acetic acid (Neville, 1983). Samples of finer particle size required more acid to obtain a pH of 5, than coarser samples because of the larger surface area to volume ratio. More acid was added to the stabilized blocks than the starting materials, probably due to the calcium added as cement which was used as additive when stabilizing the raw ashes.

The elutriates were filtered on acid washed vacuum filtration apparatus through a $0.45 \mu\text{m}$ membrane filter paper. The filterates were adjusted with distilled-deionized water to 1000 ml glass volumetric flasks, stored in 500 ml Nalgene plastic bottles and refrigerated at 5°C until they were analyzed.

Table 6.6. Final pH values and amount of acetic acid added in EPA leaching test.

<u>Sample</u> ^b	<u>pH</u>	<u>Acid added</u> ^c
Cement Block	5.07 (± 0.12) ^a	59 (± 1)
Westchester		
WAE6	8.31 (± 0.27)	200 (± 0)
W1	5.00 (± 0.12)	30 (± 4)
W2	5.09 (± 0.06)	45 (± 4)
W3	6.68 (± 0.32)	200 (± 0)
New York City		
COA2	5.24 (± 0.05)	200 (± 0)
C1	5.01 (± 0.11)	105 (± 0)
C2	5.10 (± 0.11)	165 (± 0)
C3	5.05 (± 0.04)	200 (± 0)
Huntington		
HA3	5.09 (± 0.07)	140 (± 0)
H1	4.85 (± 0.07)	25 (± 0)
H2	4.98 (± 0.09)	30 (± 0)
H3	5.02 (± 0.06)	140 (± 0)

a. Numbers in parentheses denote standard deviations.

b. Particle size ranges are listed in Table 6.1.

c. Unit is milliliter.

ASTM Extraction Procedure

Samples were leached following the method of the ASTM (1980) Proposed Method for Leaching of Waste Materials, Part A: Water Shake Extraction Procedure. For this procedure, three replicates of 75 g of each material were placed into Nalgene plastic bottles with 300 ml of distilled-deionized water. The samples were then placed on a mechanical shaker for 48 hours. After measuring pH (Table 6.7), the elutriates were filtered through a 0.45 μm millipore filter paper and stored in 500 ml plastic bottles after the addition of 1 ml nitric acid for storage.

Elemental Analysis by Atomic Absorption Spectroscopy

Three replicate samples of each elutriate were analyzed for fifteen metals by Atomic Absorption Spectrophotometer (AAS), using either flame or furnace.

Calcium Determination

The concentration of calcium was determined in accordance with the procedures outlined above.

Determination of Al, Fe, Mg, Si, As, Cd, Cr, Co, Cu, Pb, Mn, Ni, Zn and Hg

Mg, Cu and Zn concentrations in both EPA and ASTM leachates were high enough to be analyzed with acetylene/air flame without background correction. All Si analyses were done with nitrous oxide/acetylene flame without background correction. For Mn analysis, ASTM leachates were determined with graphite furnace, while EPA leachates with acetylene/air flame because the concentrations were too high to use graphite furnace. Al, Fe, As, Cd, Cr, Co, Pb and Ni concentrations in both EPA and ASTM leachates were so low that these metals were determined using the HGA 500 flameless graphite furnace with background correction. Mercury was analyzed using the Perkin Elmer MHS-10 hydride generation system.

Table 6.7. Final pH values in ASTM leaching test.

<u>Sample</u> ^a	<u>pH</u>
Cement Block	11.97 (± 0.04) ^b
Westchester	
WAE6	12.03 (± 0.01)
W1	11.29 (± 0.09)
W2	11.99 (± 0.03)
W3	12.31 (± 0.02)
New York City	
COA2	11.68 (± 0.01)
C1	8.67 (± 0.41)
C2	9.73 (± 0.34)
C3	7.81 (± 0.73)
Huntington	
HA3	11.73 (± 0.12)
H1	7.71 (± 0.28)
H2	8.20 (± 0.15)
H3	7.94 (± 0.34)

a. Values in parentheses denote standard deviations.

b. Particle size ranges are listed in Table 6.1.

Matrix modifiers, 0.5% (w/v) La_2O_3 and 1% (w/v) $(\text{NH}_4)_2\text{HPO}_4$, were used for reducing interferences for the Mg and Cd analyses respectively. A solution containing 0.1% Ultrex nitric acid and 1000 ppm Ni as $\text{Ni}(\text{NO}_3)_2$ (1:1) for As analysis in order to increase the charring temperature. Standards were serial dilutions of Fisher Scientific atomic absorption standards made up in a 0.1% Ulterx nitric acid. Potassium iodide solution (0.1%) was added to the mercury standard solutions to reduce the adsorption of Hg on the walls of glasswares.

Results and Discussion

The measured concentrations of fifteen metals analyzed for both EPA and ASTM leachates are presented in this section. Tables 6.8 and 6.9 show the elemental concentrations of EPA leachates of the starting materials and the optimum blocks respectively. Tables 6.10 and 6.11 represent values of ASTM leachates. Figures 6.2 and 6.3 again show the tendency that coarser particles result in lower concentration and larger variations between three replicate samples with some exceptions. In EPA leachates, larger particles tend to contain more Ca, Al, As and Cr in NYCFA: in ASTM leachates, coarser particles have higher concentration of Mg in WCA, Si, Cd, Cr, Mn, Ni and Zn in NYCFA, and Ca and Mg in HCA than smaller particles do. The concentrations of several elements were lower than the detection limits of the graphite furnace atomic absorption method, which is designated by b.d.l. (below detection limit) in Tables 6.8 through 6.11.

In order to compare EPA leachates versus ASTM leachates, it is necessary to consider differences between test conditions. The ratio of total liquid volume to sample mass is 20 : 1 for EPA leachates and 4 : 1 for ASTM leachates. Total leaching time is 24 h and 48 h for EPA and ASTM leachates respectively. The pH values in Tables 6.6 and 6.7 show that metals were leached under the acidified condition for EPA method, while ASTM extraction procedure were done under the basic condition. In general, metal concentrations were higher in the EPA leachates than in ASTM leachates both for the optimum blocks and the starting materials. Chromium is the only exception.

Table 6.8 Metal concentrations in EPA leachates of starting materials.

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash			
	W1 ^a	W2	W3	C1	C2	C3	H1	H2	H3	
Ca (ppm)	504	995	2878	759	1105	968	450	732	1792	
	356	921	2878	746	1088	874	443	706	1658	
	302	827	2878	699	1088	840	423	652	1558	
	AVERAGE	387	914	2878	735	1094	894	439	697	1669
	STD.DEV	85	69	0	26	8	54	11	34	96
Al (ppm)	1.28	0.97	3.66	11.46	13.95	18.95	0.10	0.16	0.31	
	0.52	0.91	2.32	11.46	12.37	16.63	0.09	0.14	0.26	
	0.39	0.80	1.77	11.39	11.94	16.08	0.08	0.09	0.24	
	AVERAGE	0.73	0.89	2.58	11.43	12.75	17.22	0.09	0.13	0.27
	STD.DEV	0.39	0.07	0.79	0.03	0.86	1.24	0.01	0.03	0.03
Fe (ppb)	671	151		30.5	26.0	90.9	324	336	246	
	237	124		19.6	22.0	51.3	265	230	218	
	191	122		17.9	20.3	39.9	210	105	161	
	AVERAGE	366	132	b.d.l. ^b	22.7	22.8	60.7	266	224	208
	STD.DEV	216	13		5.6	2.4	21.9	47	94	35
Mg (ppm)	25.4	46.3	184	155	174	274	30.5	42.6	65.5	
	17.2	45.9	131	154	167	274	30.1	38.0	59.3	
	10.1	41.8	116	150	166	257	26.3	37.6	57.2	
	AVERAGE	17.6	44.7	144	153	169	268	29.0	39.4	60.6
	STD.DEV	6.2	2.1	29	2	3	8	1.9	2.3	3.5
Si (ppm)	12.6	19.7	6.23	27.9	31.3	55.6	6.60	9.97	16.3	
	10.0	17.8	6.23	26.8	30.9	54.1	6.23	8.47	15.2	
	8.1	16.3	3.99	26.0	30.9	52.6	5.86	8.10	14.8	
	AVERAGE	10.2	17.9	5.48	26.9	31.0	54.1	6.23	8.85	15.5
	STD.DEV	1.8	1.4	1.06	0.8	0.2	1.2	0.31	0.81	0.6

Table 6.8. Continued.

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash		
	W1	W2	W3	C1	C2	C3	H1	H2	H3
As (ppb)			4.75	10.69	22.3	30.4		1.90	5.23
			2.85	9.98	21.6	29.5		1.66	4.28
			2.38	7.60	15.0	15.9		0.95	3.56
	AVERAGE	b.d.l.	b.d.l.	3.33	9.42	19.6	25.3	b.d.l.	1.50
STD.DEV			1.03	1.32	3.3	6.6		0.40	0.68
Cd (ppm)	0.27	0.31	0.07	31.8	25.4	48.4	0.05	0.10	0.26
	0.22	0.27	0.04	29.7	24.5	47.8	0.05	0.08	0.23
	0.13	0.22	0.03	26.3	23.5	46.9	0.05	0.08	0.21
	AVERAGE	0.21	0.27	0.05	29.3	24.5	47.7	0.05	0.09
STD.DEV	0.06	0.04	0.02	2.3	0.8	0.6	0.00	0.01	0.02
Cr (ppb)	3.99	5.46	75.4	9.15	13.0	98.3		1.48	4.13
	3.25	4.72	63.0	8.41	12.0	30.6		1.33	3.54
	1.18	4.13	60.3	7.68	10.6	24.7		1.48	3.10
	AVERAGE	2.80	4.77	66.2	8.41	11.9	51.2	b.d.l.	1.43
STD.DEV	1.19	0.54	6.6	0.60	1.0	33.4		0.07	0.42
Co (ppb)		9.58	7.94	94.2	76.1	146	12.0	22.7	34.2
		7.94	7.94	87.6	69.6	145	12.0	14.5	28.5
		7.12	4.65	86.0	66.3	134	11.2	14.5	27.7
	AVERAGE	b.d.l.	8.21	6.85	89.3	70.6	142	11.8	17.3
STD.DEV		1.02	1.55	3.5	4.1	6	0.4	3.9	2.9
Cu (ppm)	0.38	0.58	0.38	1.39	1.17	8.01	1.91	1.23	2.56
	0.38	0.47	0.38	1.32	1.01	7.96	1.12	0.92	2.29
	0.34	0.47	0.36	1.30	0.97	7.92	0.83	0.85	1.86
	AVERAGE	0.37	0.51	0.37	1.34	1.05	7.96	1.29	1.00
STD.DEV	0.02	0.05	0.01	0.04	0.09	0.04	0.46	0.17	0.29
Pb (ppm)	3.42	1.82		23.2	26.3	23.2	0.04	0.04	0.05
	3.33	1.68		22.8	25.9	21.9	0.03	0.02	0.05
	2.86	1.44		22.5	25.5	21.0	0.02	0.02	0.04
	AVERAGE	3.20	1.65	b.d.l.	22.8	25.9	22.0	0.03	0.03
STD.DEV	0.24	0.16		0.3	0.3	0.9	0.01	0.01	0.01

Table 6.8. Continued.

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash			
	<u>W1</u>	<u>W2</u>	<u>W3</u>	<u>C1</u>	<u>C2</u>	<u>C3</u>	<u>H1</u>	<u>H2</u>	<u>H3</u>	
Mn (ppm)	0.44	0.57	0.61	6.02	4.36	9.44	3.57	6.63	12.0	
	0.32	0.48	0.54	5.76	4.36	9.12	3.57	5.23	11.2	
	0.19	0.44	0.39	5.41	4.18	9.12	3.48	4.97	10.4	
	AVERAGE	0.32	0.50	0.52	5.73	4.30	9.22	3.54	5.61	11.2
	STD.DEV	0.1	0.05	0.09	0.25	0.08	0.15	0.04	0.73	0.7
Hg (ppb)										
	AVERAGE	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	
	STD.DEV									
Ni (ppb)	23.2	30.9	22.7	316	259	757	219	167	403	
	18.7	25.2	19.5	304	257	741	123	109	372	
	9.8	24.4	12.9	296	247	706	94	107	354	
	AVERAGE	17.3	26.8	18.4	306	254	735	145	128	376
	STD.DEV	5.6	2.9	4.1	8	5	21	53	28	20
Zn (ppm)	15.7	18.0	2.12	824	703	1169	11.0	17.3	31.4	
	12.0	15.4	0.95	795	699	1161	10.3	12.9	28.6	
	7.8	14.4	0.83	720	678	1069	8.0	12.5	24.1	
	AVERAGE	11.8	15.9	1.30	779	693	1133	9.8	14.2	28.0
	STD.DEV	3.2	1.5	0.58	44	11	45	1.3	2.2	3.0

- a. Partilce size rangws are listed in Table 6.1
 b. Below detection limits

Table 6.9. Metal concentrations^a in EPA leachates of optimum blocks and cement block.

<u>Element</u>	<u>Cement Block</u>	<u>WAE6^b</u>	<u>COA2</u>	<u>HA3</u>
Ca (ppm)	504	2027	2010	2043
	470	1976	1926	1524
	403	1943	1876	1507
	AVERAGE 459	1982	1937	1692
	STD.DEV 42	34	55	249
Al (ppm)	0.58	0.04	0.13	1.22
	0.22	0.01	0.00	1.18
	0.16	0.01	0.00	0.55
	AVERAGE 0.32	0.02	0.04	0.98
	STD.DEV 0.18	0.01	0.06	0.30
Fe (ppb)	47.0	2.50	1.59	606
	28.3	2.32	1.22	346
	18.3	1.59	0.86	241
	AVERAGE 31.2	2.14	1.22	398
	STD.DEV 11.9	0.40	0.30	153
Mg (ppm)	3.6	50.1	85.5	33.8
	3.1	45.9	68.4	28.1
	2.2	37.6	61.3	24.3
	AVERAGE 3.0	44.5	71.8	28.7
	STD.DEV 0.6	5.2	10.1	3.9
Si (ppm)	14.1	11.5	55.9	33.5
	13.0	9.6	25.7	31.6
	10.7	8.8	25.7	31.3
	AVERAGE 12.6	10.0	35.8	32.1
	STD.DEV 1.4	1.1	14.3	1.0
As (ppb)		2.61	7.84	3.80
		2.38	0.00	3.33
		2.14	0.00	3.09
	AVERAGE	b.d.l. ^c	2.38	3.40
	STD.DEV		0.19	0.30

Table 6.9. Continued.

<u>Element</u>	<u>Cement Block</u>	<u>WAE6</u>	<u>COA2</u>	<u>HA3</u>	
Cd (ppm)		0.04	8.48	0.07	
		0.01	7.99	0.05	
		0.00	7.51	0.04	
	AVERAGE	b.d.l.	0.02	7.99	0.05
	STD.DEV		0.01	0.39	0.01
Cr (ppb)	35.6	75.9	43.7	18.45	
	32.6	42.2	39.0	5.02	
	29.8	19.3	19.9	1.77	
	AVERAGE	32.7	45.8	34.2	8.41
	STD.DEV	2.4	23.2	10.3	7.22
Co (ppb)			16.2	6.30	
			13.7	6.30	
			11.2	5.48	
	AVERAGE	b.d.l.	b.d.l.	13.7	6.02
	STD.DEV			2.0	0.39
Cu (ppm)	0.02	0.18	0.67	1.28	
	0.02	0.18	0.16	1.28	
	0.02	0.18	0.16	1.26	
	AVERAGE	0.02	0.18	0.33	1.27
	STD.DEV	0.00	0.00	0.24	0.01
Pb (ppm)			9.33	0.07	
			1.65	0.07	
			1.44	0.07	
	AVERAGE	b.d.l.	b.d.l.	4.14	0.07
	STD.DEV			3.67	0.00
Mn (ppm)	0.06	0.28	0.85	1.37	
	0.04	0.16	0.75	1.23	
	0.03	0.15	0.70	1.11	
	AVERAGE	0.04	0.19	0.77	1.24
	STD.DEV	0.01	0.06	0.06	0.11

Table 6.9. Continued.

<u>Element</u>	<u>Cement Block</u>	<u>WAE6</u>	<u>COA2</u>	<u>HA3</u>
Hg (ppb)				
	AVERAGE	b.d.l.	b.d.l.	b.d.l.
	STD.DEV			
Ni (ppb)		14.5	87.4	78.1
		10.4	72.2	74.5
		9.6	64.4	71.4
	AVERAGE	b.d.l.	74.7	74.7
	STD.DEV		9.6	2.7
Zn (ppm)	0.03	0.35	191	5.67
	0.02	0.08	138	4.83
	0.02	0.05	135	4.83
	AVERAGE	0.16	155	5.11
	STD.DEV	0.14	26	0.40

- a. Values are the highest, medium, lowest, average and standard deviation of the three replicates.
- b. WAE6 : Westchester composite ash with 15% portland cement and 17% moisture content, cured at 49°C for 1 day.
 COA2 : New York City fly ash with 15% portland cement and 23% moisture content. cured at 49°C for 3 days.
 HA3 : Huntington composite ash with 15% portland cement and 18% moisture content, cured at 23°C (air) for 7 days.
- c. Below detection limit.

Table 6.10. Metal concentrations in ASTM leachates of starting materials.

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash			
	W1 ^a	W2	W3	C1	C2	C3	H1	H2	H3	
Ca (ppm)	311	492	785	613	706	672	204	335	505	
	268	472	732	593	652	652	194	308	492	
	254	468	712	586	586	633	194	301	391	
	AVERAGE	278	477	743	597	648	652	198	315	463
	STD.DEV	24	10	31	11	49	16	5	14	51
Al (ppm)	4.57	0.38	0.03	1.14	20.53	0.07	0.16	0.10	0.23	
	2.92	0.08	0.02	0.60	1.03	0.01	0.07	0.02	0.21	
	2.30	0.05	0.02	0.12	0.20	0.01	0.03	0.01	0.04	
	AVERAGE	3.27	0.17	0.02	0.62	7.25	0.03	0.09	0.04	0.16
	STD.DEV	0.96	0.15	0.00	0.41	9.40	0.03	0.06	0.04	0.08
Fe (ppb)	6.37	4.88	9.34	9.48	12.7	9.69	129.2	41.2	71.6	
	5.94	3.82	8.91	6.68	9.7	7.32	53.5	13.6	59.9	
	5.31	2.55	3.61	5.81	8.4	6.68	5.6	5.8	35.8	
	AVERAGE	5.87	3.75	7.29	7.32	10.3	7.90	62.7	20.2	55.8
	STD.DEV	0.44	0.95	2.61	1.56	1.8	1.30	50.9	15.2	14.9
Mg (ppm)	0.06	0.03	0.41	98.6	7.19	227	43.3	69.8	83.0	
	0.05	0.03	0.09	23.4	1.35	187	41.6	66.1	45.8	
	0.04	0.03	0.02	17.0	0.31	177	41.6	64.0	36.7	
	AVERAGE	0.05	0.03	0.17	46.3	2.95	197	42.2	66.6	55.2
	STD.DEV	0.01	0.00	0.17	37.1	3.03	21	0.8	2.4	20.1
Si (ppm)	4.93	2.32	1.01	3.62	2.75	7.10	1.88	5.80	2.75	
	4.93	1.88	1.01	1.88	1.88	4.49	1.88	5.80	1.88	
	3.62	1.45	0.58	1.01	1.45	3.62	1.01	1.88	1.01	
	AVERAGE	4.49	1.88	0.87	2.17	2.03	5.07	1.59	4.49	1.88
	STD.DEV	0.62	0.36	0.21	1.08	0.54	1.48	0.41	1.85	0.71

Table 6.10. Continued

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash		
	W1	W2	W3	C1	C2	C3	H1	H2	H3
As (ppb)		2.92		4.72	8.71	8.71			
		2.53		2.73	5.52	8.31			
		2.33		0.93	4.12	6.12			
	AVERAGE	b.d.l. ^b	2.59	b.d.l.	2.79	6.12	7.71	b.d.l.	b.d.l.
STD.DEV		0.25		1.55	1.92	1.14			
Cd (ppb)				1085	29.4	25254	2.05	1.63	2.25
				335	20.6	15382	1.45	1.61	2.16
				52	16.3	2476	0.96	1.58	1.50
	AVERAGE	b.d.l.	b.d.l.	b.d.l.	491	22.1	14371	1.49	1.61
STD.DEV				436	5.5	9327	0.45	0.02	0.34
Cr (ppb)	63.9	123	216	93.1	103.8	223		1.38	3.07
	51.1	119	214	42.0	50.1	137		1.07	1.99
	24.2	111	200	32.7	44.9	80		0.92	0.61
	AVERAGE	46.4	118	210	55.9	66.3	147	b.d.l.	1.12
STD.DEV	16.5	5	7	26.6	26.6	59		0.19	1.00
Co (ppb)						30.11			
						7.34			
						0.51			
	AVERAGE	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12.65	b.d.l.	b.d.l.
STD.DEV						12.66			
Cu (ppm)	0.27	0.40	0.54	0.07	0.09	0.09	0.13	0.13	0.16
	0.25	0.40	0.49	0.07	0.09	0.09	0.11	0.13	0.16
	0.25	0.40	0.40	0.07	0.07	0.09	0.09	0.11	0.11
	AVERAGE	0.25	0.40	0.48	0.07	0.08	0.09	0.11	0.13
STD.DEV	0.01	0.00	55.81	0.00	0.01	0.00	0.02	0.01	0.02
Pb (ppb)	9.17	908	3188	11.91	24.7	40.5	3.91		
	8.12	781	3112	11.60	4.5	5.1	2.37		
	7.37	348	2959	3.45	4.4	4.1	0.06		
	AVERAGE	8.22	679	3086	8.99	11.2	16.6	2.11	b.d.l.
STD.DEV	0.74	240	96	3.92	9.5	16.9	1.58		

Table 6.10. Continued.

Element	Westchester Composite Ash			New York City Fly Ash			Huntington Composite Ash			
	W1	W2	W3	C1	C2	C3	H1	H2	H3	
Mn (ppb)	2.39	3.32	9.58	869	225.5	6667	354	375	491	
	2.05	3.21	4.60	227	17.7	5828	345	316	424	
	1.82	2.74	3.44	25	14.2	1173	334	288	237	
	AVERAGE	2.09	3.09	5.87	374	85.8	4556	344	326	384
	STD.DEV	0.24	0.25	2.66	360	98.8	2416	8	36	107
Hg (ppb)										
	AVERAGE	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	
	STD.DEV									
Ni (ppb)		36.5		12.8	12.6	96.1	28.5	17.3	24.8	
		33.7		11.7	10.6	16.6	15.5	16.4	20.3	
		30.4		7.1	10.0	13.1	12.0	15.0	12.8	
	AVERAGE	b.d.l.	33.6	b.d.l.	10.5	11.1	42.0	18.7	16.2	19.3
	STD.DEV		2.5		2.5	1.1	38.3	7.1	1.0	5.0
Zn (ppm)	0.02	0.20	1.03	0.12	0.06	81.6	0.13	0.14	0.13	
	0.02	0.18	0.92	0.05	0.05	1.9	0.08	0.05	0.09	
	0.02	0.14	0.88	0.04	0.05	0.1	0.08	0.03	0.07	
	AVERAGE	0.02	0.18	0.94	0.07	0.05	27.9	0.10	0.07	0.10
	STD.DEV	0.00	0.02	0.06	0.04	0.01	38.0	0.02	0.05	0.02

- a. Particle size range is listed in Table 6.1
- b. Below detection limits

Table 6.11. Metal concentrations^a in ASTM leachates of optimum blocks and cement block.

<u>Element</u>	<u>Cement Block</u>	<u>WAE6^b</u>	<u>COA2</u>	<u>HA3</u>	
Ca (ppm)	712	311	732	251	
	480	278	732	234	
	460	278	726	201	
	AVERAGE	551	289	730	229
	STD.DEV	115	16	3	21
Al (ppm)	0.61	0.72		13.02	
	0.61	0.64		10.02	
	0.24	0.48		9.99	
	AVERAGE	0.49	0.61	b.d.l. ^c	11.01
	STD.DEV	0.18	0.10		1.42
Fe (ppb)	57.9	63.0	9.55	294	
	53.7	58.2	8.91	188	
	53.5	50.7	7.85	172	
	AVERAGE	55.0	57.3	8.77	218
	STD.DEV	2.1	5.1	0.70	54
Mg (ppm)	10.78	3.21	42.1	2.87	
	3.27	2.98	40.4	2.64	
	1.21	2.87	37.1	1.84	
	AVERAGE	5.08	3.02	39.9	2.45
	STD.DEV	4.11	0.14	2.1	0.44
Si (ppm)	0.58	2.32	3.62	2.75	
	0.58	1.45	3.62	2.75	
	0.58	1.45	3.19	2.75	
	AVERAGE	0.58	1.74	3.48	2.75
	STD.DEV	0.00	0.41	0.21	0.00
As (ppb)			5.32	8.31	
			5.12	5.52	
			4.32	4.92	
	AVERAGE	b.d.l.	b.d.l.	4.92	6.25
	STD.DEV			0.43	1.48

Table 6.11. Continued.

<u>Element</u>	<u>Cement Block</u>	<u>WAE6</u>	<u>COA2</u>	<u>HA3</u>
Cd (ppb)				
	AVERAGE	b.d.l.	b.d.l.	b.d.l.
	STD.DEV			
Cr (ppb)	11.8	68.4	390	20.5
	11.5	43.1	389	16.9
	10.6	39.7	372	16.4
	AVERAGE	11.3	384	17.9
	STD.DEV	0.5	8	1.9
Co (ppb)				
	AVERAGE	b.d.l.	b.d.l.	b.d.l.
	STD.DEV			
Cu (ppm)	0.02	0.29	0.09	1.86
	0.02	0.27	0.09	1.63
	0.02	0.25	0.09	1.45
	AVERAGE	0.02	0.09	1.65
	STD.DEV	0.00	0.00	0.16
Pb (ppb)	15.18	750	505	42.1
	7.37	556	493	37.9
	9.02	510	478	31.9
	AVERAGE	10.52	492	37.3
	STD.DEV	3.36	11	4.2
Mn (ppb)	2.74	1.58	8.07	3.09
	2.16	1.35	5.41	2.86
	2.16	1.24	4.13	2.63
	AVERAGE	2.36	5.87	2.86
	STD.DEV	0.27	1.64	0.19

Table 6.11. Continued.

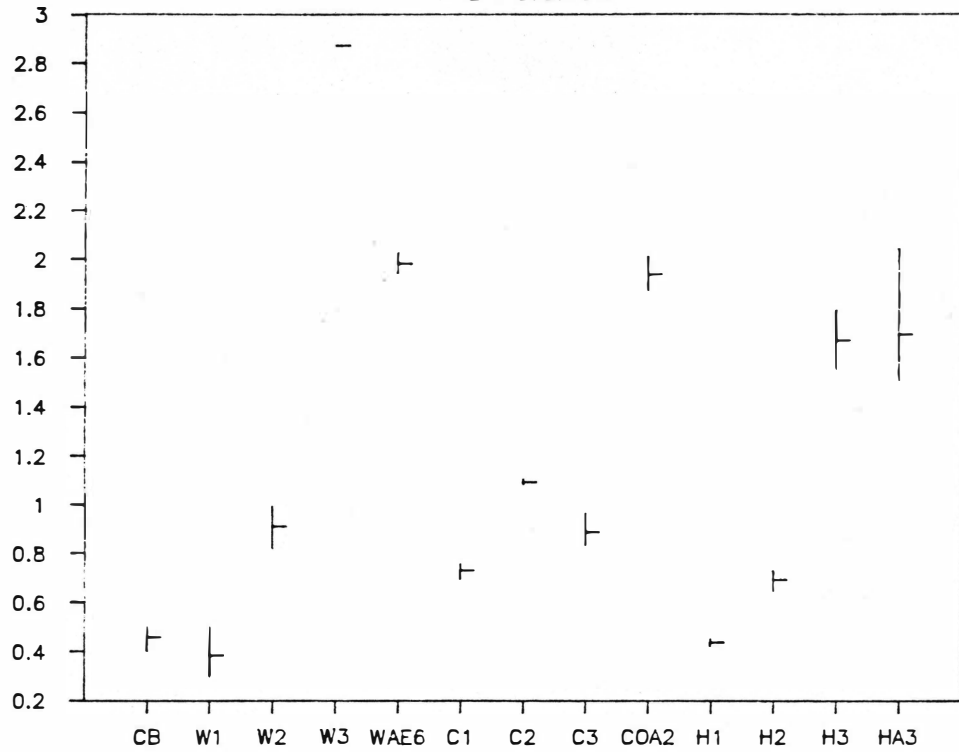
<u>Element</u>	<u>Cement Block</u>	<u>WAE6</u>	<u>COA2</u>	<u>HA3</u>
Hg (ppb)				
	AVERAGE	b.d.l.	b.d.l.	b.d.l.
	STD.DEV			
Ni (ppb)				
			14.1	73.2
			13.1	64.5
			10.0	58.9
	AVERAGE	b.d.l.	12.4	65.5
	STD.DEV		1.8	5.9
Zn (ppm)				
	0.04	0.23	1.32	0.05
	0.02	0.22	1.22	0.05
	0.01	0.17	1.20	0.05
	AVERAGE	0.20	1.25	0.05
	STD.DEV	0.02	0.05	0.00

- a. Values are the highest, medium, lowest, average and standard deviation of the three replicates.
- b. WAE6 : Westchester composite ash with 15% portland cement and 17% moisture content, cured at 49°C for 1 day.
 COA2 : New York City fly ash with 15% portland cement and 23% moisture content, cured at 49°C for 3 days.
 HA3 : Huntington composite ash with 15% portland cement and 18% moisture content, cured at 23°C (air) for 7 days.
- c. Below detection limit.

Figure 6.2 Metal concentrations in EPA leachates.

in EPA Leachate

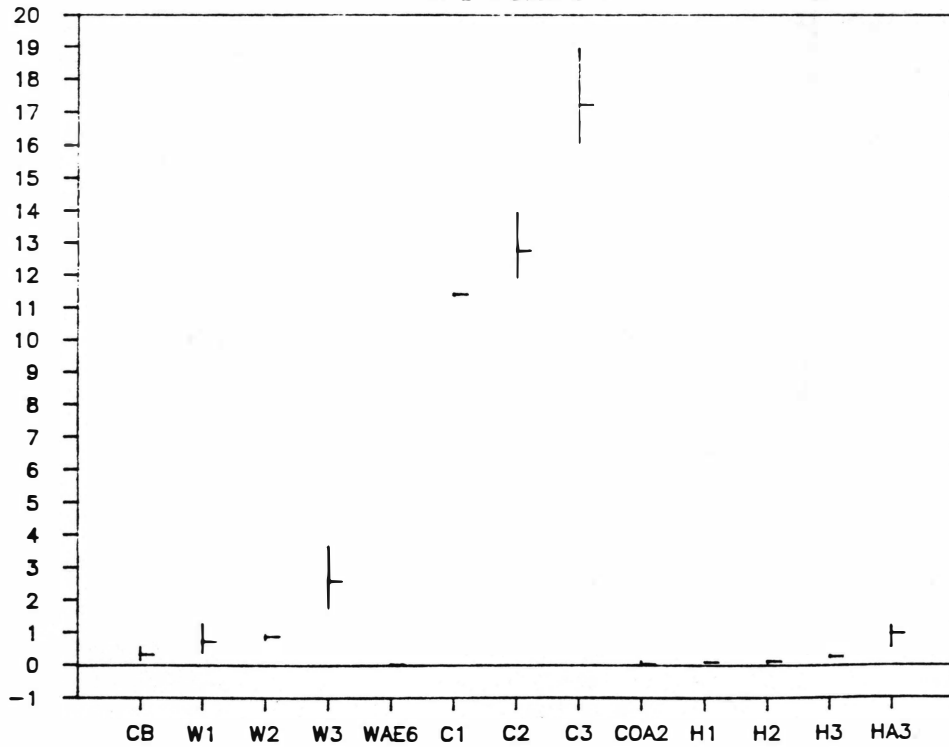
Ca Conc. (ppm)
(Thousands)



Al Concentration

in EPA Leachate

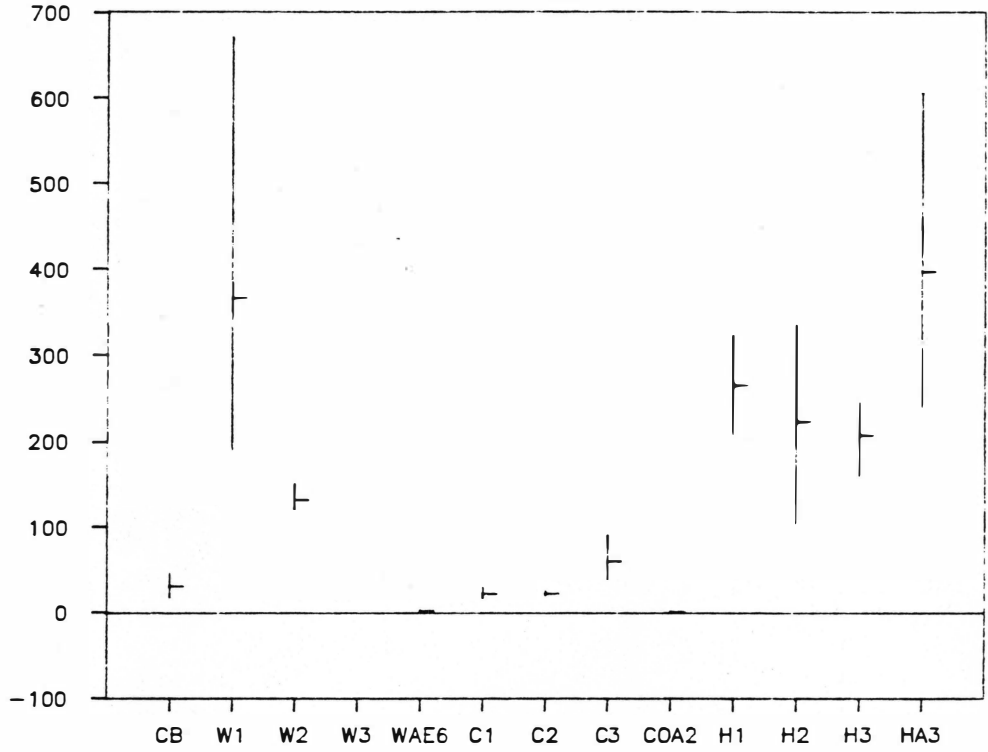
Al Conc. (ppm)



Fe Concentration

in EPA Leachate

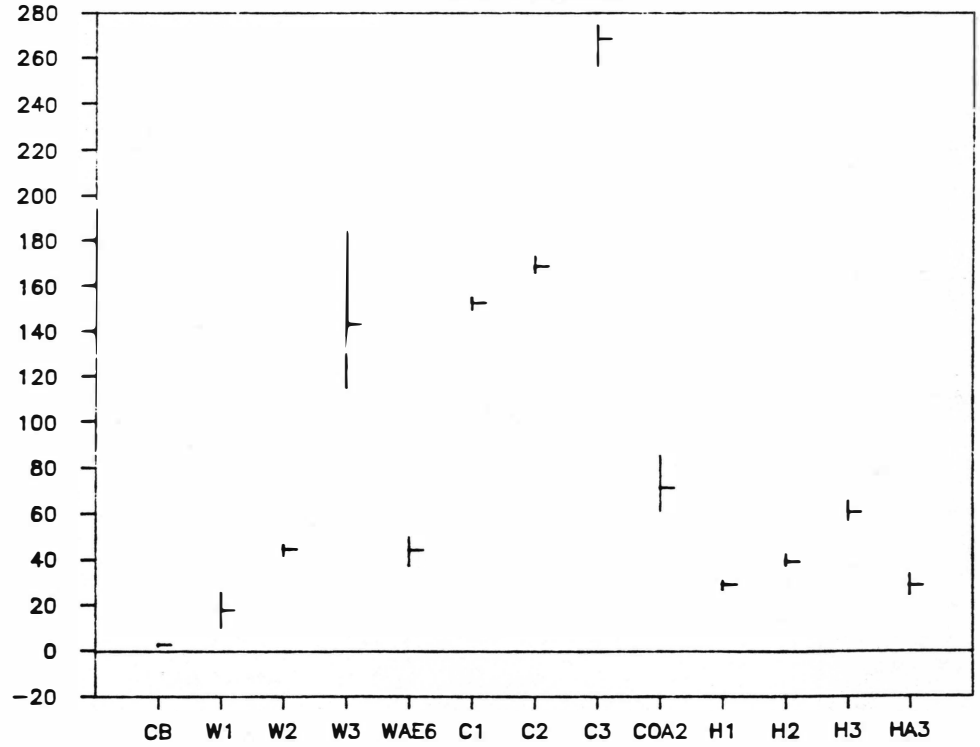
Fe Conc. (ppb)



Mg Concentration

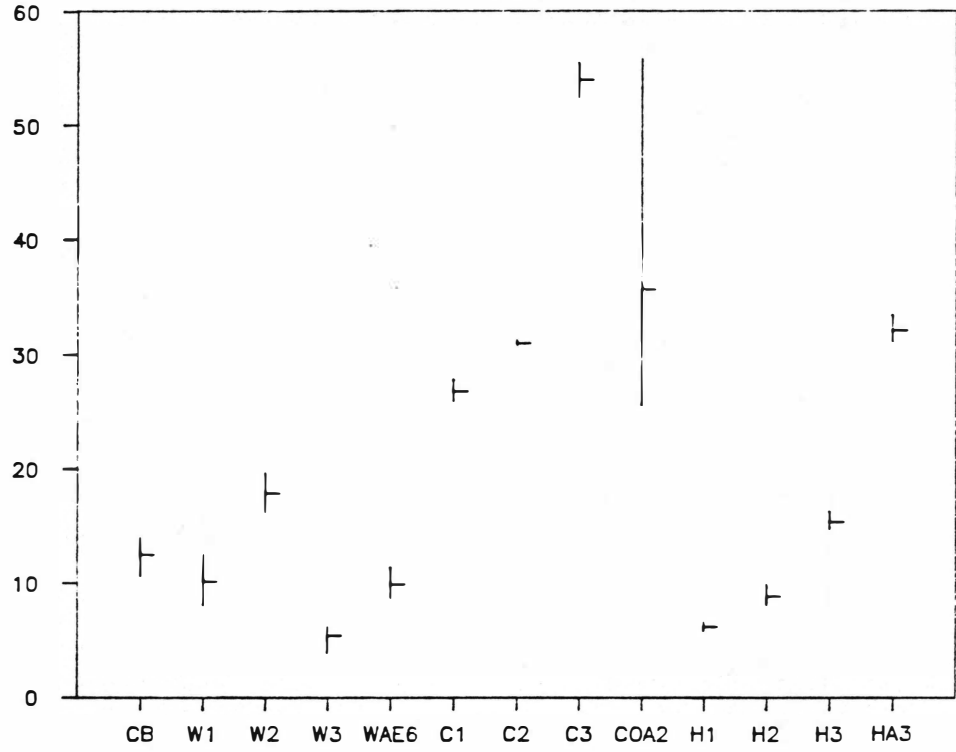
in EPA Leachate

Mg Conc. (ppm)



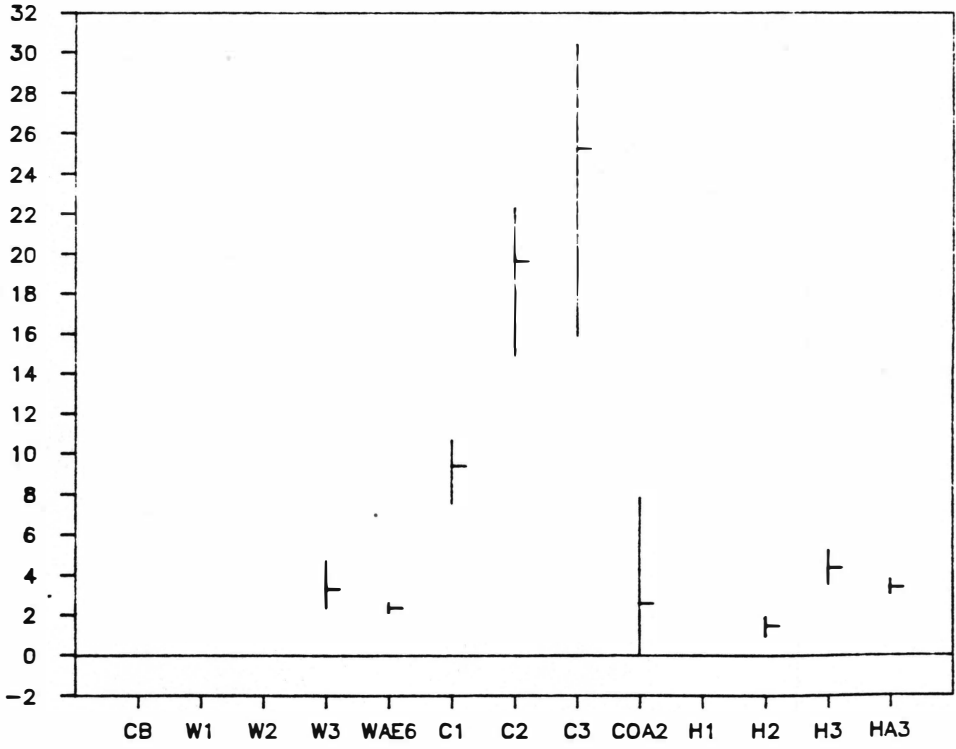
Si Concentration in EPA Leachate

Si Conc. (ppm)



As Concentration in EPA Leachate

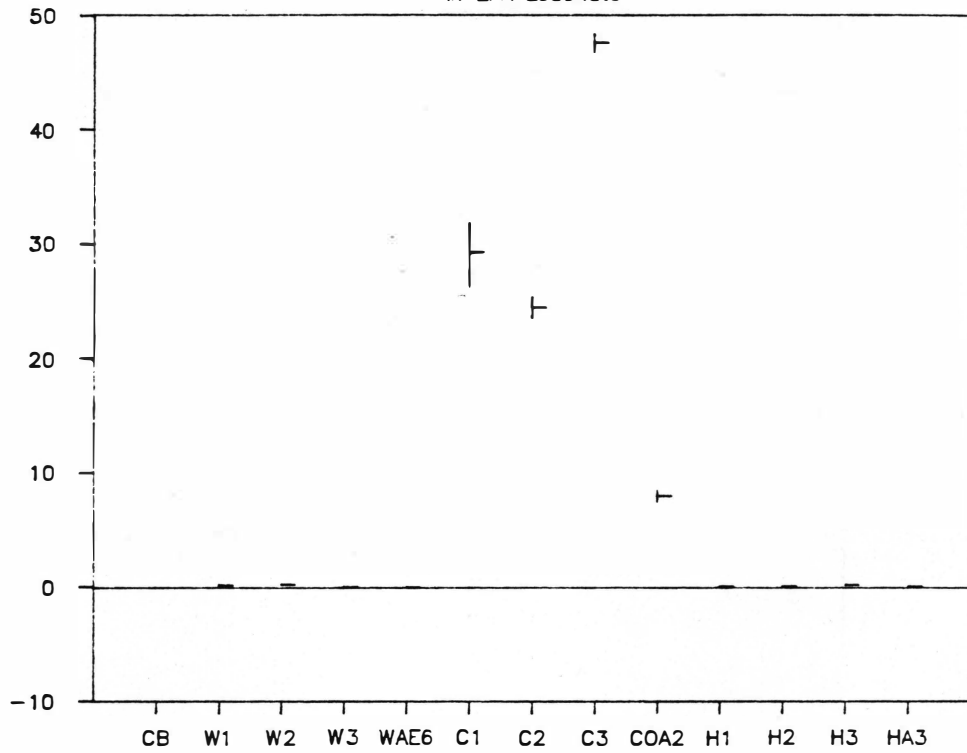
As Conc. (ppb)



Cd Concentration

in EPA Leachate

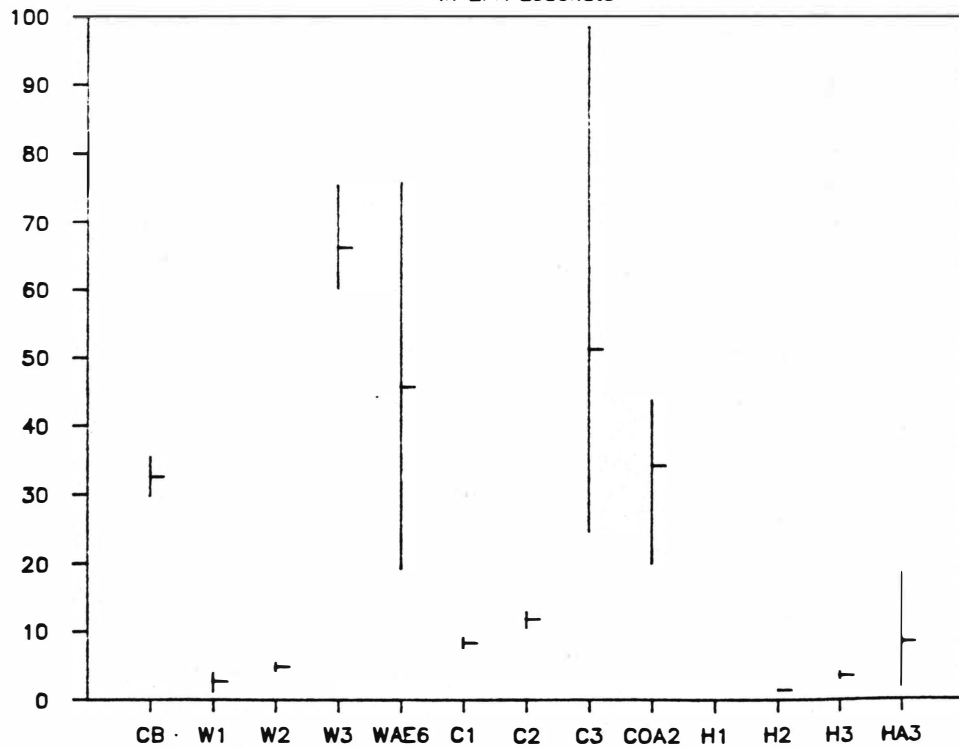
Cd Conc. (ppm)



Cr Concentration

in EPA Leachate

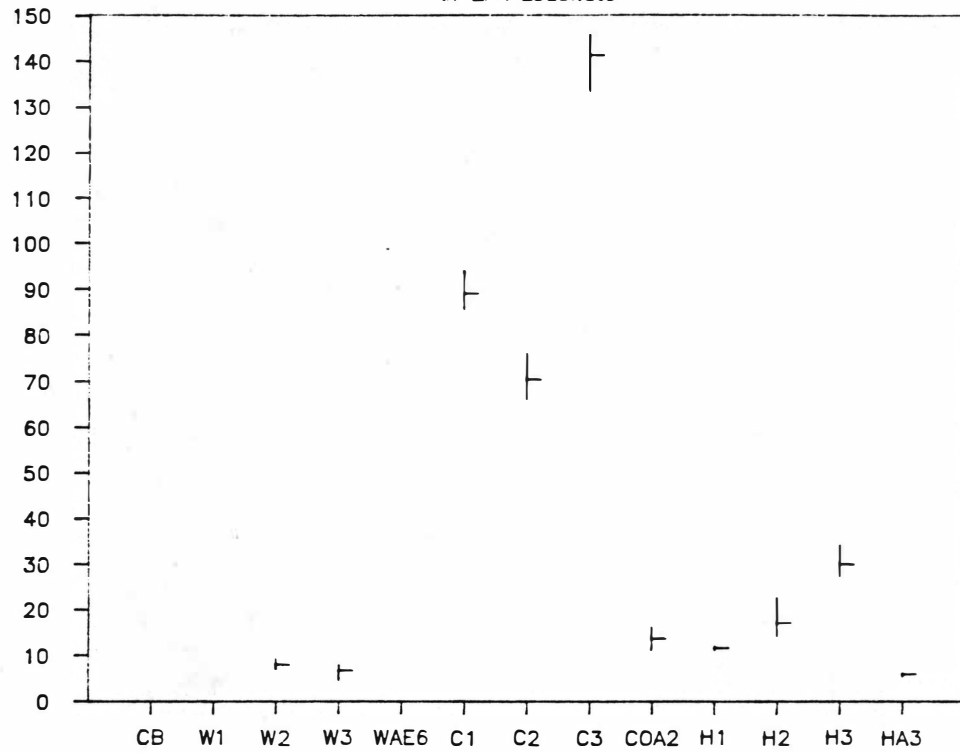
Cr Conc. (ppb)



Co Concentration

in EPA Leachate

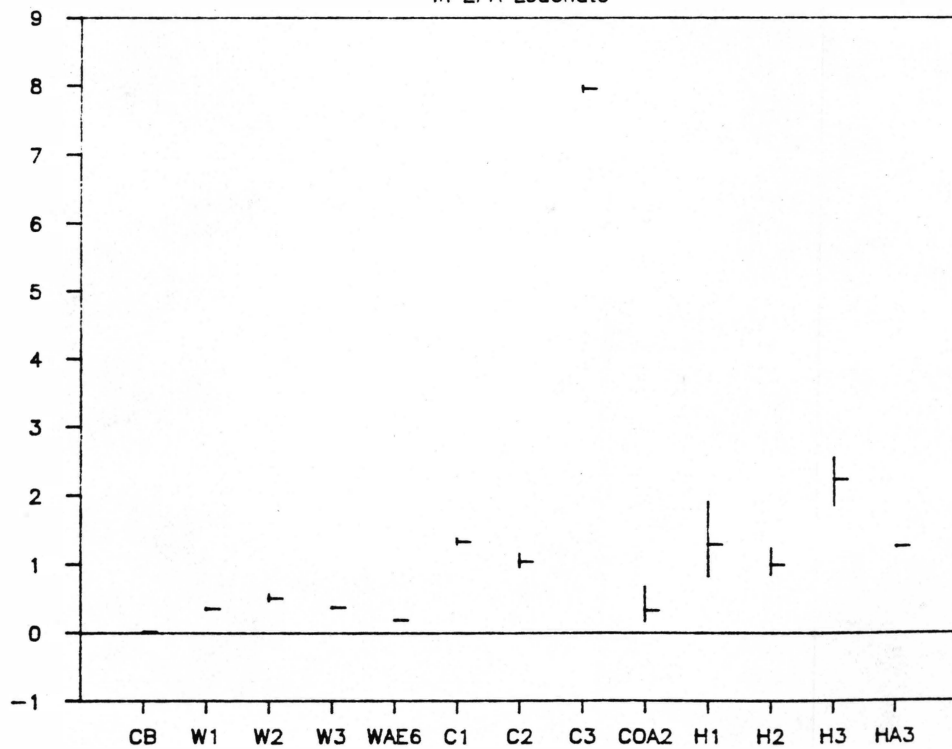
Co Conc. (ppb)



Cu Concentration

in EPA Leachate

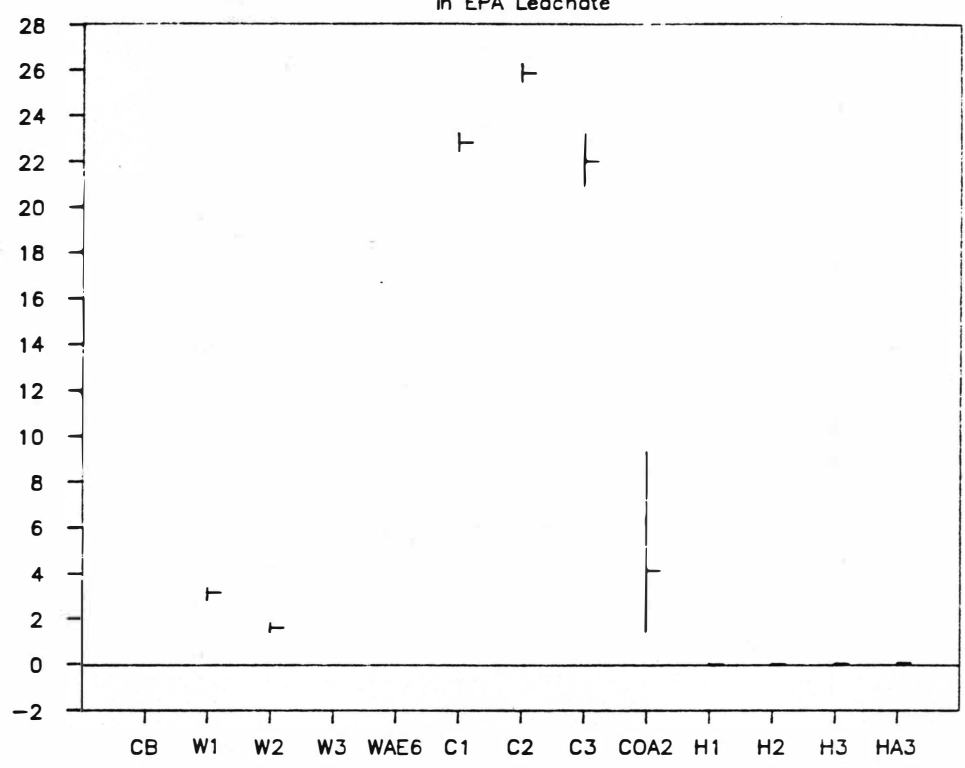
Cu Conc. (ppm)



Pb Concentration

in EPA Leachate

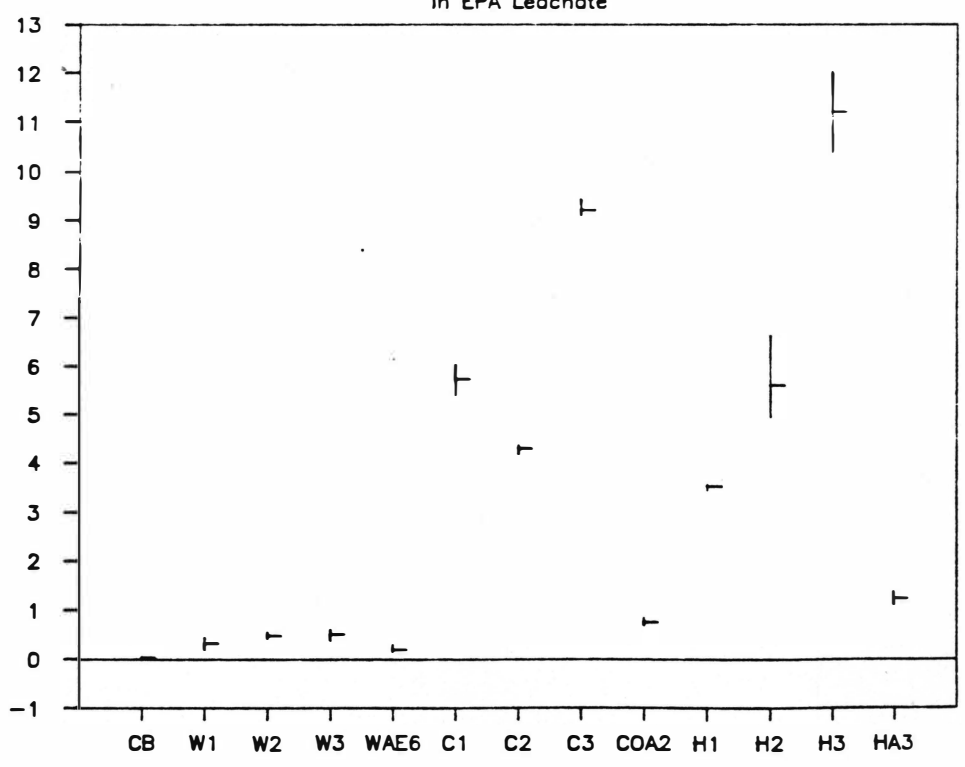
Pb Conc. (ppm)



Mn Concentration

in EPA Leachate

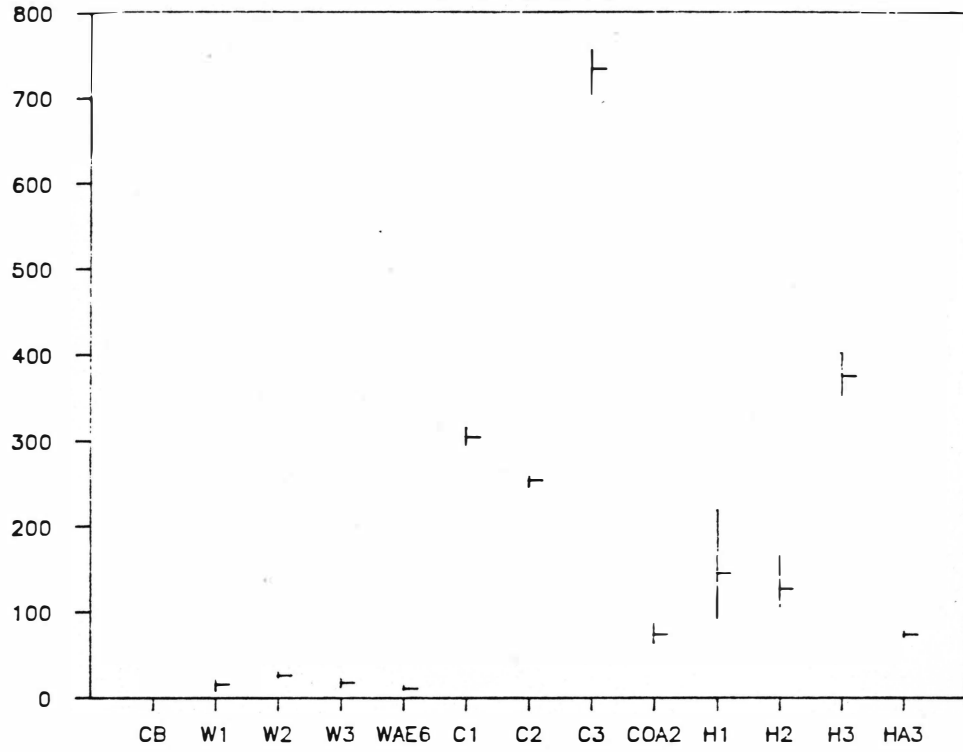
Mn Conc. (ppm)



Ni Concentration

in EPA Leachate

Ni Conc. (ppb)



Zn Concentration

in EPA Leachate

Zn Conc. (ppm)
(Thousands)

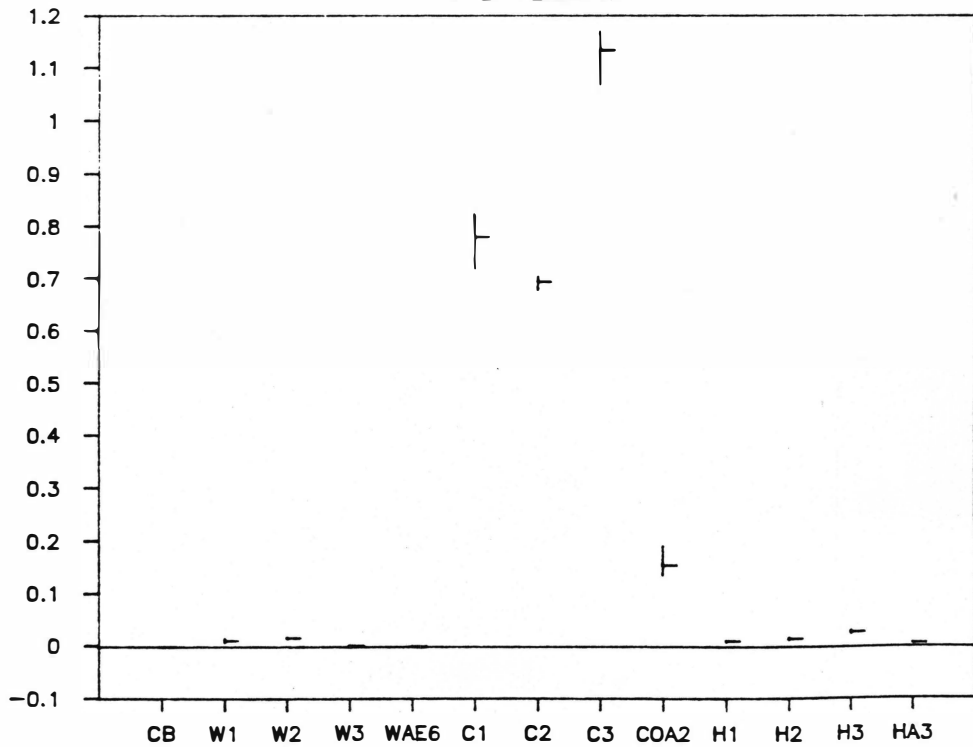
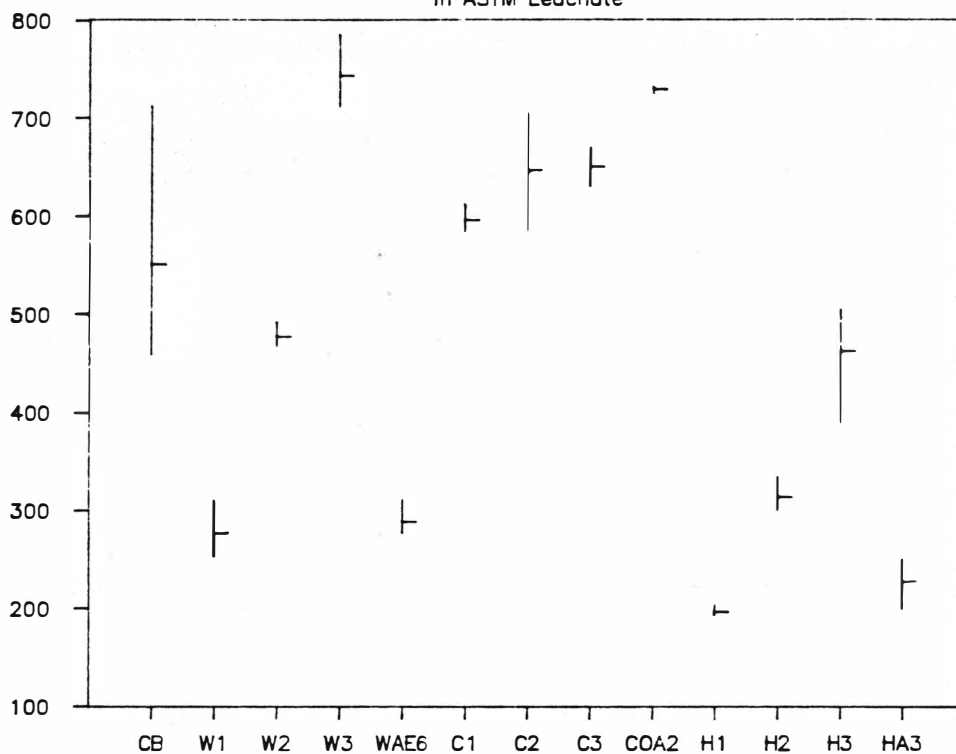


Figure 6.3 Metal concentrations in ASTM leachates.

Ca Concentration

in ASTM Leachate

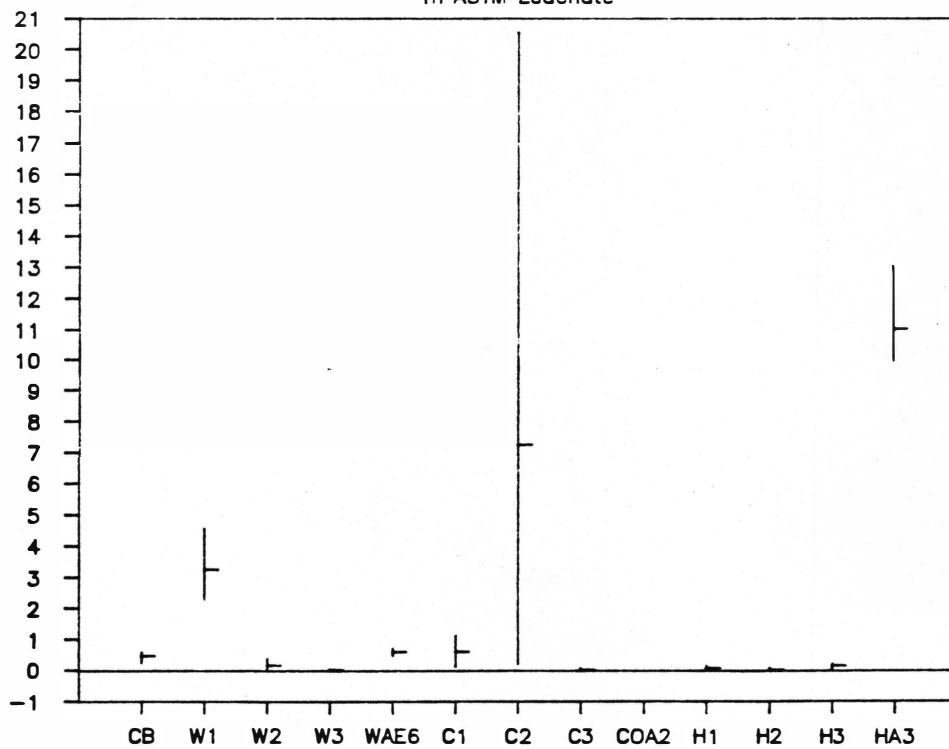
Ca Conc. (ppm)



Al Concentration

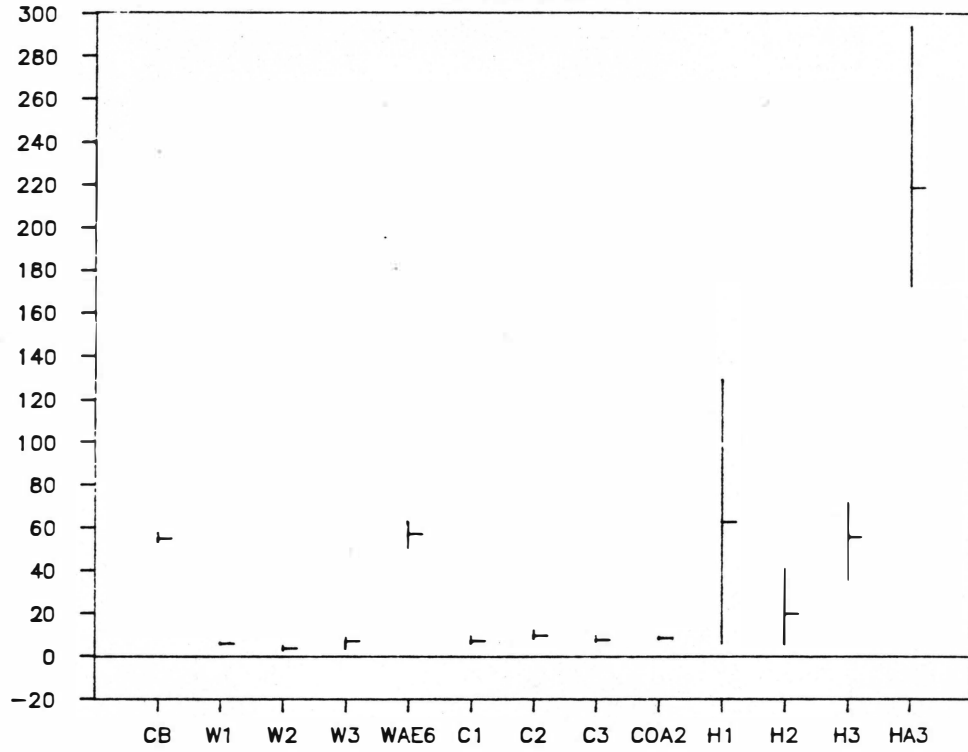
in ASTM Leachate

Al Conc. (ppm)



in ASTM Leachate

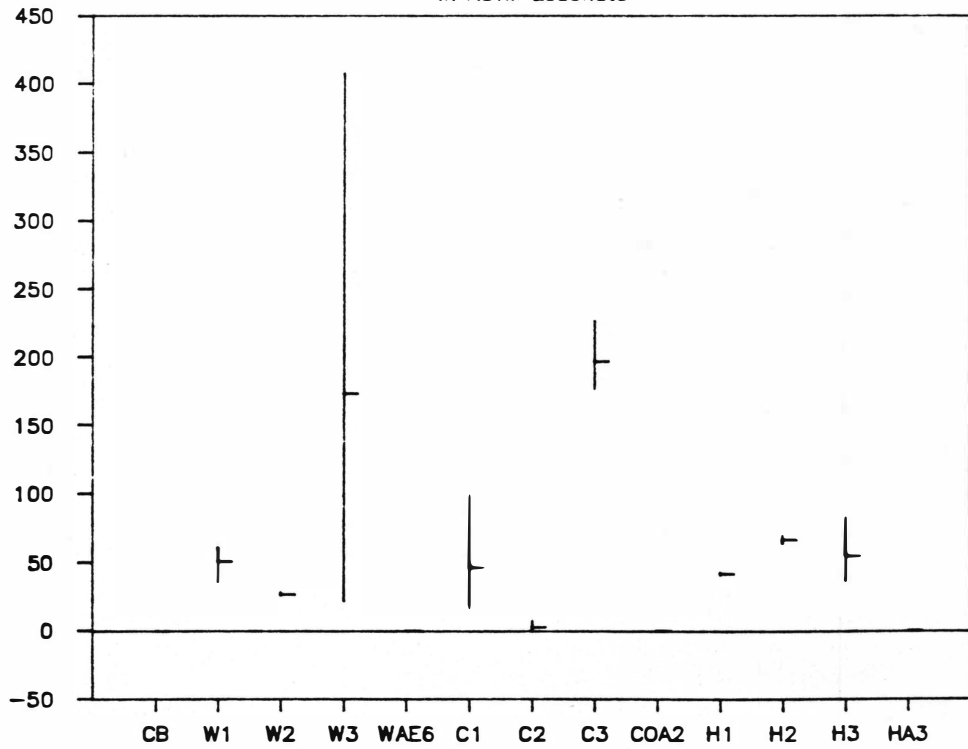
Fe Conc. (ppb)



Mg Concentration

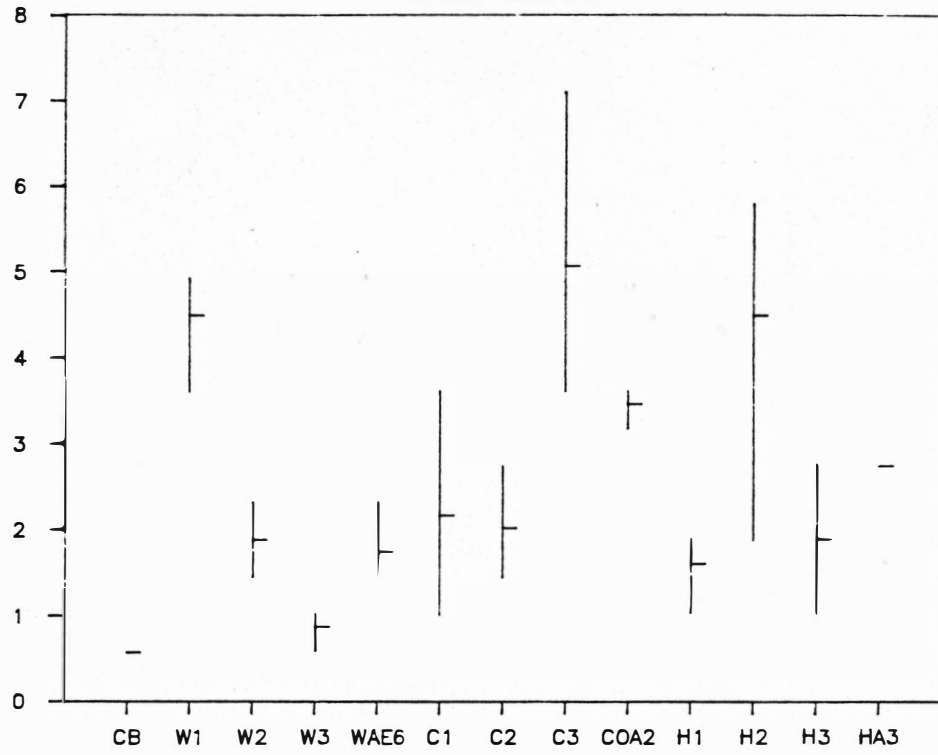
in ASTM Leachate

Mg Conc. (ppm)



in ASTM Leachate

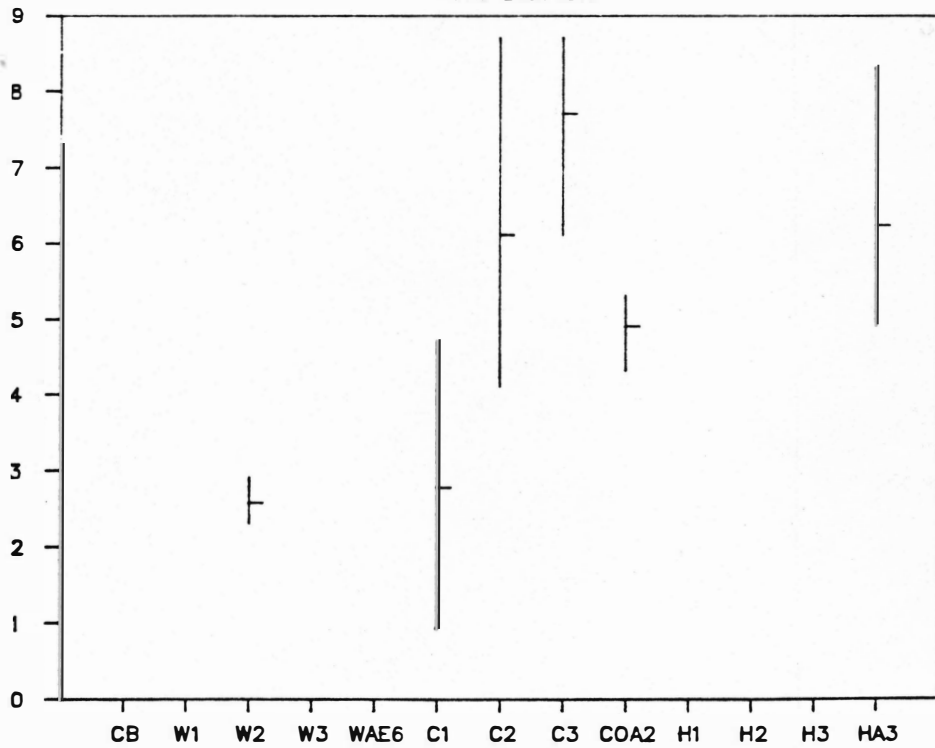
Si Conc. (ppm)



As Concentration

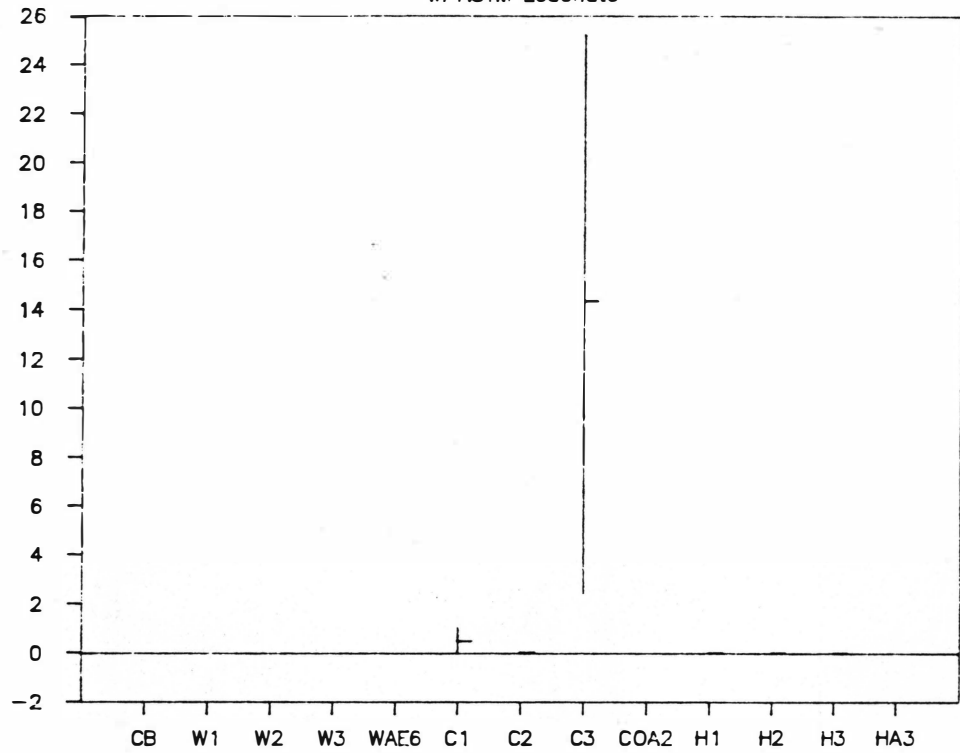
in ASTM Leachate

As Conc. (ppb)



in ASTM Leachate

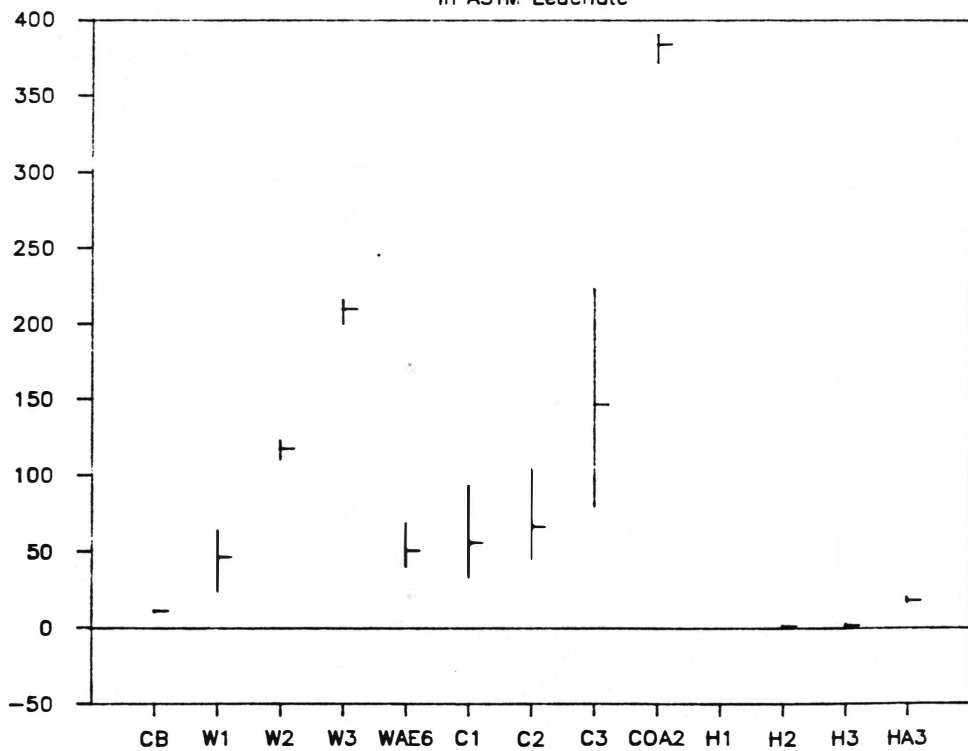
Cd Conc. (ppm)



Cr Concentration

in ASTM Leachate

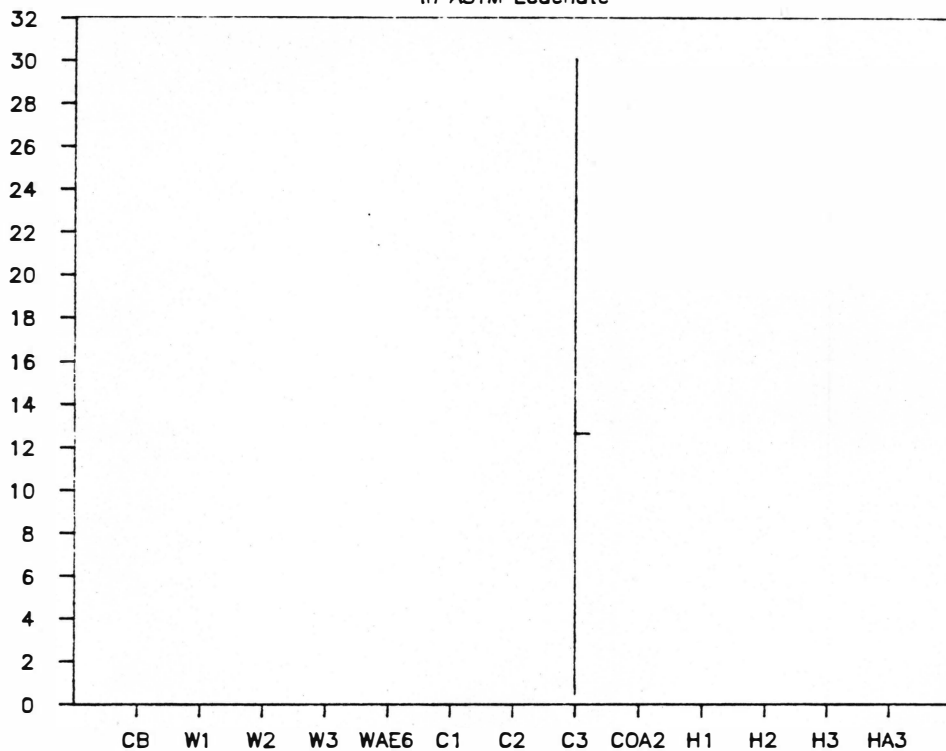
Cr Conc. (ppb)



Co Concentration

in ASTM Leachate

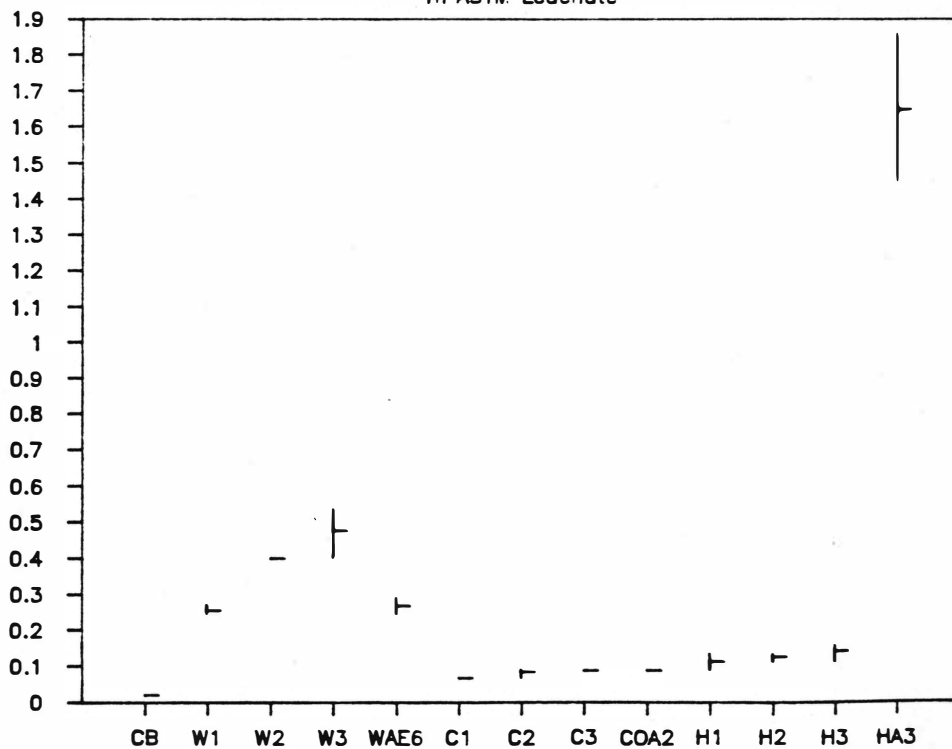
Co Conc. (ppb)



Cu Concentration

in ASTM Leachate

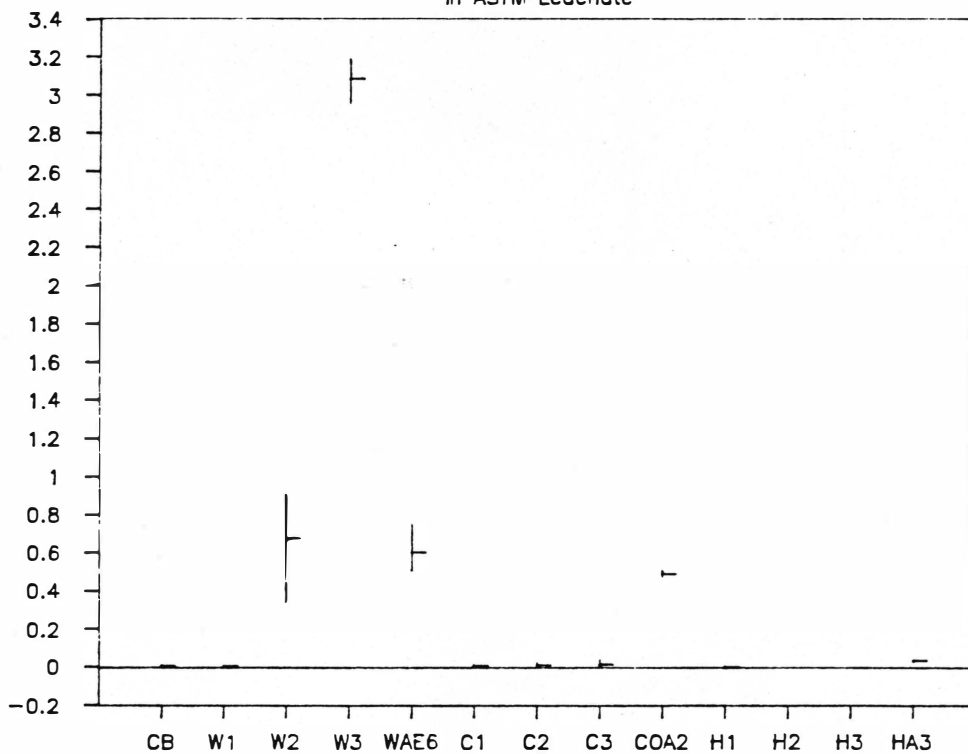
Cu Conc. (ppm)



Pb Concentration

in ASTM Leachate

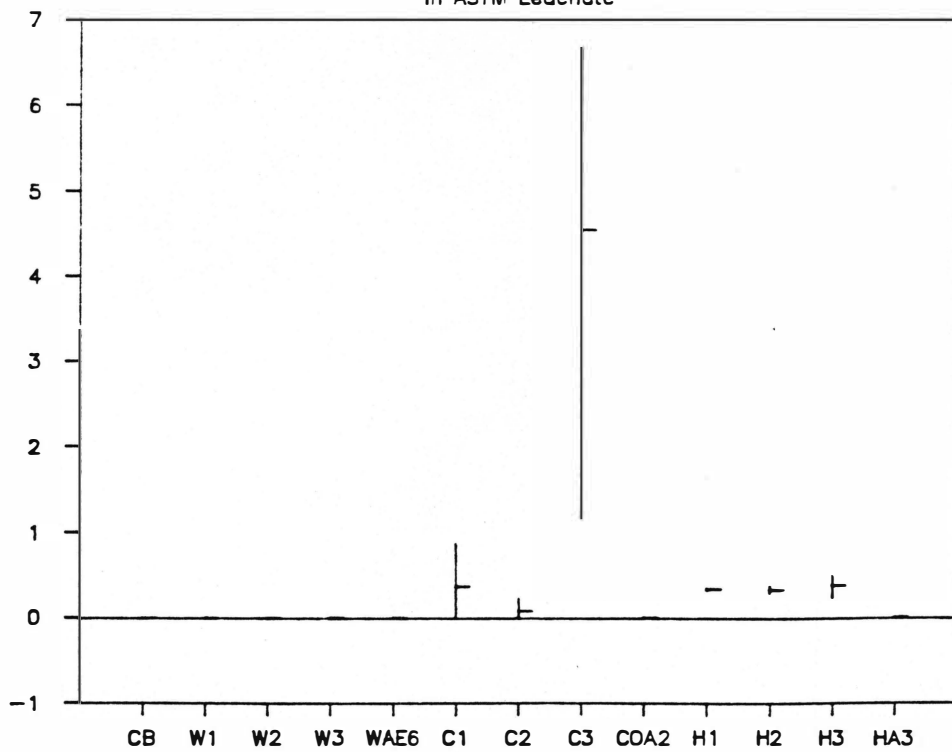
Pb Conc. (ppm)



Mn Concentration

in ASTM Leachate

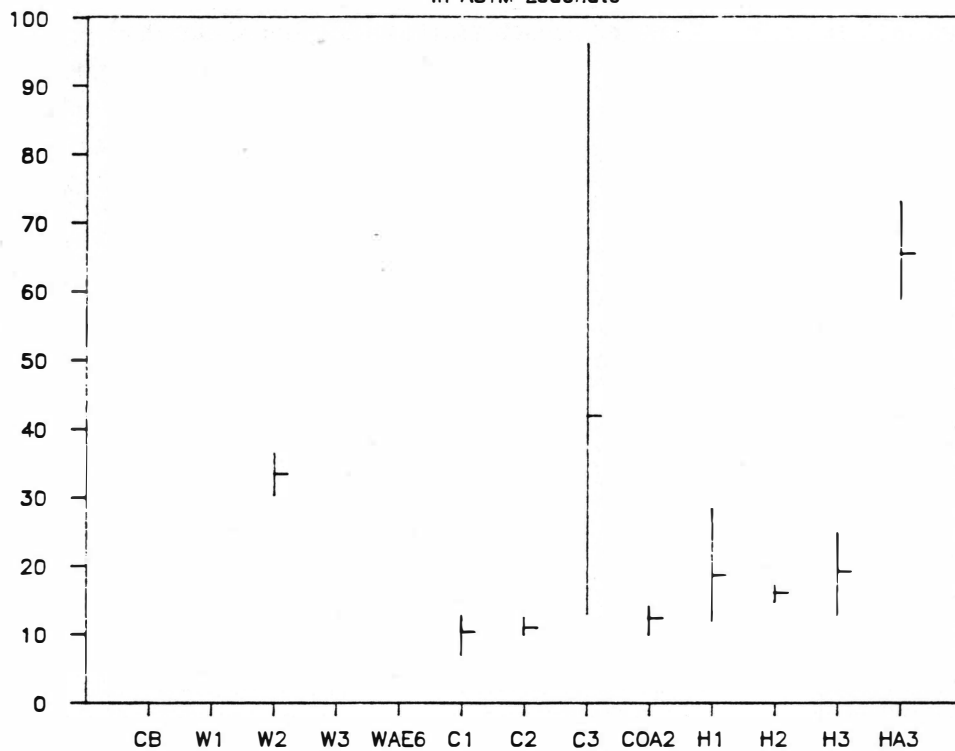
Mn Conc. (ppm)



Ni Concentration

in ASTM Leachate

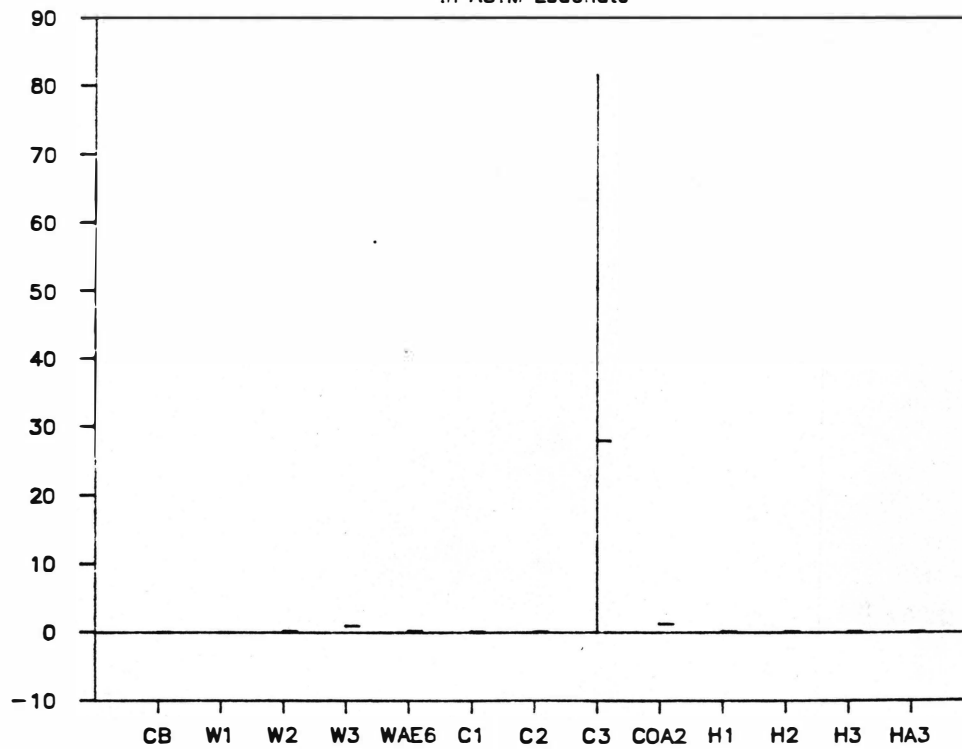
Ni Conc. (ppb)



Zn Concentration

in ASTM Leachate

Zn Conc. (ppm)



The results in Table 6.8 through 6.11 permits a direct comparison of leachate concentrations before and after chemical fixation with 15% portland cement. With respect to EPA leachates, chemical fixation of Westchester composite ash (WCA : with 15% portland cement and 17% moisture content cured at 49⁰C for 1 day) decreased the leachate concentrations except Cr (relative to the WCA). Chemical fixation of New York City fly ash (NYCFA : with 15% portland cement and 23% moisture content cured at 49⁰C for 3 days) and of Huntington composite ash (HCA : with 15% portland cement and 18% moisture content cured at 23⁰C (air) for 7 days) decreased the leachate concentrations. Exceptions were Ca and Pb for NYCFA, and Ca, Al, Fe, Si and Cr for HCA. With respect to ASTM leachates, the leachate concentrations were reduced by chemical fixation for all three ashes with some exceptions; Fe for WCA, Ca, Cr and Pb for NYCFA, and Al, Fe, As, Cr, Cu, Pb and Ni for HCA. Thus it can be said that chemical fixation with 15% portland cement considerably retards the leaching process at least for WCA. The exceptions are probably due to the unknown particle sizes included in proctor fabrication, i.e., due to the inhomogeneity of raw ashes.

EPA leachate values are generally larger than ASTM leachate values. This is probably due to the acidified conditions of the EPA procedure. The ocean is alkaline and thus leaching rates would be considerably lower. Given this fact, and when taking into account the surface to volume ratio of ground-up block material, it is apparent that these results provide a worst case scenario of the leaching behavior for the elements analyzed.

It is notable that both EPA and ASTM leachate concentrations are comparable to Federal Public Water Supply Standards (Table 6.12). Considering that a more realistic test of leaching behavior in the sea, which is not an acidic medium, can be represented by the results of the ASTM test, it is remarkable that the elemental concentrations, except Pb, in the ASTM leachates of the Westchester optimum blocks in Table 6.12 did not exceed the EPA recommended concentrations for public water supplies (freshwater). Table 6.12 also show that Westchester blocks satisfy the EPA maximum limits for leachate concentration for all metals. The metal

concentrations in the EPA leachates of the New York City and Huntington blocks are higher than the EPA limits only for one or two metals.

CALCIUM LEACHING RATES - TANK DISSOLUTION EXPERIMENT

The rate at which calcium is leached from the blocks may be an important indication of a blocks' expected lifetime in the marine environment (Duedall *et al.*, 1983). Over long time periods the slow release of calcium from the waste blocks might ultimately lead to block failure either through increased porosity and/or chemical dissolution. Experiments were conducted to measure the flux of calcium from block sections suspended in seawater inside polyethylene tanks.

Equipment and Methods

The flux of calcium was examined following the methods proposed by Duedall *et al.* (1983). Optimum blocks (WAD4, COE2 and HE5) were cut into three sections, i.e., top, middle and bottom, giving triplicate tank systems for each mixture. The average surface area of each section was approximately 253 cm²; a height of 3.3 cm and a diameter of 9.8 cm. Samples were suspended with monofilament line inside polyethylene tanks containing 2 liters of filtered seawater. The seawater was taken from the Flax Pond site. Tanks were placed on individual magnetic stirrers to provide a constant motion to the seawater. Each tank had a 0.45 μ m membrane filter placed over an opening in its cover to ensure aeration. The tank configuration is shown in Figure 6.4. A control tank with seawater only was also examined.

The experiments were conducted at room temperature and lasted for 130 d. The samples were taken at the interval of 1, 2, 3, 4, 5 and 6 days, and weekly for 5 weeks, and biweekly for 6 weeks. Whenever seawater samples were taken, pH values were measured and the water within the tanks was also replaced. Table 6.13 lists the sampling intervals and the measured pH values. Reduction of pH with time was found over the period of study. Samples were filtered through a 0.45 μ m filter, acidified to pH 2 using Ultrex nitric acid and refrigerated at 5°C.

Table 6.12. Comparison of EPA and ASTM leachate concentrations with EPA regulated concentrations for Public Water Supplies and EPA Maximum Limits for leachate concentration^a.

	Cu	Cr	Mn	As	Cd	Pb	Hg	Fe	Zn
PDW Maximum Contaminant Limits ^b	1.0	0.1	0.05	0.1	0.01	0.05	0.002		
EPA Maximum Limits for Leachate Concentration	10.0	0.5	0.5	0.5	0.1	0.5		3.0	50.0
EPA Leachate Concentrations									
WAE6	0.18	0.05	0.19	0.002	0.02	< 0.001	< 0.001	0.002	0.16
COA2	0.33	0.03	0.77	0.003	8.0	4.1	< 0.001	0.001	155
HA3	1.27	0.01	1.24	0.003	0.05	0.07	< 0.001	0.4	5.11
ASTM Leachate Concentrations									
WAE6	0.26	0.05	0.001	< 0.001	< 0.001	0.60	< 0.001	0.06	0.20
COA2	0.09	0.38	0.006	0.005	< 0.001	0.49	< 0.001	0.009	1.25
HA3	1.65	0.02	0.003	0.006	< 0.001	0.04	< 0.001	0.2	0.05

a. Unit of concentration is ppm. b. Public Drinking Water (Federal Register, 1977).

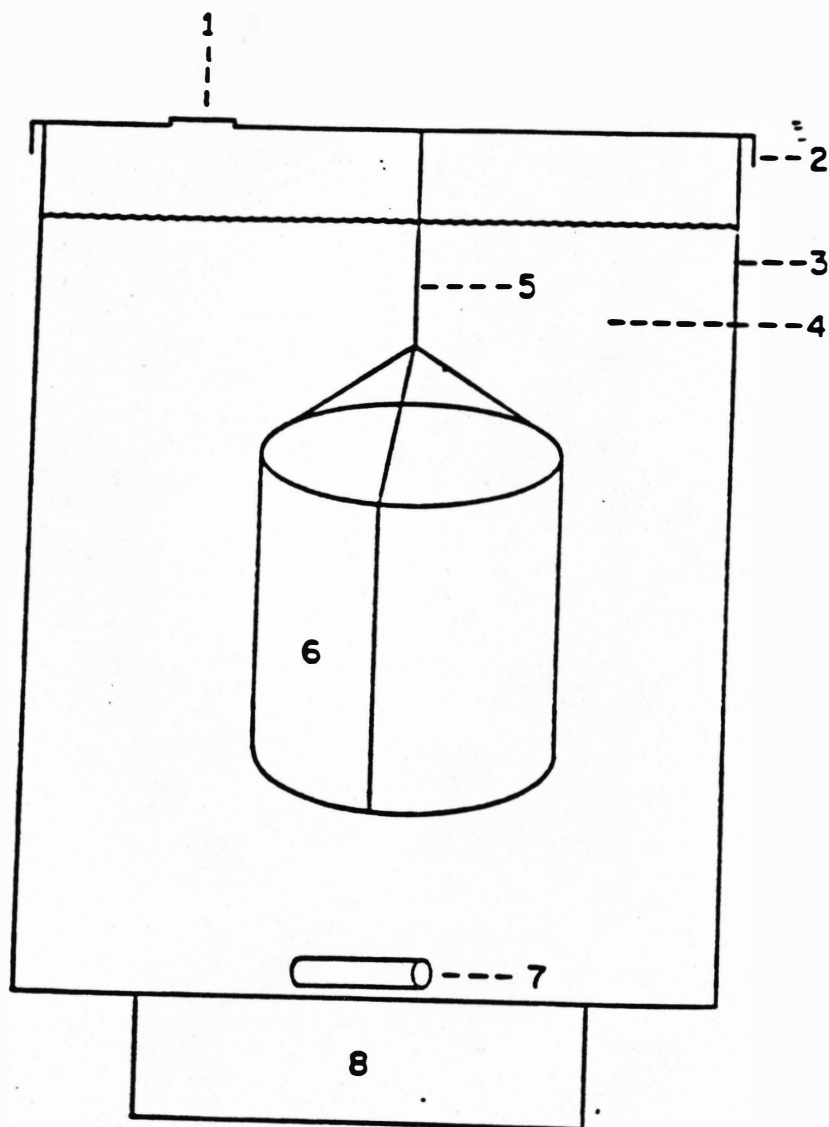


Figure 6.4 Tank configuration: (1) 0.45 um Nuclepore^R membrane filter; (2) cover; (3) plastic tank; (4) filtered seawater; (5) monofilament line; (6) stabilized incineration waste block; (7) magnetic stirring bar; (8) magnetic stirrer.

Table 6.13. Sampling intervals and measured pH in tank study.

Sample Number	Sampling Date	Sampling Interval (day)	Cumulative Time (day)	Identification and pH of Samples ^a									Blank ^b
				WAD4			COE2			HE5			
				Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom	
START	2/01/86												
1	2/02/86	1	1	9.72	9.93	9.83	9.74	9.79	9.42	9.27	8.98	9.18	8.05
2	2/04/86	2	3	9.47	9.73	9.64	9.76	9.85	9.27	9.07	9.00	8.98	8.09
3	2/07/86	3	6	9.63	9.53	9.65	9.54	9.48	9.26	8.97	8.89	8.86	8.12
4	2/11/86	4	10	9.52	9.62	9.64	9.61	9.41	9.25	8.92	8.88	8.78	8.17
5	2/16/86	5	15	9.28	9.57	9.45	9.48	9.26	9.11	8.88	8.82	8.70	8.20
6	2/22/86	6	21	8.99	9.36	9.26	9.21	9.08	9.02	8.76	8.77	8.59	8.19
7	3/01/86	7	28	8.73	9.07	8.98	9.07	8.99	8.92	8.75	8.73	8.54	8.24
8	3/08/86	7	35	8.62	8.78	8.83	8.96	8.86	8.83	8.68	8.69	8.41	8.18
9	3/15/86	7	42	8.53	8.55	8.77	8.90	8.80	8.75	8.66	8.61	8.31	8.13
10	3/22/86	7	49	8.58	8.64	8.88	8.85	8.74	8.74	8.59	8.60	8.28	8.18
11	3/29/86	7	56	8.54	8.53	8.82	8.80	8.72	8.68	8.54	8.57	8.36	8.20
12	4/12/86	14	70	8.41	8.46	8.51	8.65	8.53	8.57	8.55	8.58	8.31	8.20
13	5/10/86	28	98	8.44	8.51	8.55	8.62	8.55	8.58	8.57	8.58	8.31	8.33
14	6/11/86	32	130	8.43	8.41	8.47	8.52	8.41	8.47	8.51	8.52	8.26	8.31

- a. WAD4 : Westchester composite ash with 15% portland cement and 17% moisture content cured at 49 C for 1 day.
 COE2 : New York City fly ash with 15% portland cement and 23% moisture content cured at 49 C for 3 days.
 HE5 : Huntington bottom ash with 15% portland cement and 18% moisture content cured at 23 C (air) for 7 days.
- b. Seawater filtered with 0.45 um filter paper.

The procedures explained in an earlier section of this report were used for determining the calcium concentration, except using 0.5% (w/v) La^{+3} , added as La_2O_3 , to control interferences. Calcium fluxes were then calculated as $\text{mmole}/\text{mm}^2/\text{day}$.

Results

This study was designed to evaluate the dissolution processes of the stabilized blocks in seawater. A comparison was made between dissolution from the top, middle and bottom layers of proctors for each of the optimum mixes. Table 6.14 summarizes the concentration of Ca^{+2} in solutions taken from the test tank over 130 days. The fluxes of Ca^{+2} (Table 6.15) were calculated by dividing the incremental increase in millimoles of Ca^{+2} by the leaching period (day) and by the geometric surface area (cm^2) of the proctors. Figures 6.5, 6.6 and 6.7 represent the data in graphical form.

The amounts of calcium leached into tank waters was low in comparison to earlier studies (Parker et al., 1981; Roethel et al., 1983 and 1984). Greater variability in the Ca^{+2} flux among samples of the different layers was found in the earlier stages of the study. After 35 days the fluxes from each layer became similar. New York City blocks showed the highest Ca^{+2} fluxes, then Huntington blocks and Westchester blocks the lowest values. In general, the fluxes of Ca^{+2} decreased with increasing time.

After 4 or 5 days, the Westchester blocks showed negative Ca^{+2} fluxes which means the blocks absorbed calcium from the seawater in the test tanks.

Discussion

Concentrations and solubilities of the calcium compounds in the stabilized blocks can account for the concentration of the dissolved Ca measured during the tank studies. Parker et al. (1981) pointed out the high solubility of calcium hydroxide and calcium sulfate in seawater at 25°C . This increased solubility is attributed to the occurrence of

Table 6.14. Concentration of calaium leached during tank dissolution experiment.

Sample Number	Cumulative Time (day)	Concentration ($\mu\text{g/g}$) ^a								
		WAD4 ^b			COE2			HE5		
		Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
1	1	104	104	113	200	184	286	166	166	245
2	3	4	31	60	74	67	206	89	112	188
3	6	-35	-70	2	103	193	431	66	83	223
4	10	-61	-46	-11	401	393	672	46	46	153
5	15	-48	-54	-17	521	399	728	52	57	183
6	21	-35	-50	-63	455	505	762	-22	-44	185
7	28	-41	-63	-22	378	413	720	17	2	159
8	35	-32	-39	-26	331	479	596	-19	-4	129
9	42	-15	-34	4	311	377	507	15	19	115
10	49	-15	-4	2	315	321	456	21	2	110
11	56	8	13	27	313	372	387	61	29	114
12	70	-40	-32	-40	457	557	888	4	4	160
13	98	-29	-50	-8	904	904	1236	31	50	258
14	130	-46	-21	-25	906	887	1059	78	4	359

- a. Concentrations provided reflect subtracting the blank and the unit is $\mu\text{g/g}$.
- b. WAD4 : Westchester composite ash with 15% portland cement and 17% moisture content cured at 49 C for 1 day.
 COE2 : New York City fly ash with 15% portland cement and 23% moisture content cured at 49 C for 3 days.
 HE5 : Huntington bottom ash with 15% portland cement and 18% moisture content cured at 23 C (air) for 7 days.

Table 6.15. Flux of calcium diffused from the optimum blocks^a during tank dissolution experiment.

Time (day)	Flux $\times 10^{-8}$ mole/mm ² /day								
	WAD4			COE2			HE5		
	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
1	16.84	18.96	22.88	40.31	38.96	59.17	35.25	34.21	50.18
3	5.85	-2.34	4.20	11.88	18.34	43.91	10.99	13.41	28.04
6	-0.82	-3.51	-0.29	16.96	20.67	38.03	3.95	4.44	12.82
10	-1.55	-1.82	-0.57	18.61	16.77	28.96	2.09	2.12	6.87
15	-1.17	-1.27	-1.08	13.13	12.77	20.55	0.43	0.18	5.02
21	-0.64	-0.98	-0.81	8.00	9.26	14.60	-0.04	-0.41	3.35
28	-0.44	-0.66	-0.34	5.11	6.75	9.72	-0.01	-0.02	2.10
35	-0.34	-0.38	-0.12	3.70	5.18	6.52	-0.03	0.09	1.43
42	-0.18	-0.17	0.03	3.01	3.52	4.75	0.18	0.10	1.10
49	-0.10	0.03	0.12	2.59	3.00	3.56	0.36	0.13	0.93
56	-0.02	-0.06	-0.05	2.78	3.51	4.71	0.25	0.12	1.00
70	-0.07	-0.21	-0.14	3.93	4.42	6.28	0.11	0.16	1.22
98	-0.11	-0.13	-0.07	3.73	3.87	4.85	0.24	0.11	1.29
130	-0.09	-0.03	-0.04	1.41	1.45	1.69	0.13	0.01	0.57

- a. WAD4 : Westchester composite ash with 15% portland cement and 17% moisture content cured at 49 C for 1 day.
 COE2 : New York City fly ash with 15% portland cement and 23% moisture content cured at 49 C for 3 days.
 HE5 : Huntington bottom ash with 15% portland cement and 18% moisture content cured at 23 C (air) for 7 days.

Figure 6.5 Calcium flux in Westchester optimum blocks

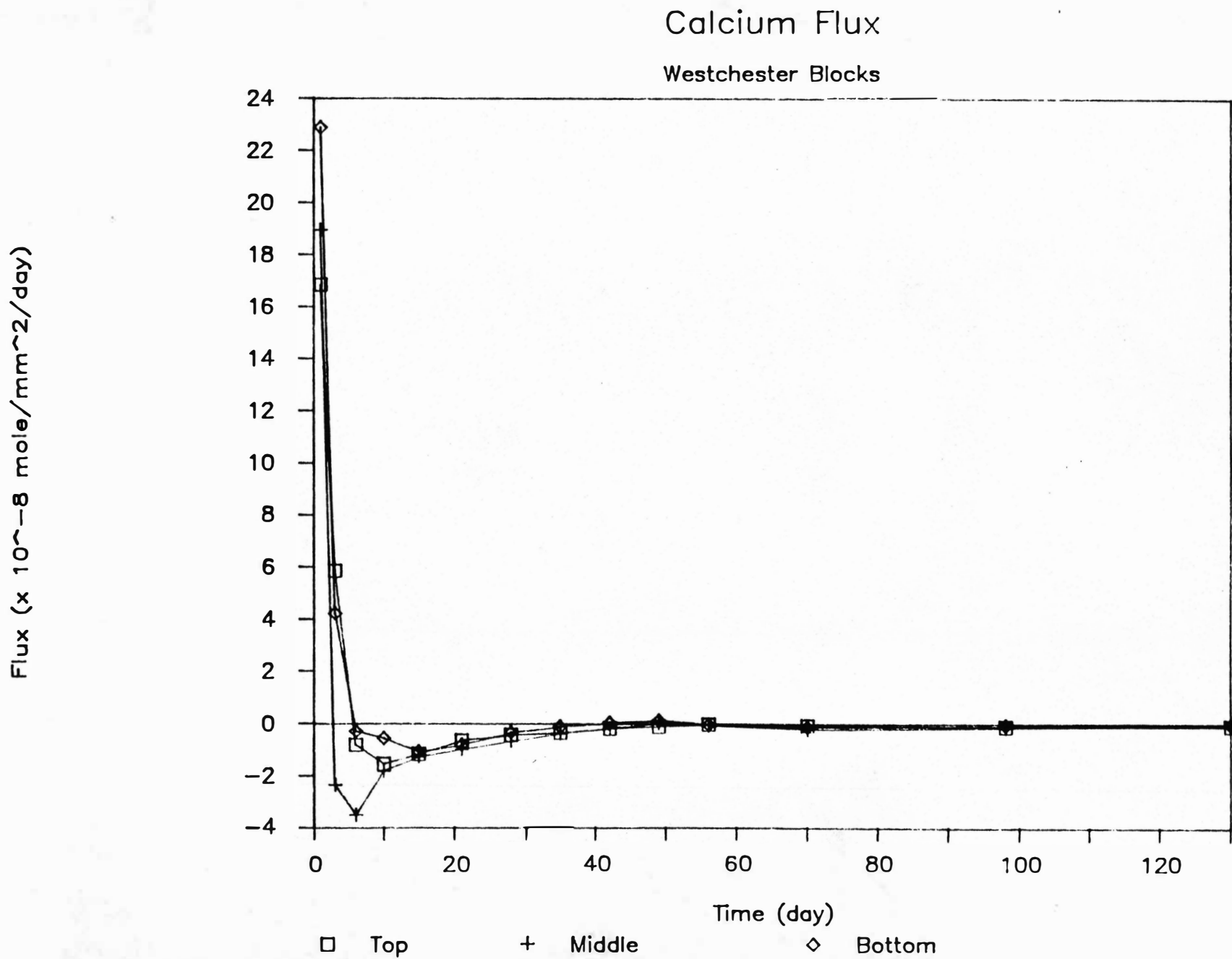


Figure 6.6 Calcium flux in New York City optimum blocks.

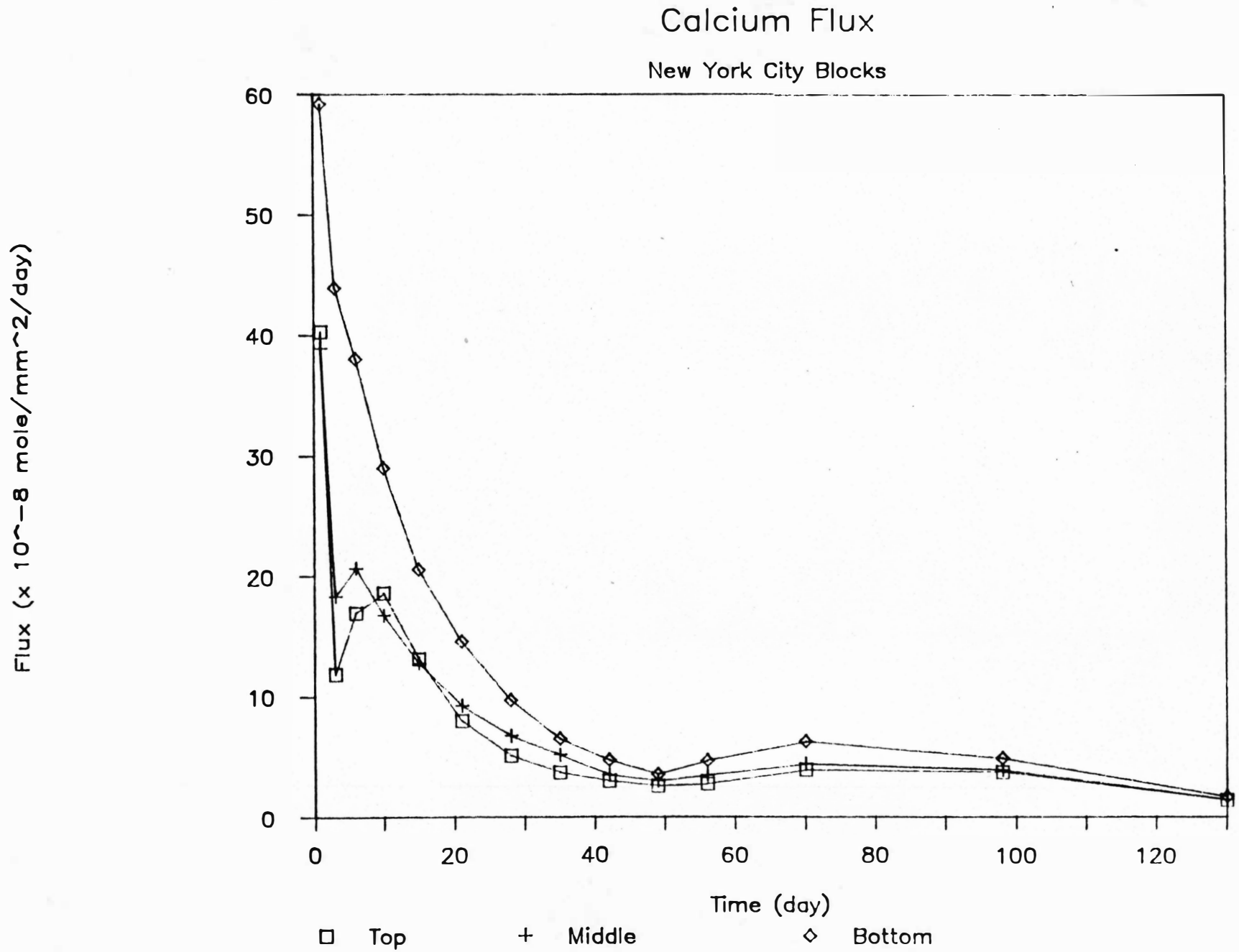
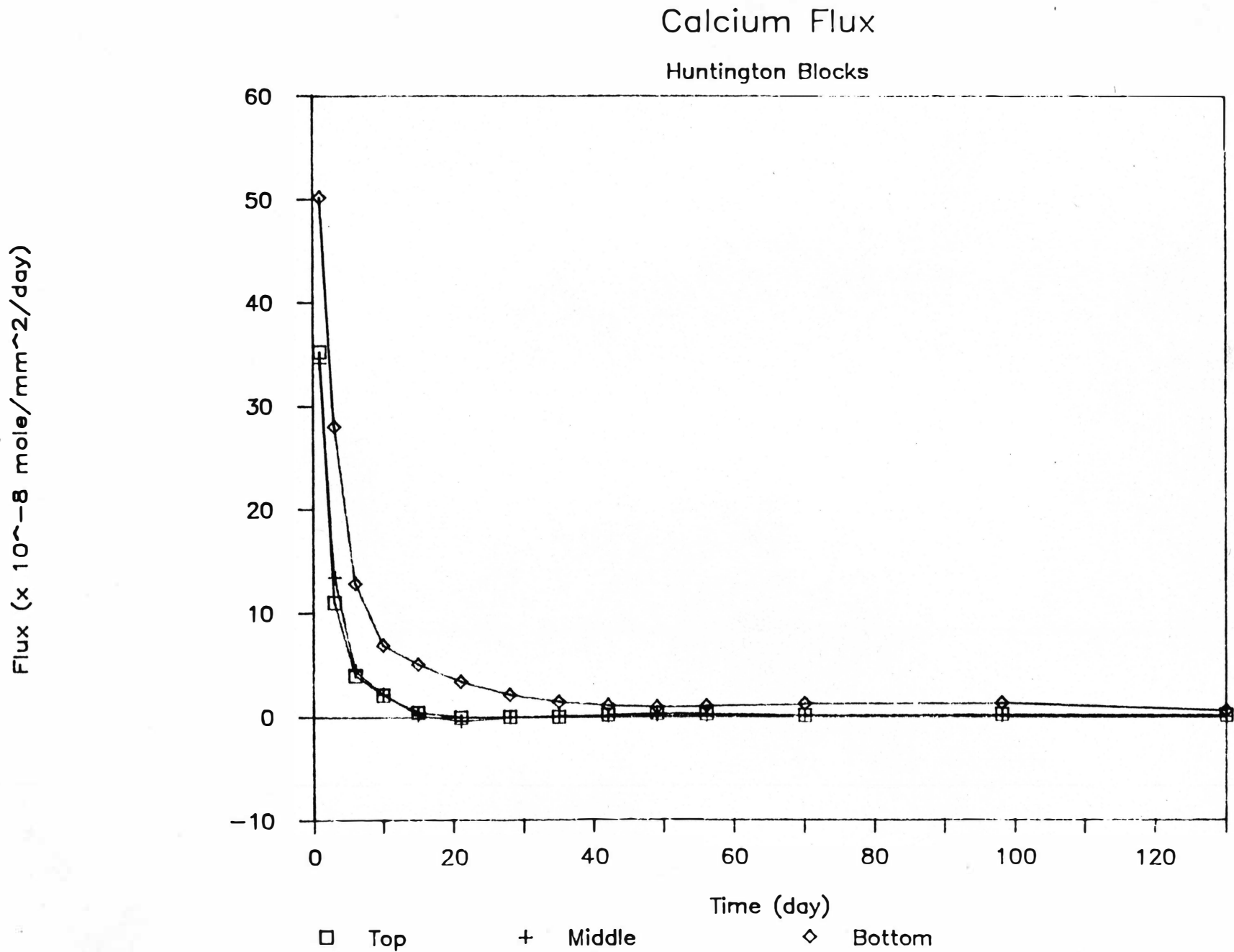


Figure 6.7 Calcium flux in Huntington optimum blocks.



ion-pairing in seawater. According to Stumm and Morgan (1981), the priority of solubility for Ca compounds in seawater at 25°C, 1 atm is: $\text{Ca(OH)}_2 > \text{CaSO}_4 \cdot 2\text{H}_2\text{O} > \text{CaCO}_3$. Ca(OH)_2 has the highest solubility in seawater and CaCO_3 is the least soluble. Although the calcium compounds were incorporated into the blocks during the curing process, some free calcium compounds were still present at the exterior portions of the proctors. Since experiments were conducted at room temperature, the relatively high Ca^{+2} fluxes in the earlier stages of the study may be due to the dissolution of the free Ca(OH)_2 and CaSO_4 present at the surface of the proctors. After dissolution of free calcium compounds, the interior calcium diffused outward to the seawater. For the tank study, since proctors were suspended in seawater, only a small portion of material was directly in contact with the seawater. The factor therefore controlling diffusion of Ca^{+2} from the proctors to the surrounding seawater, was tortuosity, the diffusion path needed for ions to pass through the proctor, rather than permeability. The exponential drop in Ca flux with increasing time demonstrates that the surfaces of the proctors became rapidly depleted in Ca^{+2} . Diffusion of Ca^{+2} from the proctor sub-layer to the tank solution is apparently retarded by the increase in the path length of the diffusing ions, with the net result that the flux of Ca^{+2} decreased with increasing time.

The negative Ca^{+2} flux observed in Westchester blocks after 3 days might be due to the incorporation of calcium from the seawater to form the cementitious crystals. Seligman (1978) observed the precipitation of calcium aluminosilicate in the cementation process. This means seawater immersion does not result in the progressive losses of the block's integrity but continue to form cementitious products (Roethel, 1981 and Duedall et al., 1983), which was also seen at the submersion (seatable) test (refer to Table 5.5).

DIFFUSION MODEL

Theory

A one-dimensional diffusion model was examined to ascertain the impact of the calcium leaching from the stabilized blocks to the surrounding seawater on the structural integrity of blocks. According to the model given by Duedall et al. (1983), the flux of ions through the interface is given by,

$$J = h S_0 \exp(h^2/D) \operatorname{erfc} [h(t/D)^{1/2}]$$

where

- J = flux of ion in millimoles/cm²/sec,
- h = transfer coefficient,
- S₀ = concentration in the block in millimoles/cm³,
- D = diffusion coefficient in cm²/sec, and
- t = time in second.

For $t \gg D/h^2$, the flux is approximately expressed,

$$J = S_0 \cdot (D/\pi \cdot t)^{1/2}.$$

Thus, J is proportional to $t^{1/2}$ as time progresses. And the diffusion coefficient (D) can be estimated as,

$$D = \pi \cdot t(D/S_0)^2.$$

The effective distance of diffusion (X_c), defined as the depth where there is a change in the Ca⁺² concentration due to diffusion, is given by,

$$X_c = (2 \cdot D \cdot t)^{1/2}.$$

Estimation of Expected Lifetime of Block in Seawater

Using the calculated value of D, X_c can be determined for various times. As an example for Westchester Block (WAD4) :

$$t = 130 \text{ days}$$

Table 6.16. Calculated distance (Xc) of the diffusion zone in optimum blocks.

Time (day)	Xc (cm) ^a		
	WAD4	COE2	HE5
100	0.002	0.057	0.009
200	0.003	0.080	0.012
365 (1 y)	0.003	0.108	0.016
730 (2 y)	0.005	0.153	0.023
1095 (3 y)	0.006	0.187	0.028
1825 (5 y)	0.008	0.242	0.036
3650 (10 y)	0.011	0.342	0.051
10950 (30 y)	0.019	0.593	0.089
18250 (50 y)	0.024	0.765	0.115
36500 (100 y)	0.034	1.082	0.163

a. Refer to the equations in Section 6.5.1.

b. Diffusion coefficients (cm²/sec) ; WAD4 : 5.17×10^{-13}
 COE2 : 2.86×10^{-10}
 HE5 : 2.09×10^{-12}

c. When calculating diffusion coefficients (D), average values of top, middle and bottom sections were used for the ion flux (J₀).

d. Wet density (g/cm³) ; WAD4 : 1.97
 COE2 : 1.64
 HE5 : 1.77

$$J = - 5.41 \times 10^{-5} \text{ millimoles/cm}^2/\text{day}$$

$$S_0 = 3.21 \text{ millimoles/g}$$

$$= 6.32 \text{ millimoles/cm}^3 \text{ (Wet density = } 1.97 \text{ g/cm}^3\text{)}$$

thus

$$D = 1.61 \times 10^{-8} \text{ cm}^2/\text{day}$$

$$= 1.86 \times 10^{-13} \text{ cm}^2/\text{sec.}$$

For the City and Huntington blocks, D equals 1.86×10^{-10} and 4.20×10^{-12} cm^2/sec , respectively. Table 6.16 represents the effective distance (X_c) of the diffusion zone in the stabilized blocks. It is shown that it will take more than a century for diffusion to affect the outer 0.04 cm of the Westchester block.

Discussion

The model used to predict the life-time of the stabilized blocks in the seawater is based on two assumptions: (1) All the soluble calcium compounds contained in the blocks will eventually diffuse to the ocean during the prolonged exposure time. (2) Molecular diffusion is the principal process for the loss of major components. van der Sloot et al. (in press) modified the Duedall diffusion model with respect to assumption (1) and incorporated a term, fractionation coefficient, for the leachable fraction to evaluate the effective diffusion coefficient. They argued that the ultimate leachable fraction from a certain product is important for its leaching behavior. However, since the work of van der Sloot et al. has not yet been subjected to critical review, we continued along with the Duedall diffusion model.

The diffusivity of Ca^{+2} at room temperature (25°C) for the Westchester blocks is 1.86×10^{-13} cm^2/sec . The model predicts that in 100 years, at 25°C and at salinity 26, only an outer 0.04 cm of the Westchester blocks would be affected by loss of Ca^{+2} . In coastal marine environments, temperatures cycle annually between 1°C and 25°C and the experiment was performed at room temperature (25°C) and above due to heating from the electric stirring motors. Since diffusivity decreases with decreasing temperature (Li and Gregory, 1974), the model predictions

presented here probably represent maximum values for the effective depth of the diffusion zone for the blocks exposed in the open sea.

The above model does not however account for the physico-chemical and biological processes except the diffusion behavior. Ion exchange process may be another regulating factor in controlling the Ca^{+2} flux. Edward (1983) observed that Ca^{+2} fluxes were greater in seawater than in freshwater because of the replacement of Ca^{+2} by Mg^{+2} in seawater. Furthermore, biological colonization processes which may be either destructive or stabilizing in the marine environment, may have a greater detrimental effect than diffusion of major components. Earlier studies with blocks of fly ash and flue gas desulfurization sludge (Roethel *et al.*, 1980, Humphries, 1982 and Duedall *et al.*, 1983), showed that the clam Zirfaea crispata, the mud crab Rhithropanopeus harissii, the tube dwelling amphipod Corophium lacustre, and the barnacle Balanus improvisus, were able to bore into or otherwise bio-erode block surfaces. On the other hand, the finding of encrusting organisms such as bryozoan colonies (organisms with calcium carbonate exoskeletons) overgrowing some blocks may indicate reduction of calcium flux. Bioerosion and biostabilization may well have a greater influences on blocks in the marine environment and further extrapolation of the laboratory results to the actual marine environment would not be warranted. Obviously more work needs to be done with respect to the effect of biological activities on the leaching and/or adding of metals from/onto the stabilized blocks.

Section 7

MINERALOGY: COMPOSITION AND ALTERATIONS

The mineralogy of the various incinerators' residues, optimum strength blocks and seawater submerged blocks was examined using the techniques of powder x-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD was used to identify mineral phases present in the different specimens. The SEM was used (1) to determine particle size and morphology of different end members and (2) to observe crystal growth in order to infer chemical processes that may be occurring in the stabilized mixes both prior to and following submersion. Photomicroscopy was very useful in the identification of microcrystalline minerals normally not observed by light microscopy or by standard XRD techniques.

APPARATUS AND PROCEDURES

X-ray Diffraction Analysis

In order to evaluate the effects of ash stabilization and seawater submersion, x-ray diffraction patterns were taken of the raw ash material, optimum strength blocks and submerged blocks to follow the change in mineral structure that occurs. The mineralogical composition of the specimen was determined by x-ray diffraction analysis of unoriented mounts of powdered samples. The powdered samples were prepared by grinding a freeze-dried sample and passing it through a No. 200 sieve (mesh size 75 μm). A portion of the sample was spread in a thin layer on a glass slide and analyzed on a Picker (New Hyde Park, New York) x-ray diffractometer using Cu-K α radiation at 35 Kv and 23 mA and a 70° to 5° 2 θ scan.

The diffractograms were examined for the presence of minerals using for peak identification the alphabetical index for inorganic materials compiled by the Joint Committee on Powder Diffraction Standards, (JCPDS, 1979). Classification of mineral phase presence as major or minor was based upon the number of diffraction peaks identified as well as peak

intensities. Since the intensity of x-ray diffraction by a given mineral phase is a function of the degree of mineral crystallinity as well as crystal size, this classification is qualitative. An authigenically precipitated phase, such as ettringite for example, may yield a weak diffraction pattern even though present in large quantity since it will be poorly crystallized in incineration residues.

Scanning Electron Microscopy

Scanning electron microscopy was used to determine morphological changes in the residues at various stages of the project. Ash samples were mounted onto stainless steel stubs with PC-7 epoxy and then gold coated or graphite coated to increase resolution. Samples then were observed on a JEOL model 35C (Tokyo, Japan) scanning electron microscope with resolution capability of 100Å which is located at the Department of Ecology and Evolution of the State University of New York at Stony Brook.

RESULTS

Incineration Residues

X-ray diffraction patterns for the various incineration residues are shown in Figure 7.1. Table 7.1 summarizes the important characteristics of these diffractograms.

The mineralogical composition of Westchester ash appears to be dominated by the presence of calcite (CaCO_3), Anhydrite (CaSO_4), and Quartz (SiO_2) as major mineral phases while Portlandite [$\text{Ca}(\text{OH})_2$] and Ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 25\text{H}_2\text{O}$] were present as minor constituents. Huntington ash is similar to Westchester ash with its major peaks attributable to calcite and quartz, however anhydrite is present in minor proportion while portlandite and ettringite are not present. New York City ash is rather different from the other as is observed by the minor presence of calcite and quartz and $\text{CaSO}_3\cdot 1/2\text{H}_2\text{O}$ while anhydrite and NaCl are present as major phases.

Table 7.1. Mineral composition of incineration residues.

Westchester		New York City		Huntington		Mineral
<u>2 θ</u>	<u>d</u>	<u>2 θ</u>	<u>d</u>	<u>2 θ</u>	<u>d</u>	
23.1	3.86	23.1	3.85	29.4	3.04	Calcite
29.5	3.03	29.7	3.01	36.0	2.49	
39.5	2.28			39.5	2.28	
43.1	2.10			47.6	1.91	
				48.3	1.88	
25.6	3.48	25.6	3.48	25.4	3.51	Anhydrite
31.5	2.84	31.5	2.84	31.4	2.85	
38.8	2.32	38.6	2.33	33.2	2.70	
41.0	2.20	41.0	2.20	41.0	2.20	
				43.3	2.09	
				48.3	1.88	
18.2	4.87					Portlandite
34.2	2.62					
47.2	1.93					
50.9	1.79					
20.9	4.25	26.7	3.34	26.6	3.35	Quartz
26.9	3.31			36.6	2.46	
50.2	1.82			50.2	1.82	
				60.0	1.54	
9.2	9.61					Ettringite
15.8	5.61					
22.9	3.88					
32.3	2.77					
		31.8	2.81			NaCl
		45.6	1.99			
		56.6	1.63			
		28.4	3.14			CaSO ₃ ·1/2H ₂ O
		34.5	2.60			

Figure 7.1 X-ray diffractograms of incineration residues.

- (a) New York City
- (b) Westchester
- (c) Huntington

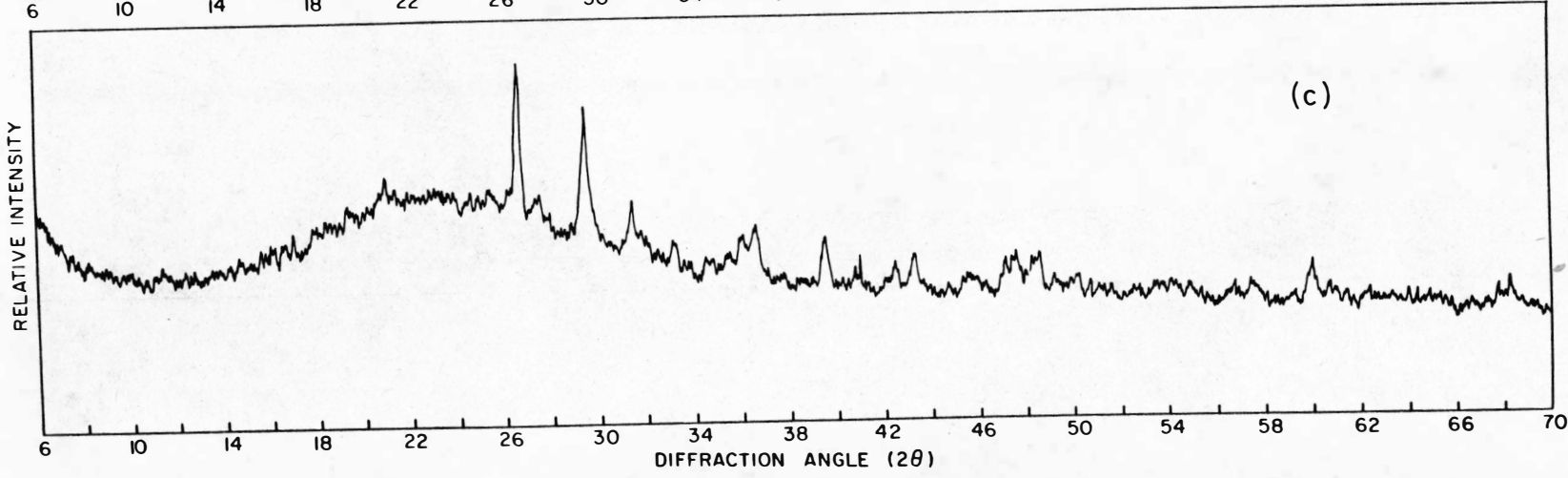
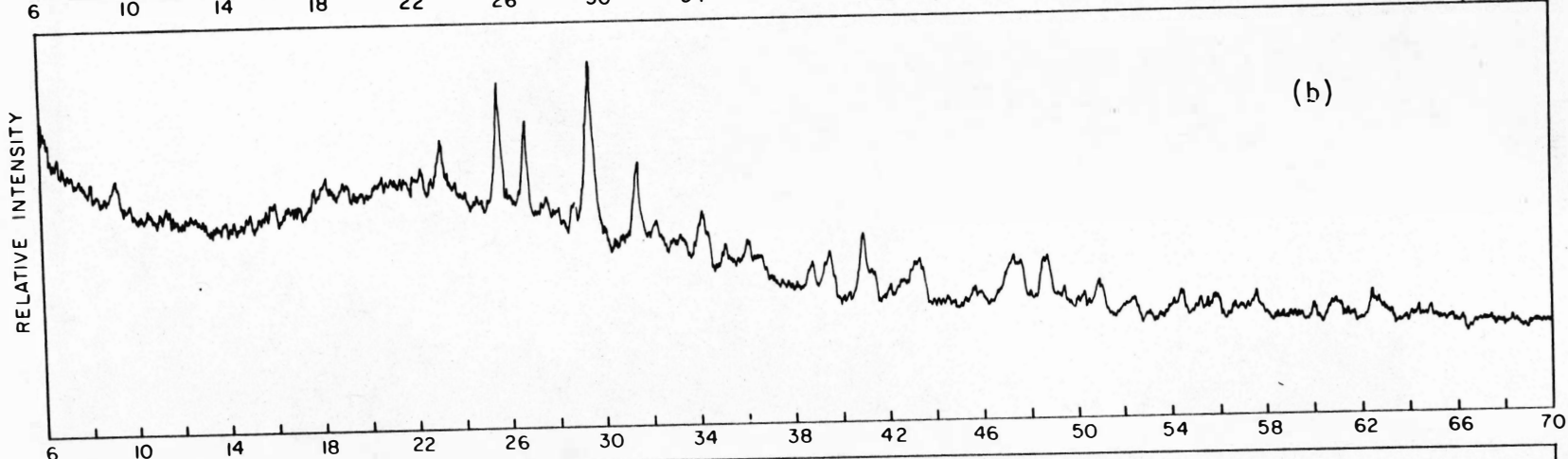
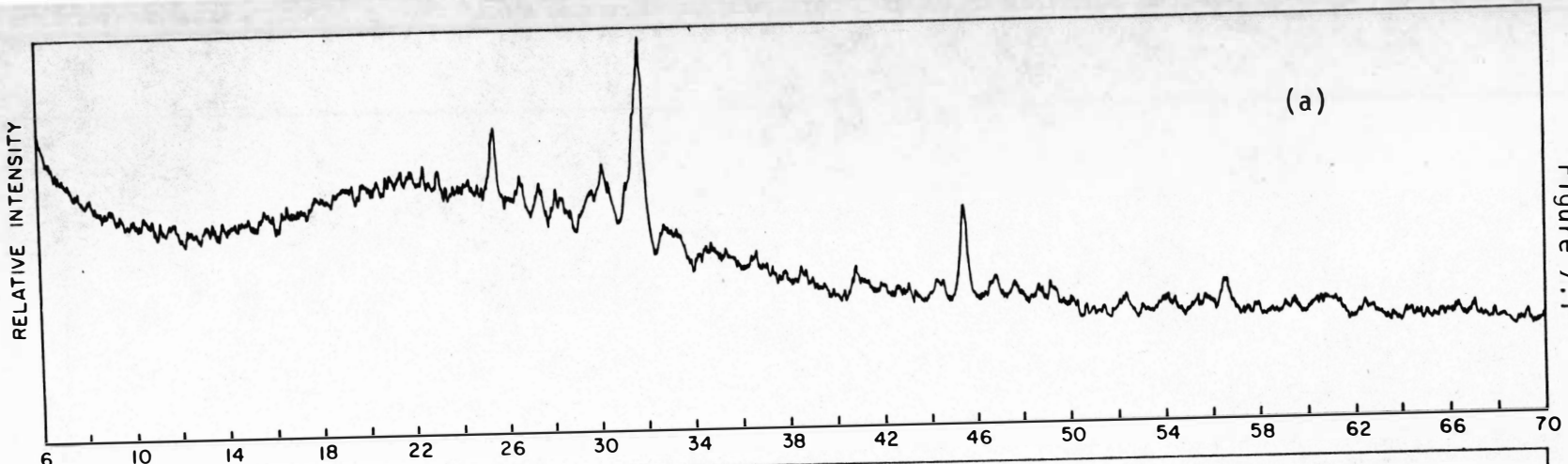


Figure 7.1

The x-ray diffractograms of the various residues exhibit a lower signal to noise ratio than that observed for the optimum mix blocks. This can be attributed to the presence of large amounts of amorphous material which may also have a shielding for any crystalline material present in the sample thus obscuring smaller peaks. The increase in the baseline as the scan proceeds downscale is attributable to large amounts of glass and amorphous phases of iron.

Scanning electron micrographs of incineration residues are shown in Figure 7.2. The majority of crystal development observed was associated with the Westchester residue. Tubular crystals 1 - 5 μm in lateral dimension and 0.1 - 0.5 μm in thickness were uniformly dispersed throughout the residue. New York City ash also exhibited a high degree of crystal development, numerous spherically shaped particles ranging in size from 1 - 40 μm were observed. Huntington samples were notable in the reduced amount of crystal development seen when compared to the two other ash types. Flat platelets 10 - 100 μm dominate the photomicrographs.

Stabilized Incineration Residues

X-ray diffraction patterns of the optimum blocks are shown in Figure 7.3 with a summary of the important characteristics presented in Table 7.2.

All blocks show very much the same mineralogical patterns in comparison to their respective ash sources. The Westchester optimum mix block differs only by the loss of the anhydrite peaks and the change of Portlandite to a major mineral phase. The increase in portlandite can be expected since the stabilization additive (Type 1 Portland cement) contains large amounts of portlandite. The loss of the anhydrite peak may result from partial hydration of the CaSO_4 during block fabrication forming poorly crystallized $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This would account for its loss from the pattern. Huntington block follows the same changes in mineralogy from ash to block as Westchester block. Anhydrite is lost, portlandite is gained and, in addition, ettringite is formed. New York City block shows no change.

Figure 7.2 Scanning electron micrographs of incineration residues.

- (a) Westchester residue - upper
- (b) New York City fly ash - middle
- (c) Huntington residue - lower

Figure 7.2

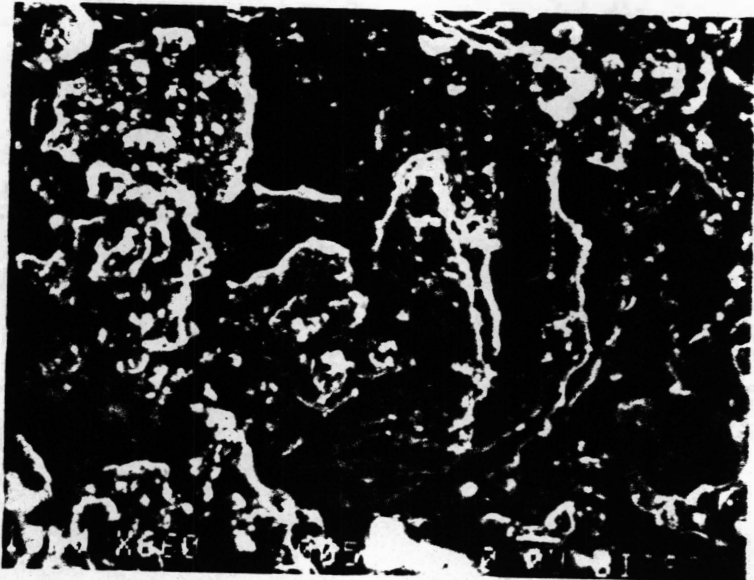
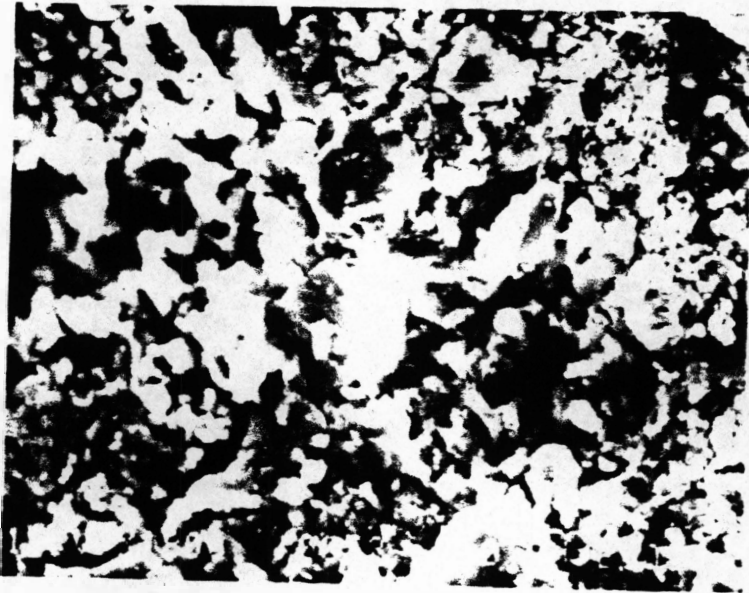
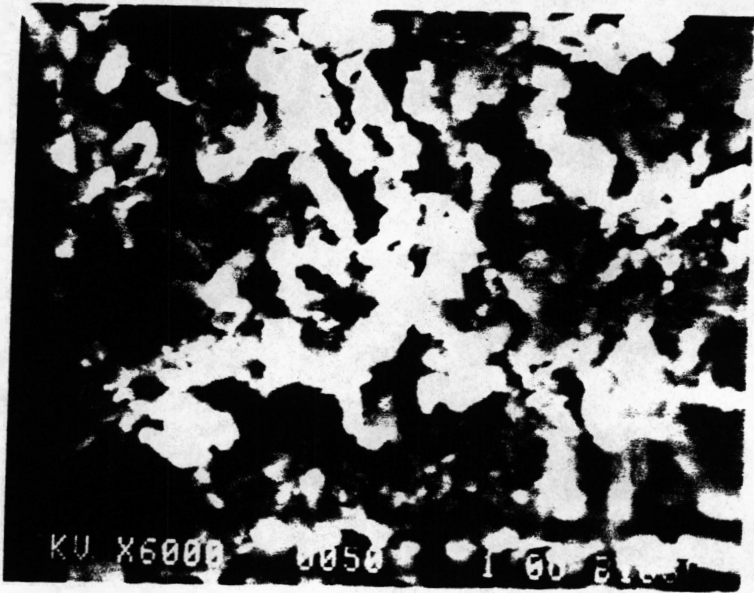


Table 7.2. Mineral composition of stabilized incineration residues.

Westchester		New York City		Huntington		Mineral
2 θ	d	2 θ	d	2 θ	d	
29.5	3.03	23.2	3.83	29.6	3.02	Calcite
39.5	2.28	29.7	3.01	36.1	2.49	
47.6	1.91	36.1	2.49	39.7	2.27	
		39.2	2.30	47.8	1.90	Anhydrite
		25.8	3.45	48.3	1.88	
		31.6	2.83			
		41.1	2.20			
18.2	4.87			18.2	4.87	Portlandite
34.2	2.62			34.4	2.61	
47.2	1.93			47.4	1.92	
26.7	3.34	26.9	3.31	26.7	3.34	Quartz
36.7	2.45	60.3	1.53	50.4	1.81	
60.1	1.54			60.3	1.53	
9.1	9.72			9.3	9.51	Ettringite
15.9	5.57			16.0	5.54	
32.3	2.77			32.4	2.76	
				35.4	2.54	
		32.0	2.80			NaCl
		45.8	1.98			
		56.8	1.62			
		28.6	3.12			CaSO ₃ ·1/2H ₂ O
		34.7	2.59			

Figure 7.3 X-ray diffractograms of stabilized incineration residues.

- (a) New York City
- (b) Westchester
- (c) Huntington

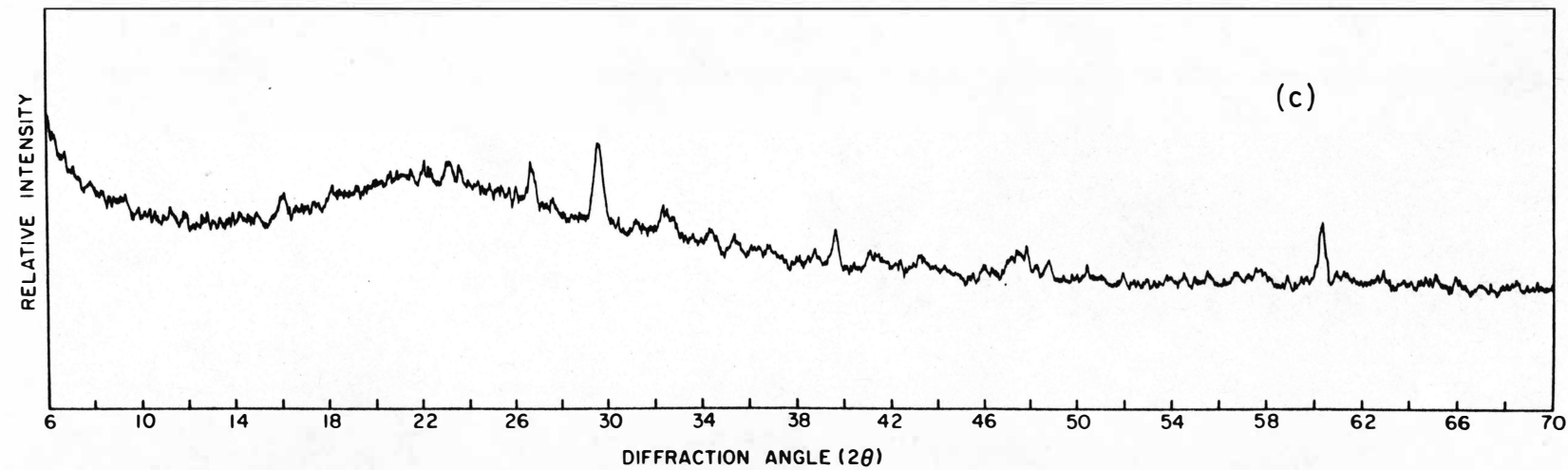
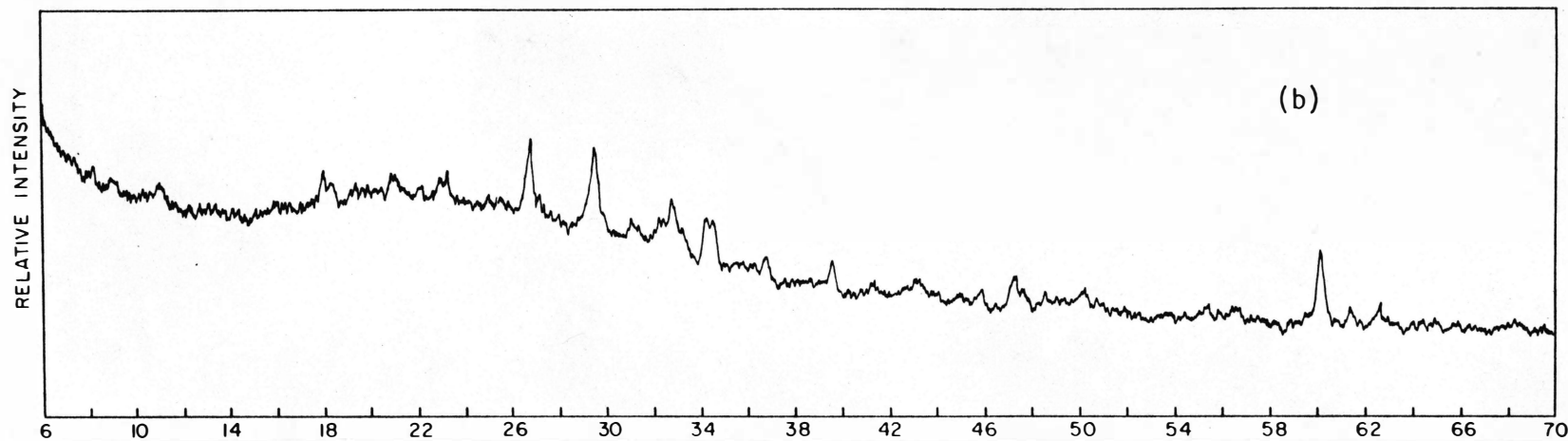
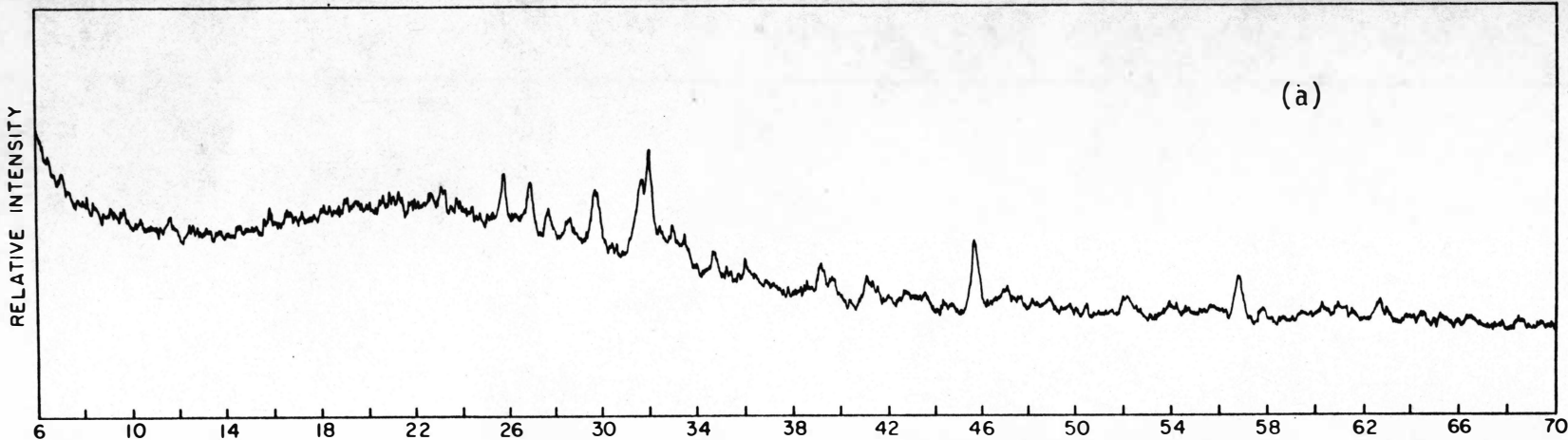


Figure 7.3

Results from SEM are shown in Figure 7.4. Samples were taken from optimum blocks of each ash type. Improved crystal development was observed in two areas:

- (1) the numbers of crystals per "group" (or area of development)
- (2) and/or the number of groupings.

For all three ash types, crystal development was increased in both manners.

Westchester and New York City stabilized proctor samples were observed to possess a tight assemblage of interlocking crystals. Well defined crystals and amorphous material appear to be evenly woven together, indicating a homogeneous mixture of the principal components. Huntington residue shows less well defined crystal development relative to the other residue types.

Effects of Seawater Submersion

Optimum mix blocks were submerged in seawater, for 60 days removed and subsequently prepared for x-ray diffraction analysis. The XRD patterns are presented in Figure 7.5. Table 7.3 summarizes changes in mineral phases that occur.

It is observed that all blocks form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) after 60 days of seawater exposure. Gypsum development was extensive in the New York City blocks, a fact that will lead to the failure of this material in the weeks ahead. In addition, Huntington proctors following submersion loose portlandite and ettringite while New York City block shows a reduction in anhydrite and NaCl.

Scanning electron micrographs of the submerged blocks are shown in Figure 7.6. Westchester blocks showed a further increase in crystal development after submersion. New York City blocks showed a significant increase in crystal development. Tightly packed gypsum crystals dominate the photomicrographs. Finally, Huntington blocks exhibited an uncharacteristic "flaky" appearance that seemed to contain no noticeable crystal development, even at higher magnifications.

Figure 7.4 Scanning electron micrographs of stabilized incineration residues.

- (a) Westchester residue - upper
- (b) Huntington residue - middle
- (c) New York City - lower



Table 7.3. Mineral composition of stabilized blocks after 60 days submersion in seawater.

Westchester		New York City		Huntington		Mineral
<u>2 θ</u>	<u>d</u>	<u>2 θ</u>	<u>d</u>	<u>2 θ</u>	<u>d</u>	
23.2	3.83	23.2	3.83	23.2	3.83	Calcite
29.5	3.03	29.6	3.02	29.6	3.02	
39.5	2.28			39.6	2.28	
43.1	2.10					
47.7	1.91					
		25.5	3.49			Anhydrite
		31.3	2.86			
		40.9	2.21			
18.2	4.87					Portlandite
34.2	2.62					
47.3	1.92					
26.7	3.34	26.6	3.35	26.8	3.33	Quartz
50.2	1.82			60.2	1.54	
60.1	1.54					
9.1	9.72					Ettringite
15.8	5.61					
32.3	2.77					
		31.8	2.81			NaCl
		28.1	3.18			CaSO ₃ .1/2H ₂ O
		34.6	2.59			
11.2	7.90	11.8	7.50	11.3	7.83	Gypsum
20.8	4.27	20.9	4.25			
29.1	3.07	29.2	3.06			
31.2	2.87					

Figure 7.5 X-ray diffractograms of stabilized incineration blocks after 60 days submersion in seawater.

- (a) New York City
- (b) Westchester
- (c) Huntington

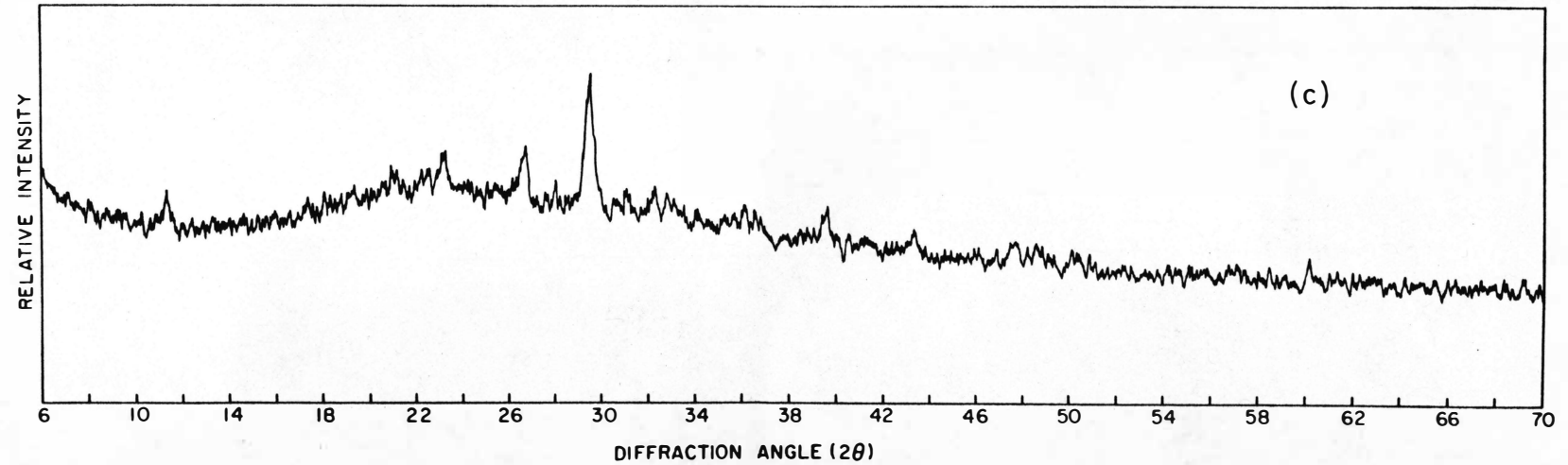
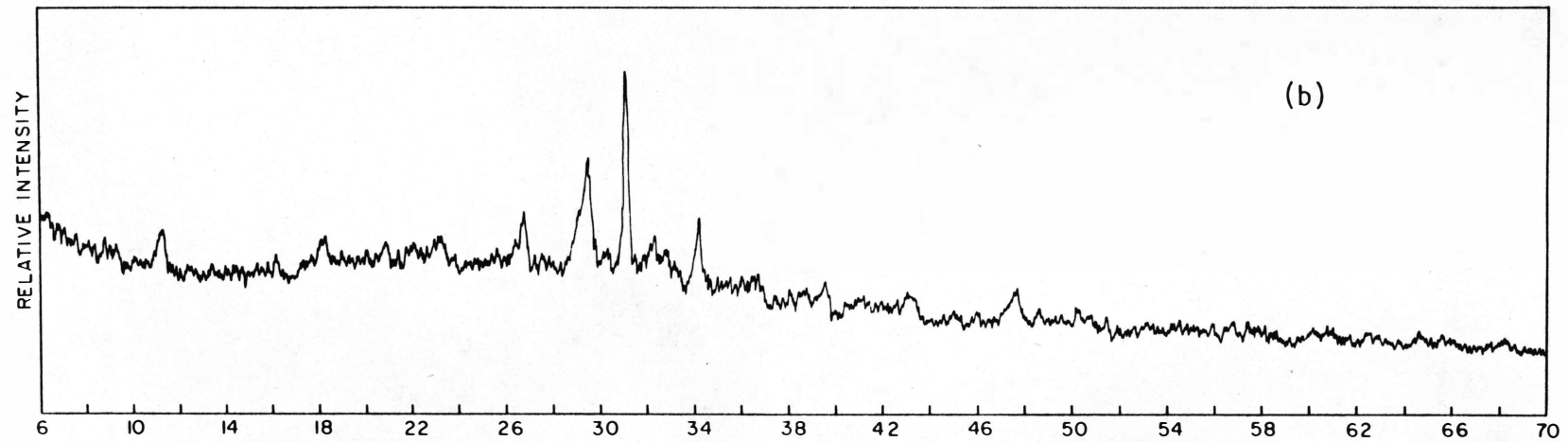
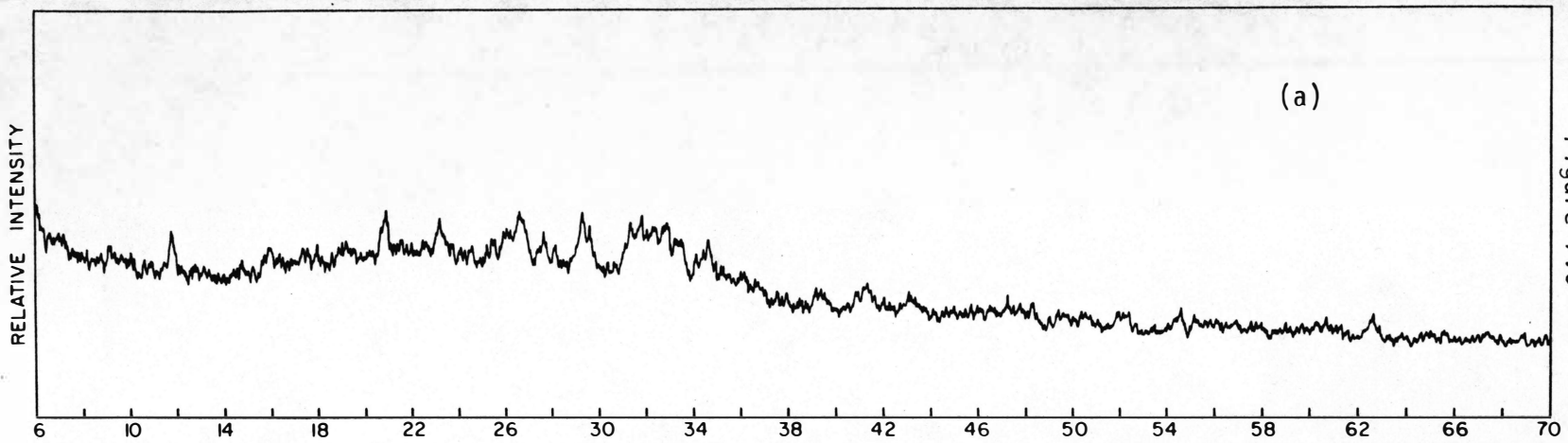
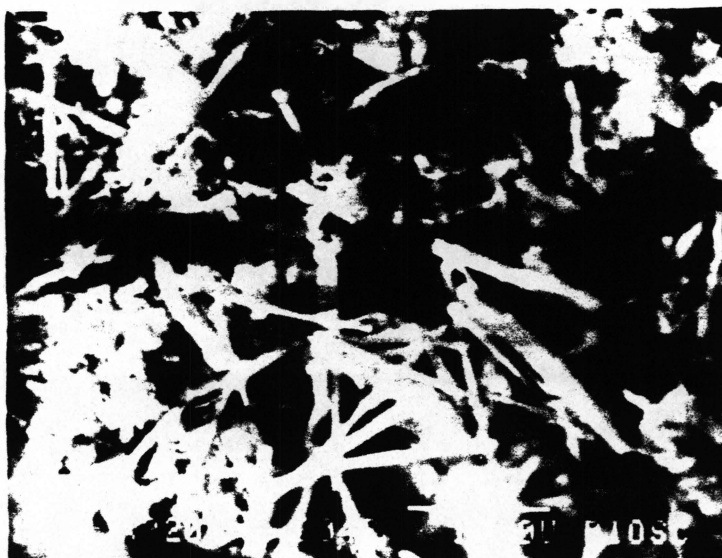
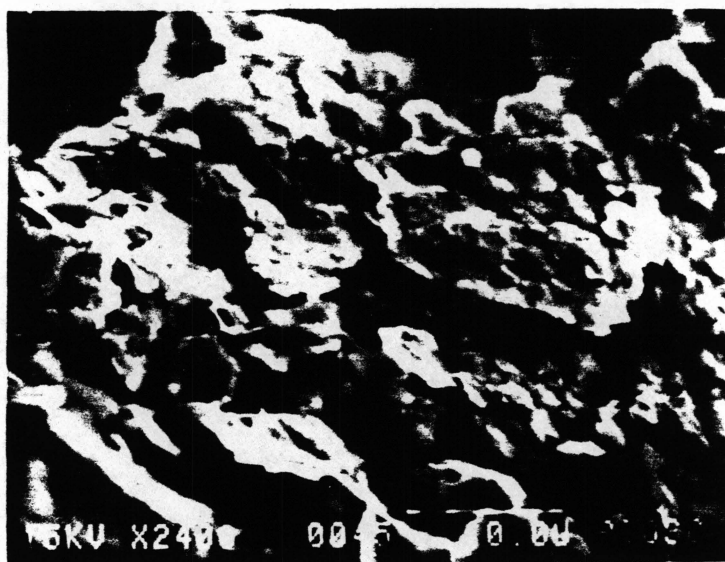


Figure 7.5

Figure 7.6 Scanning electron micrographs of stabilized blocks after 60 days of submersion in seawater.

- (a) Westchester residue - upper
- (b) Huntington residue - middle
- (c) New York City fly ash - lower



DISCUSSION

The stabilization mechanisms responsible for the development of strength in the stabilized blocks have their origin in the mineralogy of the reactant end members. The outstanding property that makes fly ash a viable material in the stabilization process is its pozzolanic nature. A pozzolan is a siliceous material or alumino-siliceous material which is not cementitious in itself, but which, in finely divided form and in the presence of moisture, reacts with alkali and alkaline-earth constituents producing cementitious products (ASTM, 1975). The pozzolanic reactions between the incineration waste and the stabilization additive can be greatly influenced by the mineralogy of each of the residues. The reactivity, defined as the bonding capability of ash, is a function of several factors (Barber, 1970; Thorn and Walt, 1965; Vincent *et al.*, 1961) some of which are:

- a. total amount of quartz and alumina associated with the fly ash
- b. amount of free lime present in the fly ash
- c. presence of carbon in the fly ash
- d. fineness of the fly ash, and
- e. surface characterization of the fly ash

For items a, b, d, and e it appears that the greater the quality, value or degree of, the greater the pozzolanic reactivity. For item c, carbon beyond certain concentrations will inhibit the reactivity of the fly ash (Vincent *et al.*, 1961).

Knowledge pertaining to any alterations in the mineralogy of the reactants subsequent to stabilization may provide information as to the structure of bonding components. All ash types benefited from the stabilization process. Crystal development increased following fabrication leading to a strong block. X-ray diffraction patterns clearly identify quartz and a variety of calcium compounds in each of the residues. These materials are necessary for the development of structurally important reaction products such as ettringite and calcium silicates.

Submersion affected each ash type differently. Westchester blocks exhibited an increase in their strength after 60 days of submersion. SEM data showed that the blocks also underwent an increase in crystal development for the same period. This increase in crystals led to a more strongly knit block that was able to withstand higher pressures than before submersion. New York City blocks exhibited a decrease in crystal development after submersion that correlates well with the decline in strength also noted for that time frame. In fact, after being submerged for ~120 days, the blocks fell apart altogether. This however was not surprising due to the large amounts of anhydrite observed in the x-ray diffraction patterns of the unstabilized ash. Submersion in seawater resulted in a significant alteration in the major mineral phase present in this mix type. Upon exposure to seawater anhyrrite, the predominant mineral phase in the New York City ash was converted to its hydrated form, gypsum. This conversion results in an expansion of the blocks components. The expansion is difficult to calculate as it is a function of dissolution, temperature and kinetics, all of which little data are available. However the expansion exceeded the porosity of the block, causing the bonding crystals to rupture and resulting in the structural failure of the material.

Finally, Huntington blocks exhibited only a slight decrease in strength in total contrast to the results one would expect on viewing the SEM photos. Crystal development seemed to be totally lacking in the blocks after submersion whereas the development before submersion was quite evident. The reason for this change, and how the block maintained its integrity is unknown.

Section 8

MARINE DISPOSAL IMPACTS

Model Estimates of Leachate Diffusion Zone in the Sea

Using data derived from the leachate studies, it is possible to use a model to obtain a first approximation of the size of the plume of leached components from a localized source, such as a disposal block reef. From measurements in the sea of turbulent and dispersive processes near the seafloor, Professor Akira Okubo (personal communication) has developed a general relationship for dispersion/dilution from a source near the seafloor:

$$D = \frac{q}{2\pi^{1/2} W S_p X}$$

where D = downstream distance, m
 q = source strength, g/sec
 W = diffusion velocity, cm/sec
 S_p = ambient concentration, g/cm³
 x = height of mixing, m

This general relationship can be applied to calculate the distance downstream from a source where the dispersive plume from a disposal reef site is diluted/dispersed to concentrations approaching ambient levels (Roethel and Woodhead, 1983). Using this model, the plume length of each of the fifteen elements investigated during the leachate studies was calculated, and is presented in Tables 8.1 and 8.2. Figure 8.1 illustrates the situation modelled; a disposal reef of 1000 tons of waste blocks on the seafloor in water with a diffusion velocity of 1 cm/sec and a conservative height of diffusion of 5 m. Ambient water column concentrations of elements used in the model are those for oceanic waters, (Goldberg, 1961), which are significantly lower than in many populated coastal regions such as the New York Bight. These factors, when combined

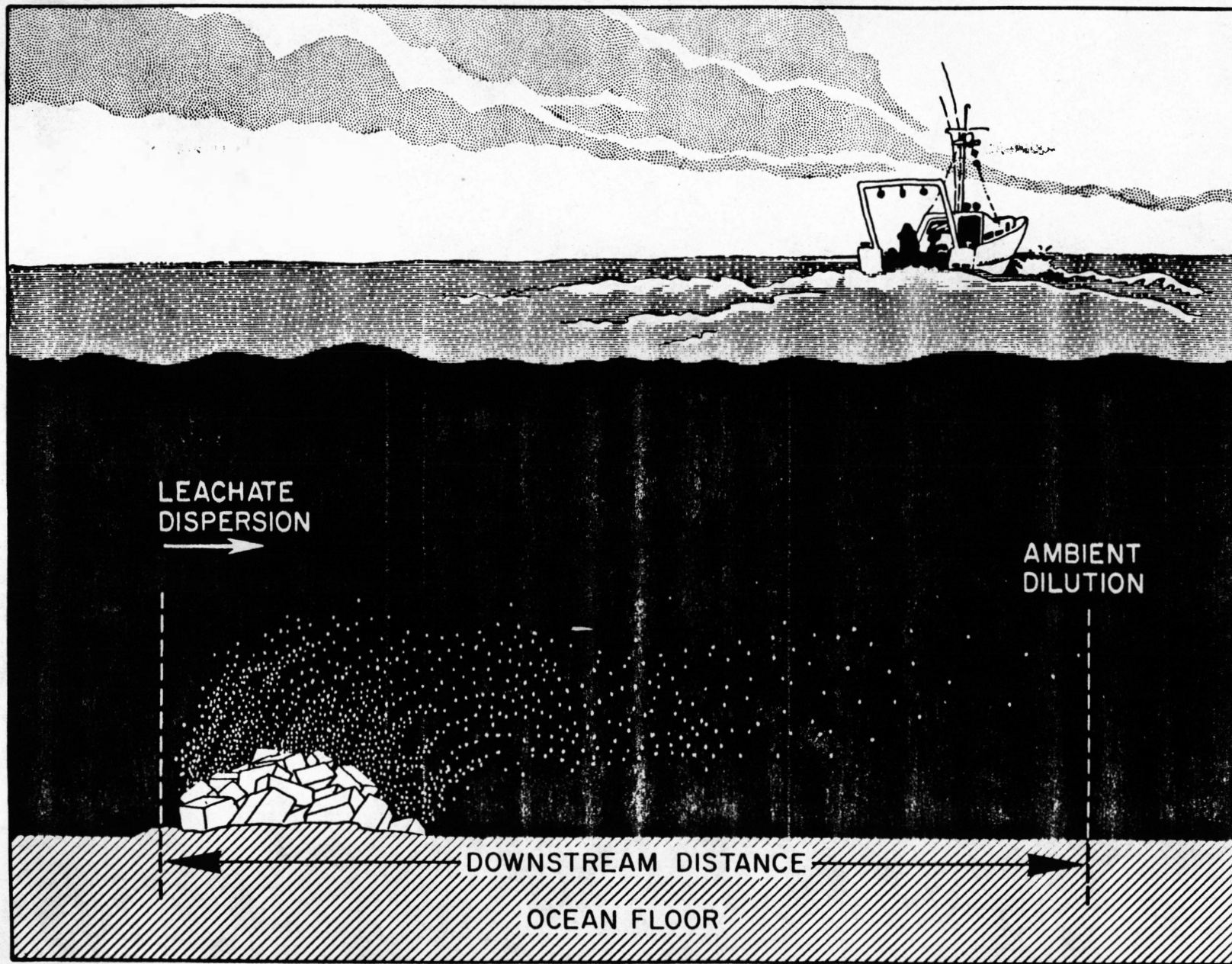


Figure 8.1. Diagram of downstream dispersion of leachate, modelled to calculate rates of dilution to ambient concentrations.

Table 8.1 Model calculations of plume length (m) applying EPA protocols

ELEMENT	SOURCE	TOTAL CONCENTRATION (ppm)	PERCENT LEACHED (%)	SOURCE STRENGTH (g/sec)	AMBIENT CONCENTRATION (g/cm ³)	DOWNSTREAM DISTANCE (m)
CADIMUM	WESTCHESTER	43.9	0.046	2.12E-04	1.00E-10	11.98
	HUNTINGTON	12.6	0.4	5.30E-04	1.00E-10	29.89
	NEW YORK	731	1.09	8.37E-02	1.00E-10	4725.54
LEAD	WESTCHESTER	5137	0	0.00E+00	3.00E-11	0.00
	HUNTINGTON	1040	0.007	7.65E-04	3.00E-11	143.92
	NEW YORK	7278	0.06	4.59E-02	3.00E-11	8632.75
COPPER	WESTCHESTER	4668	0.004	1.96E-03	3.00E-09	3.69
	HUNTINGTON	1446	0.09	1.37E-02	3.00E-09	25.73
	NEW YORK	606	0.05	3.18E-03	3.00E-09	5.99
CHROMIUM	WESTCHESTER	142	0.03	4.48E-04	5.00E-11	50.53
	HUNTINGTON	141	0.006	8.89E-05	5.00E-11	10.03
	NEW YORK	190	0.018	3.59E-04	5.00E-11	40.57
NICKEL	WESTCHESTER	109	0.01	1.15E-04	2.00E-09	0.32
	HUNTINGTON	54.6	0.14	8.03E-04	2.00E-09	2.27
	NEW YORK	78.1	0.096	7.88E-04	2.00E-09	2.22
COBALT	WESTCHESTER	19.8	0	0.00E+00	5.00E-10	0.00
	HUNTINGTON	11.6	0.05	6.10E-05	5.00E-10	0.69
	NEW YORK	19.7	0.7	1.45E-03	5.00E-10	16.36
MANGANESE	WESTCHESTER	825	0.02	1.73E-03	2.00E-09	4.89
	HUNTINGTON	806	0.15	1.27E-02	2.00E-09	35.85
	NEW YORK	1065	0.07	7.83E-03	2.00E-09	22.11
ALUMINUM	WESTCHESTER	58000	0.000036	2.19E-04	1.00E-08	0.12
	HUNTINGTON	39600	0.0025	1.04E-02	1.00E-08	5.87
	NEW YORK	69600	0.000061	4.46E-04	1.00E-08	0.25
IRON	WESTCHESTER	49000	0.000004	2.27E-05	1.00E-08	0.01
	HUNTINGTON	73000	0.00055	4.22E-03	1.00E-08	2.38
	NEW YORK	15600	0.000007	1.28E-05	1.00E-08	0.01

Table 8.1 Continued

ELEMENT	SOURCE	TOTAL CONCENTRATION (ppm)	PERCENT LEACHED (%)	SOURCE STRENGTH (g/sec)	AMBIENT CONCENTRATION (g/cm ³)	DOWNSTREAM DISTANCE (m)
ARSENIC	WESTCHESTER	4.8	0.05	2.52E-05	3.00E-09	0.05
	HUNTINGTON	15.7	0.02	3.30E-05	3.00E-09	0.06
	NEW YORK	72.5	0.0036	2.74E-05	3.00E-09	0.05
MAGNESIUM	WESTCHESTER	13700	0.32	4.61E-01	1.35E-03	0.00
	HUNTINGTON	9600	0.3	3.03E-01	1.35E-03	0.00
	NEW YORK	13400	0.54	7.60E-01	1.35E-03	0.00
SILICON	WESTCHESTER	161000	0.0062	1.05E-01	3.00E-06	0.20
	HUNTINGTON	137000	0.023	3.31E-01	3.00E-06	0.62
	NEW YORK	102000	0.035	3.75E-01	3.00E-06	0.71
CALCIUM	WESTCHESTER	137000	1.44	2.07E+01	4.00E-04	0.29
	HUNTINGTON	130000	1.56	2.13E+01	4.00E-04	0.30
	NEW YORK	128000	1.51	2.03E+01	4.00E-04	0.29
ZINC	WESTCHESTER	4482	0.0036	1.70E-03	1.00E-08	0.96
	HUNTINGTON	2294	0.22	5.30E-02	1.00E-08	29.93
	NEW YORK	18618	0.83	1.62E+00	1.00E-08	916.47

Table 8.2 Model calculations of plume length (m) applying ASTM protocols

ELEMENT	SOURCE	TOTAL CONCENTRATION (ppm)	PERCENT LEACHED (%)	SOURCE STRENGTH (g/sec)	AMBIENT CONCENTRATION (g/cm ³)	DOWNSTREAM DISTANCE (m)
CADMIUM	WESTCHESTER	43.9	0	0.00E+00	1.00E-10	0.00
	HUNTINGTON	12.6	0	0.00E+00	1.00E-10	0.00
	NEW YORK	731	0	0.00E+00	1.00E-10	0.00
LEAD	WESTCHESTER	5137	0.01	2.70E-03	3.00E-11	507.77
	HUNTINGTON	1040	0.003	1.64E-04	3.00E-11	30.84
	NEW YORK	7278	0.007	2.68E-03	3.00E-11	503.58
COPPER	WESTCHESTER	4668	0.005	1.23E-03	3.00E-09	2.31
	HUNTINGTON	1446	0.11	8.36E-03	3.00E-09	15.72
	NEW YORK	606	0.014	4.46E-04	3.00E-09	0.84
CHROMIUM	WESTCHESTER	142	0.03	2.24E-04	5.00E-11	25.26
	HUNTINGTON	141	0.012	8.89E-05	5.00E-11	10.03
	NEW YORK	190	0.2	2.00E-03	5.00E-11	225.37
NICKEL	WESTCHESTER	109	0	0.00E+00	2.00E-09	0.00
	HUNTINGTON	54.6	0.12	3.44E-04	2.00E-09	0.97
	NEW YORK	78.1	0.015	6.16E-05	2.00E-09	0.17
COBALT	WESTCHESTER	19.8	0	0.00E+00	5.00E-10	0.00
	HUNTINGTON	11.6	0	0.00E+00	5.00E-10	0.00
	NEW YORK	19.7	0	0.00E+00	5.00E-10	0.00
MANGANESE	WESTCHESTER	825	0.0002	8.67E-06	2.00E-09	0.02
	HUNTINGTON	806	0.0003	1.27E-05	2.00E-09	0.04
	NEW YORK	1065	0.0006	3.36E-05	2.00E-09	0.09
ALUMINUM	WESTCHESTER	58000	0.001	3.05E-03	1.00E-08	1.72
	HUNTINGTON	39600	0.03	6.24E-02	1.00E-08	35.23
	NEW YORK	69600	0	0.00E+00	1.00E-08	0.00
IRON	WESTCHESTER	49000	0.0001	2.57E-04	1.00E-08	0.15
	HUNTINGTON	73000	0.0003	1.15E-03	1.00E-08	0.65
	NEW YORK	15600	0.00006	4.92E-05	1.00E-08	0.03

Table 8.2 Continued

ELEMENT	SOURCE	TOTAL CONCENTRATION (ppm)	PERCENT LEACHED (%)	SOURCE STRENGTH (g/sec)	AMBIENT CONCENTRATION (g/cm ³)	DOWNSTREAM DISTANCE (m)
ARSENIC	WESTCHESTER	4.8	0	0.00E+00	3.00E-09	0.00
	HUNTINGTON	15.7	0.04	3.30E-05	3.00E-09	0.06
	NEW YORK	72.5	0.0067	2.55E-05	3.00E-09	0.05
MAGNESIUM	WESTCHESTER	13700	0.00002	1.44E-05	1.35E-03	0.00
	HUNTINGTON	9600	0.00003	1.51E-05	1.35E-03	0.00
	NEW YORK	13400	0.0003	2.11E-04	1.35E-03	0.00
SILICON	WESTCHESTER	161000	0.001	8.46E-03	3.00E-06	0.02
	HUNTINGTON	137000	0.002	1.44E-02	3.00E-06	0.03
	NEW YORK	102000	0.003	1.61E-02	3.00E-06	0.03
CALCIUM	WESTCHESTER	137000	0.21	1.51E+00	4.00E-04	0.02
	HUNTINGTON	130000	0.18	1.23E+00	4.00E-04	0.02
	NEW YORK	128000	0.57	3.83E+00	4.00E-04	0.05
ZINC	WESTCHESTER	4482	0.0004	9.42E-05	1.00E-08	0.05
	HUNTINGTON	2294	0.002	2.41E-04	1.00E-08	0.14
	NEW YORK	18618	0.007	6.85E-03	1.00E-08	3.86

with data derived from the conservative leachate methods such as used in this study, provide a "worst case" scenario.

Plume length for EPA (Figure 8.2) and ASTM (Figure 8.3) leachate values are graphically presented and it is seen that for stabilized Westchester and Huntington residues, with the exception of lead, the plume length is less than 100 meters regardless of the leachate protocol applied. New York City stabilized fly ash extends a few kilometers for cadmium and lead using EPA leachate values; but the model implies a significant reduction in the plume length under ASTM leaching conditions.

SPACE FOR DISPOSAL ON SEABED

It is estimated that the New York Metropolitan region will produce approximately 12.6×10^6 tons of incineration residue annually in the near future (Table 8.3). Assuming 15% stabilization additives would be necessary for fixation then approximately 3×10^6 tons of SIA blocks would require disposal. If ocean disposal of fixated SIA blocks should be adopted what space on the seabed would be required?

Taking one (1) square mile of seabed at a depth of 80 ft, off Long Island, it is assumed that the site may be filled to a depth of 50 ft. The volume disposal capacity would then be $1 \text{ mile}^2 \times 30 \text{ ft} = 8.36 \times 10^8 \text{ ft}^3$.

If pore space between blocks is 35% = $2.93 \times 10^8 \text{ ft}^3$.

Volume capacity for blocks = $8.36 - 2.93 \times 10^8 = 5.43 \times 10^8 \text{ ft}^3$.

Unit SIA block volume = 0.593 ft^3 .

Total number of SIA blocks in disposal volume = 9.2×10^8 .

Average weight of block at density of $110 \text{ lb/ft}^3 = 65 \text{ lbs}$.

Then total weight capacity of block disposal = $30 \times 10^6 \text{ tons}$.

Figure 8.2

ELEMENTAL PLUME LENGTH BASED UPON EPA PROTOCOL

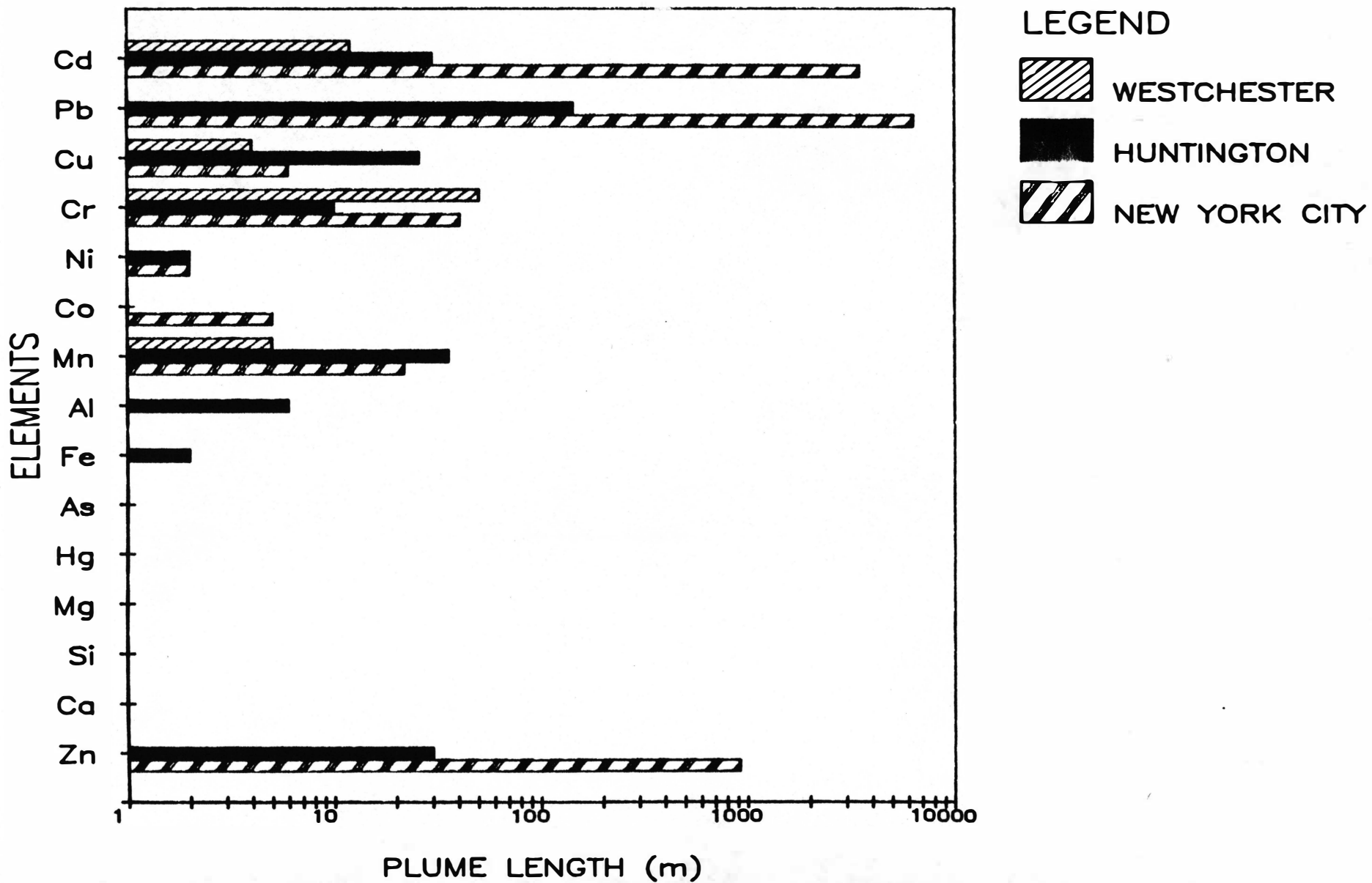
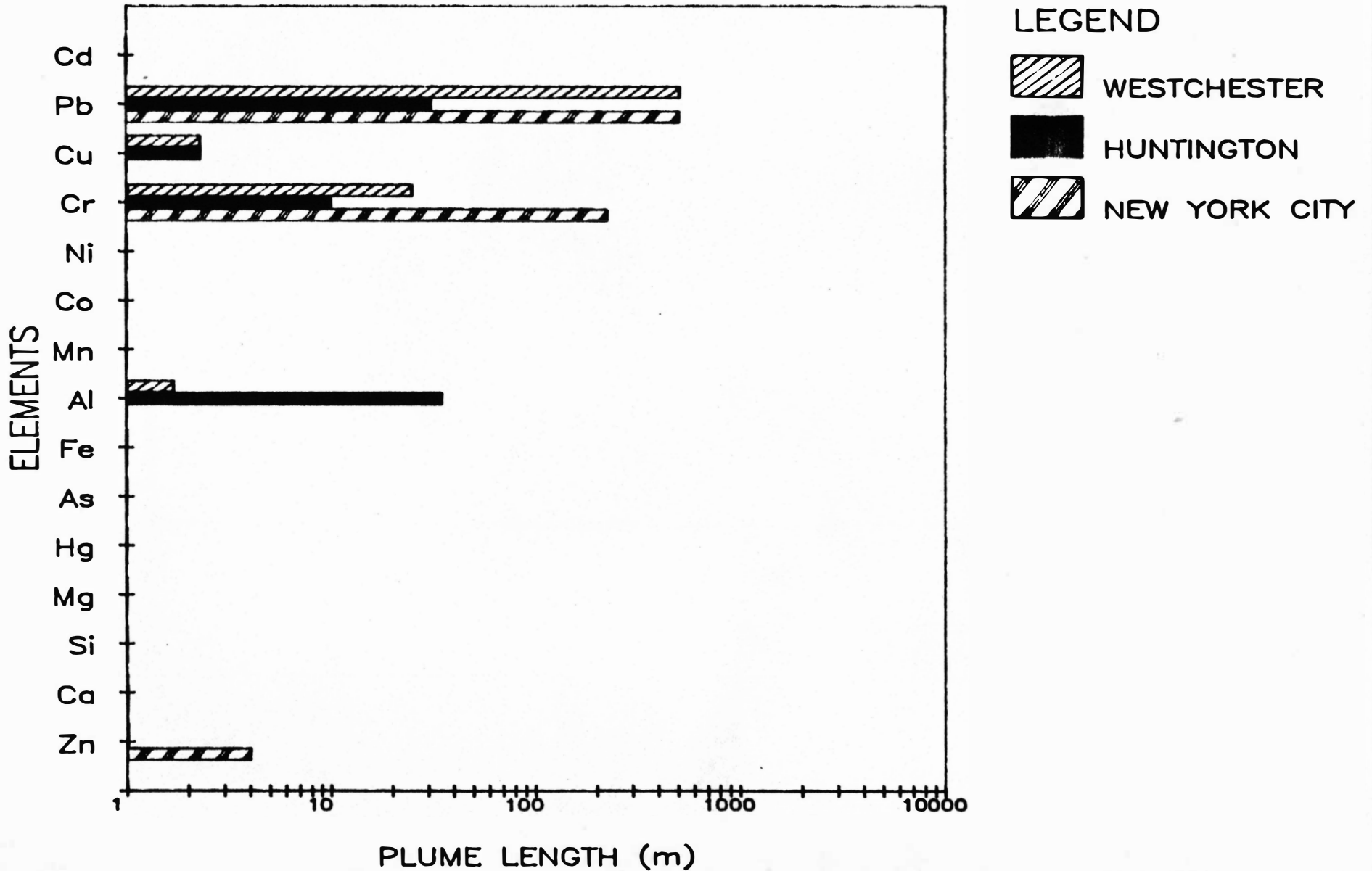


Figure 8.3

ELEMENTAL PLUME LENGTH BASED UPON ASTM PROTOCOL



Regional production of SIA for fixation based upon the estimate in Table 8.3.

Incineration Residues = 2.6×10^6 tons.

Stabilization additives required for fixation = 3.9×10^5 tons.

Total annual weight of SIA block production = 3×10^6 tons.

Time to fill disposal site to 30 ft at this rate = 10 years.

Table 8.3 Years of residue disposal necessary to create an artificial reef

LOCATION	REFUSE COLLECTED PER YEAR	RESIDUE PRODUCED PER YEAR	TOTAL WEIGHT OF STABILIZED BLOCKS	TIME TO FILL DISPOSAL SITE
<u>NEW YORK CITY</u>				
MANHATTAN	3,385,375	677,075	778,636	38
BROOKLYN	2,540,400	508,080	584,292	51
QUEENS	2,202,775	440,555	506,638	59
BRONX	1,202,675	240,535	276,615	108
STATEN ISLAND	359,525	71,905	82,691	362
<u>CITY WIDE TOTAL</u>	9,690,750	1,938,150	2,228,873	13
<u>NASSAU COUNTY</u>				
GLEN COVE	46,000	9,200	10,580	2828
HEMPSTEAD	803,000	160,600	184,690	162
LONG BEACH	36,500	7,300	8,395	3564
NORTH HEMPSTEAD	274,000	54,800	63,020	475
OYSTER BAY	311,000	62,200	71,530	418
<u>COUNTY TOTAL</u>	1,470,500	294,100	338,215	88
<u>SUFFOLK COUNTY</u>				
BABYLON	274,000	54,800	63,020	475
BROOKHAVEN	511,000	102,200	117,530	255
EAST HAMPTON	110,000	22,000	25,300	1183
HUNTINGTON	292,000	58,400	67,160	446
ISLIP	328,500	65,700	75,555	396
RIVERHEAD	110,000	22,000	25,300	1183
SHELTER ISLAND	18,250	3,650	4,198	7128
SMITHTOWN	110,000	22,000	25,300	1183
SOUTHAMPTON	76,000	15,200	17,480	1712
SOUTHOLD	45,625	9,125	10,494	2851
<u>COUNTY TOTAL</u>	1,875,375	375,075	431,336	69
<u>NEW YORK REGIONAL TOTAL</u>	13,036,625	2,607,325	2,998,424	10

Section 9

Summary and Conclusions

The object of this study was to stabilize incineration ash (SIA) with chemical additives to form solid blocks for evaluating an alternative method of marine disposal of this waste material. Laboratory studies were conducted on the physical and chemical properties of the SIA proctor sized samples in the laboratory and in seawater.

The results of this investigation confirmed that incineration residues can be stabilized in block form using lime (CaOH_2) or Portland cement as stabilizing additives. This investigation has developed data that suggests SIA blocks can maintain their physical integrity and minimize elemental leaching following submersion in the sea. Both physical and chemical properties of the stabilized materials will significantly affect their behaviors in the sea.

Specific conclusions reached as a result of this study are as follows:

- (a) Fixation additives, moisture content and curing protocols all affect the physical properties of the stabilized proctors.
- (b) Addition of sulfates significantly reduce the structural integrity of the stabilized proctors, Na_2CO_3 addition to the mix has no effect.
- (c) Moisture content was a function in part of the mean particle size of the mix.
- (d) Temperature accelerates the development of compressive strength as well as increased curing time.
- (e) Permeabilities of approximately 10^{-7} cm/sec were observed over a period of 30 days.

- (f) Stabilization significantly alter leaching behavior, for combined residue proctors, EPA leachate limits were not exceeded.
- (g) Fly ash contains significantly higher concentrations of volatile metal when compared to bottom ash.
- (h) Stabilized blocks of combined residue should maintain their structural integrity in the sea for an extended period of time, one century appears likely based upon the leaching of Calcium an element central to the structural integrity of the material.
- (i) Incineration residue may prove to be an acceptable substitute for natural aggregates in the fabrication of cement blocks.
- (j) Should marine disposal of stabilized incineration ash be undertaken, one reef approximately one square mile in area could accommodate the residue of the entire New York Metropolitan region for a decade.

REFERENCES

- American Society for Testing and Materials. 1975. Standard specification for fly ash and other Pozzolans for use with lime - Procedure C593-69 In: 1975 Annual Book of ASTM Standards, Vol. 13, Philadelphia, Pa. pp. 340-344.
- American Society of Testing and Materials. 1980. Proposed methods for leaching waste materials (Method A) Water shake extraction procedure. In: Annual Book of ASTM Standards, Part 31, Water, Philadelphia, PA., pp. 1369-1372.
- Barber, E. G. 1970. The utilization of Pulverized Fuel Ash. Journal of the Institute of Fuels, 43, 4-9.
- Duedall, I.W., J.S. Buyer, M.G. Heaton, S.A. Oakley, A. Okubo, R. Dayal, M. Tatro, F.J. Roethel, R.J. Wilke, J.P. Hershey. 1983. Diffusion of calcium and sulfate ions in stabilized coal wastes. In: Wastes in the Ocean, I.W. Duedall, B.H. Ketchum, P.K. Park and D.R. Kester (Eds.). John Wiley & Sons, Inc. New York, 1983, Vol. 1, chapter 19. pp. 375-395.
- Edwards, T. 1983. Dissolution rates of calcium in stabilized coal wastes in freshwater and seawater. Master Thesis, Marine Sciences Research Center, State University of New York at Stony Brook, 69 pp.
- Environmental Protection Agency Hazardous Waste Guidelines and Regulations. Federal Register, Vol. 43, No. 243. pp. 58955-58957. 1978.
- Goldberg, E.D. 1961. Chemistry of the Oceans. In: Oceanography, M. Sears Ed., American Association for the Advancement of Science, Washington D.C. 583pp.

- Harder, P. J., M. J. Marcinak, N. J. Schlotter, A. I. Labotka, and I. W. Duedall. 1981. The fixation of fly ash: Physical and leachate properties. Final Report to the Consolidated Edison Company of New York, Inc., New York, N. Y. 10003, pp. 264.
- Humphries, E.M. 1982. Section 2. Biological investigations. In: Stabilized coal waste in the Chesapeake Bay-Choptank River Estuary: Environmental Investigations, I.W. Duedall and E.M. Humphries (Principal Investigators). Technical Report PPRP-49, Maryland Power Plant Siting Program, Annapolis, Maryland, 2 sections (paginated separately).
- JCPDS. 1979. Power Diffraction File, Inorganic Materials Alphabetical Index, Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, Swathmore, Pennsylvania.
- Lechich, A.F. 1984. Stabilization of titanium processing wastes within a fly ash matrix. Master Thesis, Marine Sciences Research Center, State University of New York at Stony Brook, 100 pp.
- Li, Y-H., and S. Gregory. 1974. Diffusion of ions in seawater and in deep-sea sediment. *Geochimica et Cosmochimica Acta*, 38, 703-714.
- Neville, A.M. 1983. Properties of concrete. Halsted Press, Div. of Wiley & Sons, New York, NY.
- Parker, J.H., P.M.J. Woodhead, and I.W. Duedall. 1981. Experimental test blocks and demonstration reef construction. Coal Waste Artificial Reef Program, EPRI CS-2009, Vol. 2, Project 1341-1, Interim Report, Prepared for : Electric Power Research Institute, Palo Alto, California 94304, pp. 51-77.
- Roethel, F.J., I.W. Duedall, H.B. O'Connors, J.H. Parker and P.M.J. Woodhead. 1980. The interactions of stabilized scrubber sludge and fly ash with the marine environment. Journal of Testing and Evaluation, 8, 250-254.