New Jersey Institute of Technology

Digital Commons @ NJIT

12-31-1990

Stabilization/solidification of organic containing wastes using organophilic clay and coal fly ash

Edith Lagoutte
New Jersey Institute of Technology

Follow this and additional works at: https://digitalcommons.njit.edu/theses

Part of the Environmental Sciences Commons, and the Toxicology Commons

Recommended Citation

ABSTRACT

Title of the Thesis: Stabilization/Solidification of Organic

                Containing Wastes Using Organophylic

                Clay and Coal Fly Ash.

Edith Lagoutte, Master of Science, 1990.

Thesis directed by: Dr.Dana KNOX, Associate Professor, Department

                of Chemical Engineering Chemistry and Envi

                ronmental Science.

The relative merits of eight different coal fly ashes for use in the stabilization/Solidification of a waste containing both heavy metals and pentachlorophenol were investigated. Also studied, was the possible use of either untreated or treated (with hexadecyl ammonium bromide) clay to enhance the stabilization of the organic. The sample composition was : 62% foundry baghouse dust (or 60% if 2% clay as added to the sample), 4.5% cement, 14% coal fly ash, 19.5% water. Pentachlorophenol was chosen as representative of the organic contamination. All tests were performed after curing the samples at $22^\circ C$, 98% Rh for 28 days. The tests consisted of: water content, true density, bulk density, unconfined compressive strength, porosity, and the Toxic Characteristic Leaching Procedure Test (TCLP).

The results showed promising results, based on the physical resistance of the samples and the reduction of the concentration of chromium, lead and cadmium in the leachate. However, after 28 days curing, no differences in the physical or chemical properties could be observed amoung S/S samples made with different fly ashes. Physical tests show an average true density of 2.3, and a strength resistance of about 300 psi. The resitance to the wet/dry testing was excellent, as samples had lost less than 1% corrected cumulative weight loss. However, the resistance to freeze/thaw cycles was not as satisfactory.

A comparison of the results obtained after 28 days, between the untreated and treated clay show that the use of treated clay can enhance the strength and weathering resistance of the cubes. It also reduces the PCP concentration in the leachate by a factor of 10.

STABILIZATION/SOLIDIFICATION OF

ORGANIC CONTAINING WASTES USING

ORGANOPHILIC CLAY AND COAL FLY ASH

By:

Edith Lagoutte

Thesis submitted to the Faculty of the Graduate school of
the New Jersey Institute of Technology in partial fullfillment
of the requirement for the degree of
Master of science
1990

APPROVAL SHEET

Title of Thesis: Stabilization/Solidification of Organic

                     Containing Wastes Using Organophilic Clay

                     and Coal Fly Ash.

Name of Candidate: Edith Lagoutte

                   Master of Science, 1990

Thesis and Abstact Approved: _____   _____

                                 Dr. Dana Knox   Date
                                 Associate Professor
                                 Dept. of Chemical Eng.,
                                 Chemistry and Environ-
                                 mental Science.

                                 _____   _____

                                 Dr.John Liskowitz   Date
                                 Distinguished Professor
                                 Dept. of Civil and
                                 Environmental Engineering

                                 _____   _____

                                 Dr.James Grow   Date
                                 Associate Professor
                                 Dept. of Chemical Eng.,
                                 Chemistry and Environ-
                                 mental Science.

VITA

Name: Edith Lagoutte

Permanent address:

Degree and date to be conferred: Master of Science, toxic option,

1990.

Date of birth:

Place of birth:

Secondary Education: Lycee agricole de Valence, France.

Collegiate institutions attended	Dates	Degree	Date of degree
Institut Universitaire de tours, France	09/83-06/85	B.S.	June 1985
University de Chambery France	09/85-06/87	M.S.	June 1987
Institut National des Sciences Appliquees, France	09/87-08/88	D.E.A	Aug.1988
New Jersey Institute of Technology, U.S.A.	09/88-10/90	Master of Science	Dec.1990

Major: Environmental Science, Toxicology option

Position held: Research Assistant, NJIT 09/88-present.

Blank Page

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

CHAPTER   Page

(iii)

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDIX

CHAPTER I: INTRODUCTION

Based on an environmental point of view, one of the main concerns is to avoid any additional contamination of our land due to inconsiderate dumping of industrial waste. Strong regulations have been established for treatment and disposal of hazardous waste. Several technologies are now available, such as incineration, biological treatment or chemical fixation and solidification. Although stabilization is not a destructive technology, it has received a great deal of attention from environmental scientists , lawyers, and the public. This process consists of combining waste sludges with various additives that both chemically and physically solidify the material, thus making it less susceptible to leaching.

An almost infinite variety of chemical fixation processes exist. They offer the advantage of using cheap and readily available materials, having a good long term stability both physically and chemically, having a low energy requirement, and producing a monolitic leach resistant solid.

Most of the processes now commercially available treat inorganic wastes. The most widely used method is the cement based process, sometime modified with fly ash added as a pozzolanic agent. Very good results are obtained when inorganic toxics such as heavy

metals are involved. But very little is known when the method has to be applied for organic- containing waste.

The first objective of this project was, to demonstrate the successful use of the stabilization /solidification technique when organic toxics are involved. The second objective of this project was to asseses the influence of different fly ashes on the physical/chemical properties of the treated samples.

The experimental plan was developed as follow:

Experiment I: Effect of 8 fly ash types on physical/weather
ing properties.

Experiment II: Effect of clay on physical/weathering proper
ties.

Experiment III: Effect of fly ash type on containment of
organic and metals.

Experiment IV: Effect of clay on containment of organic and
metals.

This report will first give a overview of the actual knowledge on stabilization/solidification. This will be followed by the description of the methods used , as well as a brief description of the components used for the experiments. The last chapter will give all results, in the same order as the experimental plan.

CHAPTER II: BACKGROUND

II.A TERMINOLOGY AND DEFINITION

In general, solidification/stabilization refers to a technology which uses additives to transform a waste into a more manageable form by physically, and/or chemically, immobilizing the waste constituents. This definition is simple, but words such as fixation, stabilization and solidification have been used interchangeably. EPA has defined stabilization and solidification as follows [Wiles, 1982]:

"Solidification itself is a process in which materials are added to the waste to produce a monolithic solid of high structural integrity; it may or may not involve a chemical bonding between the toxic contaminants and the additive. Contamination migration is restricted by vastly decreasing the surface area exposed to leaching and/or isolating the wastes within an impervious capsule.

Stabilization refers to a process by which a waste is converted into a more chemically stable form. It reduces the hazard of the waste by a chemical reaction which will convert the contaminant to its least soluble, toxic or mobile form."

Solidification/stabilization methods have as their goal the safe, ultimate disposal of hazardous waste through landfilling or some other productive uses [Conner, 1990].

II.B POTENTIAL ROLE OF STABILIZATION

One of the driving force for using stabilization/solidification technology is the regulatory status. The handling, storage, treatment and disposal are now regulated by the Resource Conservation and Recovery Act (RCRA) of 1976, including the subsequent 1984 amendments (HSWA). The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), otherwise known as Superfund, promotes the S/S technology applied to hazardous waste. Those regulations developed specific criteria to determine which waste are hazardous. They also establish standards for treatment, disposal and storage of waste. The Superfund Amendment and Reauthorization Act (SARA) of 1986 established a massive remedial program for the clean-up of existing sites that threaten the environment. With the promulgation of recent land-bans, specific technologies are specified as Best Demonstrated Available Technologies (BDAT). Solidification/stabilization (S/S) appears to be one of the most important of these. Land disposal is nowadays considered as the least prefered method of choice from an environmental standpoint. But it is often the only remaining solution if waste can not follow a classical treatment process such as thermal, chemical or biological destruction, or be reused in any beneficial way . Approximately 25% of the decisions for Superfund site remediation action in the

fiscal year 1988 included S/S at least as part of the treatment process. Many of these decisions involved sites contaminated with inorganic or organic constituents. Results of field application of full-scale testing have been presented during the 2nd International Symposium on S/S of Hazardous Wastes [Barth, 1990]. Several S/S processes have been evaluated in detail in the Superfund Innovative Technology Evaluation (SITE) program (USEPA, Cincinnati). Results are promising and some S/S BDAT should soon be accepted. S/S is able to achieve the primary goals of hazardous waste treatment which can be defined as follows:

- (1) improving the handling and physical characteristics of the waste,
- (2) decreasing the surface area across which transfer or loss of contained pollutants can occur,
- (3) limiting the solubility of any pollutants contained in the waste and detoxifying contained pollutants.

II.C BRIEF INVENTORY OF S/S METHODS

S/S treatment can offer numerous alternatives. S/S processes can be grouped into categories according to the type of additives and processes utilized:

II.C-1 CEMENT BASED

This is the most popular solidification agent for inorganic materials such as incinerator-generated wastes, roadways, etc. Its high pH tends to keep metals in the form of insoluble hydroxides or carbonate salts helping to minimize subsequent leaching. This method is well developed, and the chemical and physical properties of cement are well known. Portland cement is less widely used with organic toxics, since some organics are known to interfere with the overall setting and curing process [Conner, 1986, Tittlebaum, 1987].

II.C-2 LIME-BASED-POZZOLANIC METHODS

This system is characterized by compounds that contain aluminate and silicate which harden in the presence of hydrated lime . The most common are lime plus fly ash and lime plus cement-kiln dust. This process also ensures high pH conditions in the matrix. It has the same advantages as the cement-based: ready availability of material and equipment, low cost, and familiarity with pozzolanic properties [Arniella, 1990].

II C-3 THERMOPLASTIC RESINS

This involves the melting of a molten thermoplastic material such as asphalt, parafilm, bitumen, polyethylene, polypropylene, or sulfur with dried wastes at temperatures typically in the range of 130 to 230° C. The treated material is often containerized (drummed or coated) prior to disposal. This method may be used for hazardous wastes containing polychloro-bi-phenyls and dioxin as well as heavy metals. It has the advantage of decreasing the leachability by a factor of 100 to 1000 compared to that obtained using cement only. It is more expensive , requiring more complex equipment and it is necessary to ensure that the waste and resin are compatible, to avoid the risks of dissolution, slow deterioration and/or explosive reactions when sulfur is present [Arniella, 1990, Tittlebaum, 1987].

II.C-4 ORGANIC POLYMERS

These have been mostly used with nuclear wastes. The process involves the mixing of a monomer such as formaldehyde with a catalyst to form a polymer. The resulting solidified mass is spongy in texture. Only a small amount is required, so that the final product occupies about 30% less volume than cement-based systems. It has the inconvenience of being more expensive (about five times the cost of using cement), allowing some leachate (if all the water is not entrapped, metal ions can leach due to the acidic environment) , and the final product needing to be containerized to avoid biodegradation [Arniella, 1990, Tittlebaum, 1987].

II.C-5 GLASSIFICATION OR VITRIFICATION

In this case, waste may be mixed with molten borosilicate-glass (temperature on the order of 1,200°C) in a multizone furnace or can be melted by a subsurface electrode at the same time as its surrounding soil, to form a stable in situ matrix. This process offers the advantage of excellent strength, and very low porosity. However, it cannot be used on site when volatiles are involved because uncontrolled vaporization can occur during the melting process. It is also very costly [Arniella, 1990].

II.C-6 ENCAPSULATION

This consists of coating the waste material with a binder or an insoluble jacket. Polyethylene and/or polybutadiene have been used. It this case, both organic or inorganic wastes can be treated and well isolated. It is, however, expensive and requires a good selection of the binder material to ensure its compatibility with the waste [Arniella, 1990].

II.D CHARACTERIZATION OF THE ADDITIVES USED IN THE

CEMENT/FLY ASH-BASED SYSTEM

II.D-1 CEMENT

Immobilization of metals containing wastes using a cement-based matrix has been particularly well studied. It offers the advantage of reacting with the free water in the waste to form a dry matrix. Inorganic contaminant will remain immobile by encapsulating them in the resultant matrix.

The cement usually used is Ordinary Portland Cement (OPC) type I. It consist mainly of di-and tri-calcium silicates (about 77% W/W), tri-and trtra-calcium aluminate (16% W/W) and iron oxides. Cement hydration chemistry involves a complex series of reactions which begin when water and cement are mixed. Although the reaction can continue for years, most of the physical properties reach quasi-steady state values after approximately one month. The silicate phase hydrates to form calcium silicate-hydrate (C-S-H) and calcium hydroxide. The hydration of aluminate is known to contribute very little to the strength of the hydrated paste [Walsh, 1986]. In the case where cement contains sulfates, a sulfoaluminate can be formed, called ettringite. This formation is usually observed specifically in young hydrated cement and then decomposes with time.

The process of cement hydration can be modified when other compounds are present such as certain heavy metals or organic molecules. Research is being done to assess where the metals can be located in the cement [Poon, 1986]. The chemical nature of the metal in the cement and mutual influences of metal and cement are also of great interest. Spoon et al (1985) have recently demonstrated that a cement spiked with 2% zinc had a higher permeability which was not observed in the case of mercury. They attributed this to a chemical fixation mechanism for zinc and a physical isolation process that may occur in the case of mercury. The precipitation of hydroxides into the cement would provide a viable explanation for metal fixation in the cement matrix. They also found that ettringite was strongly related to the structural integrity of the solidified product. Lead nitrate was found to inhibit cement hydration by forming a impermeable coating around the calcium silicate grains [Thomas et al, 1981]. By reducing the cement hydration, the outer silicate will be in contact with water longer than the inner silicate of the cement particle, which enhances its degree of polymerization. A recent surface analysis study on cement doped with lead verified the presence of cavities and needlelike crystals, verifying this theory [Coke et al, 1990]. Poon (1986) identified a four oxygen coordinated first shell around the zinc atom in the cementitious matrix, but not in the case of mercury doped sample. This implies that the often suggested physical means of microencapsulation is not valid for metals such as zinc and lead. It occurs for mercury and other

10

similar metals, which form a particularly insoluble compound in alkaline environment while not modifying the micro-structure of the cementitious matrix [Poon, 1986]. In his experiments using acid sequential batch tests, Bishop (1990) shows that the cadmium leachability curve follows the alkalinity leaching curve, meaning that this heavy metal does not bind to the silica matrix itself. He demonstrates with a similar experiment that chromium and lead dissolution rates follow exactly the silicon dissolution rate, which again, goes against the encapsulation theory as a general rule for all heavy metals.

The mechanism whereby organic compounds interact with cement matrices is also important for the characterization of S/S technologies. Using micro-analytical techniques, Tittlebaum et al (1987) found that two waste phases are produced when p-bromophenol was spiked into type I Ordinary Portland Cement. One is concentrated and occurs as large grains, the second is a submicroscopic and heterogeneous distribution of the organics within the gel phase. Evidence exists that water soluble organics have detrimental effects on cement curing. Cement containing a high concentration of ethylene glycol has no or very little strength, a lack of crystalline formation and a high degree of porosity which reflect an increase in volume of hydrated substances [Shieffield, 1987]. In additional analysis, Walsh (1986) proposed the hypothesis that due to a molecular size close to the size of water, ethylene glycol may substitute for the water of hydration.

Non-water-soluble organic elements seem to have a smaller influ-

ence on cement curing. Sheffield (1987) found that cements containing pentachlorophenol (PCP) at a weight ratio of 1:25 and 1:10 were lower in strength through 7 days but both gained strength to the level of the control sample. This increase may be due to a delayed formation of C-S-H gel. At 1:5 concentration, strength was about 60% of the control samples after 28 days curing. TCLP tests were performed and showed less than 50% recovery of PCP in the extract. It was showed that PCP was found uniformly dispersed in the C-S-H gel phase, but had neither entered in the cement grain nor coated around the cement grains as p-bromophenol did. Phenol can also inhibit the setting of cement and produces large voids in the cement matrix, [Shieffield, 1987]. Phenol recovery from cement matrix was very much dependent on the curing time and initial phenol content [Vipulanandan, 1990]

Concerns have been expressed that over the long term organic wastes may become more mobile due to pH variation, surface tension and biological degradation of fixating agents and contaminants [Wolfe, 1986].

II.D-2 CLAY

One of the problems of S/S using a cement based matrix is the weak interaction between the organic molecules and the matrix. As a result, it has been observed that fixation using cement is very poor to nonexistent. Unfortunately, this has to be added to the detrimental effect commonly observed on the integrity of stabi-

12

lized wastes.   One possible solution is the use of an additive
that interacts with the matrix and, at the same time, will
adsorb and consequently immobilize the organic material.

Clays have been used for landfill liners to prevent leachate
migration [Wolfe, 1986]. Their capacity to adsorb most aromatic
molecules has been proved [Warren, 1986] and it has been suggest-
ed that they could be used as S/S agents for organic-containing
wastes, since the majority are aromatic and usually nonpolar in
nature.

In general, clays have alternating layers of hydrated alumina
and silica, with both tetrahedral and octahedral sites available
to retain organic molecules. Cations such as Li^+, Na^+ , K^+,
Ca^{2+}, Mg^{2+} and Fe^{2+} are usually present between alumina and
silica layers. The cations Li^+, Mg^{2+} and Fe^{2+} can be replaced by
quaternary ammonium cations, after a first exchange of the Na^+
and Ca^{2+} cations which are loosely held . This substitution
causes the clay to become organophilic and widens the interpla-
nar distances by acting as pillars.

Research has been done to establish the clay-aromatic interac-
tions, and to interpret the results obtained when using different
quaternary ammonium compounds. Mc Bride and Mortland (1955), for
example, have found that the basal spacing of ethylammonium
smectite increased as a function of the proportion exchanged with
tetra-n-propyl ammonium ions. Mc Bride and Pinnavia have found
that phenol was adsorbed to a greater extent by tetramethyl ammo-
nium smectites rather than hexa-decyl-tri-methyl-ammonium
(HDTMA) smectites.

Sheriff et al. (1987), and Mortland et al. (1986) have compared the adsorption of phenol and chlorophenols on smectite clays treated with quaternary ammonium compounds with differing substituents and hence with differing hydrophobicity. The efficiency of adsorption varies with the compounds and with the treatments. The authors were able to explain their results in terms of a relationship between the adsorbate and the treatment compound hydrophobicity. Mortland (1986) showed that trichlorophenol had penetrated interlamellar surfaces of HDTMA clay and by the increased basal spacing. In a comparative study done at the Alberta Environmental Centre and New Jersey Institute of Technology [Lagoutte, 1990], it was found that PCP was best adsorbed when the bentonite was treated with cetylpyrimidinium chloride or HDTMA rather than with tetramethylammonium. In the first two cases, the adsorption capacity was in the range of 110 mg/g of clay, compared to a capacity less than 10 mg/g in the second case. PCP/Clay isotherms are given in Figure II D-2-1 in the appendix.

Clay-organic complexes have been studied by soil scientists among others and a variety of interactions have been proposed. Of particular interest to the subject of alkylammonium treated clays is the work of Fenn and Mortland (1986) who have showed that phenol was adsorbed on tetra-ethyl-ammonium montmorillonite by an ion-dipole interaction as well as possible hydrogen bonding and electron interaction with the silicate structure of the clay.

Research is now being done to evaluate the use of clay in conjunction with cement-based S/S process, as a method of treating

hazardous waste. It is well known that, due to the chemical heterogeneity between the different classes of compounds encountered in hazardous waste disposal , uneven adsorption would occurs for a single clay system. Thus each waste would have to be treated with the appropriate clay system to give optimum adsorption of every organic. Comparative studies have been done in order to demonstrate and compare the results obtained with both a commercial treated clay and non-treated montmorillonite in the stabilization of an industrial waste. In the best case, they obtained 90% adsorption of 3-chlorophenol and dichlorophenol, but only 45% of phenol. The advantage of using a treated clay was obvious [Montgomery, 1988].

A fundamental concern is the nature of the chemical bonding between modified clay and organic waste material. Gibbons and Soundarajan (1989) worked with wastes spiked with various organics such as trichlorethylene, phenol, nitrobenzene and triethanolamines. They demonstrated that the waste materials are sandwiched between the alterning layers of silica and alumina and that there is a myriad of bonds with the stabilization binder. Dipole-dipole interaction, hydrogen bonding, coordinate covalent bonding, Lewis acid-base reactions, Friedel-Craft reactions were involved during containment. They verified that the total energy to drive those organic compounds out of the matrix is higher than their normal heats of vaporization, which suggests that the fixation is not limited to a simple asdorption on the matrix but also involves a more complex chemical binding. Based on the leachate value obtained by TCLP, they also suggested that when cement and slag powder are added and hydrated, these materials seal the

15

clay-mineral organic layers and crystallize. In the long run, there could be intertwining crystals of clay minerals and cement. The slag powder could plug any holes in the structure. Results obtained by Montgomery (1988) confirm this as they noticed, a reduction in the leachate after 56 days containment compared to after 28 days only.

The effect of clay on Unconfined Compressive Strength (UCS) in the cement matrix of a stabilized foundry baghouse waste was studied at the Alberta Environmental Centre (Figure II.D-2-2, in appendix). They concluded that at higher OPC levels (5.2%), increasing clay level can produces increases in UCS. But UCS is not linearly related to the increase in clay. Montgomery (1988) noticed an increased strength for samples stabilized with treated clay compare to the one using bentonite.

II.D-3 FLY ASH

Coal fly ash is known to possess desirable pozzolanic qualities and is often combined with Portland cement to produce high strength concretes [Swammy, 1983, Haques, 1984]. Fly ashes do not harden significantly by themselves, but can exhibit cementing activity in the presence of a sufficiently large amount of OPC. This is believed to be caused by the release of calcium hydroxide by the Portland cement as it crystallizes, which then reacts with the fly ash to form calcium aluminium silicate that hardens much as does the Portland cement itself. Such concretes have much higher strength than ordinary concretes, but generally also require longer curing, as fly ash retards the setting of cement.

Coal fly ash is thus often used as part of the cementitious binder in stabilization/solidification processes. It not only produces high-strength matrices (resulting in reduced leachability of contaminants from a less permeable, more durable waste form), but greatly reduces the cost of the treatment by reducing the amount of cement required.

Coal fly ash can vary in its chemical composition and physical properties [Liskowitz, 1986]. The average particle size distribution vary between 1 and 150 um , with an density between 1.6 and 3.2 g/cm^3 [Furuya, 1987]. Its major constituents are SiO_2, Al_2O_3, and Fe_2O_3 which represent about 90% of the oxides, with lesser amounts of CaO, K_2O, S, C, Ti, Ba, and Mn. It also contains trace amounts of Cd, Ni, Pb, Cu, Zn, Sn, and V.

The surfaces of the ash particles tend to have a higher concentration of CaO and S than is present overall. Since smaller particles have proportionately more surface area, they also have higher concentrations of CaO and S. An other work has indicated that removal of the surface layer by washing, results in higher adsorption capacity [Liskowitz, 1986].

In addition, the residual carbon content of coal fly ash, which is usually between 1 and 2%, has been shown to have ability comparable to that of activated carbon for adsorption of organics. The study shows that removal of organic pollutants depends mainly on pH characteristics, washing procedures, residual carbon content and the polarity and solubility of the compounds to be

treated [Banerjee, 1989]. Griest (1986) also found that although carbon is a minor component by mass, it strongly influences the sorptivity of organics in the large (more than 45 um) particle size fraction of fly ash. This suggests that fly ash can be used in the stabilization/solidification process when organic elements are present, instead of being considered as a waste.

Investigations have also been done to study the sorptivity of fly ash for metal in water, waste water and soils. The use of fly ash as an agent for metal removal from aqueous solutions was experienced by Panday (1985). It was found that copper(II) removal was influenced by its concentration, the pH of the solution, and the temperature. The process of adsorption was found to be diffusionnal. A 100% adsorption was obtained when the solution was at pH 8.0 and copper concentration was 1.10^{-4} M in the form of copper sulfate . In the Midatlantic Industrial Waste Conference in 1980, Benson demonstrated that fly ash can have a fixing capacity comprised between 0.6 mg/g for zinc and 1.6 mg/g for lead with intermediate capacities for chromium and cadmium at pH = 4. He established that fixing capacities vary with pH and redox potential. The precipitation process is believed to be the predominant factor with fly ash.

CHAPTER III: MATERIAL & METHOD

III.A: WASTE AND ADDITIVES DESCRIPTION

The goal of this project is to stabilize a mineral waste spiked with an organic toxic,penta-chloro-phenol) using a minimum of additives. The following compounds were chosen, based on litera- ture research and previous experiments done at the Alberta Envi- ronmental Centre:

III A-1 MONTMORILLONITE CLAY

The organophilic clay used in this research is Coarse Grade Wyoming Bentonite, from NL Baroid Industries, Inc. The bentonite was ground with a Brinkman grinder to pass a 75 micron meter sieve.

The treated clay was prepared as follows: 100 gram portions of ground bentonite were cation exchanged by treating with 1000 ml portions of 1 M NaCl solution and mixing with a rotary extractor. The mixing was maintained for 24 hours, with a rotation speed of approximately 25 rotations per minute.

The suspensions were centrifuged and the supernatant discarded. The NaCl treatment was repeated a second time as above. The bentonite was then treated with a solution of 0.14 M hexa-decyl- trimethyl-ammonium bromide (HDTMA, $(CH_3)_3N^+(CH_2)_{15}CH_3$) in 20% methanol/ 80% distilled water . After 24 hours mixing, the sus-

pensions were centrifuged and the supernatant discarded. The treated bentonite was then rinsed a minimum of three times in 20% methanol/ 80% distilled water solution, following the same procedure as the one used before.

The treated clay was dried in a 60°C oven, reground to pass a 75 micron sieve and stored in a closed container.

III A-2 WASTE

The waste chosen for this study is a foundry baghouse. It is essentially an inorganic waste containing metal oxides. The principal potential hazardous constituents are heavy metals including lead, zinc, copper, manganese, nickel, and chromium as well as iron ions.

III A-3 COAL FLY ASH

Nine different fly ashes were selected from samples collected in a previous study at NJIT (Liskowitz, 1983). The coal source, firing condition, and particle size of each are summarized below:

#1 Wellmore Cactus (I) outlet (boiler B)

#2 Wellmore Cactus (II) outlet   "

#3 Wellmore Ackiss, low power, outlet (boiler B)

#4 Militant, front hopper, intermediate power (boiler A)

#5 Deep Hollow, front hopper, high power   "

#6 Deep hollow, front hopper, low power   "

#7 Deep Hollow, back hopper, high power   "

#8 Deep Hollow, back hopper, intermediate power   "

#9 Militant, back hopper, intermediate power   "

The relative power is an indication of the temperature in the

20

boiler , and front/back hopper is an indication of larger/smaller particle size. Analysis of the particle size distribution reveals that the ashes collected from the back precipitator are in general smaller than the particles collected from the front precipitator. In general, the size analysis of the fly ash shows that 80% of the fine have an average diameter between 0.05 and 0.08 mm. Details concerning these factors and burning conditions are available in the cited references. Results from the previous study, giving concentration of silicate, aluminate and iron and lead oxides and carbon content, are given in Figure III.A, in the appendix.

III A-4 CEMENT

The cement used is Ordinary Portland Cement (OPC) type I, the most commonly used. Before being used, the OPC was passed through a 75 micron sieve to avoid any influence on physical/chemical results due to its particle size heterogeneity.

III A-5 ORGANIC TOXIC

Pentachlorophenol (PCP) was the organic toxic used for this study. It is a common environmental contaminant, mostly used in the industry of wood preservation. Because of the low solubility of PCP in water (about 50 ppm in normal conditions, getting lower in acidic condition), the sodium salt PCP (C_6Cl_5ONa, xH_2O) was used for all the experiments. In this way, the entire amount of NaPCP could be dissolved in the exact quantity of water necessary for the experiment, ensuring a homogenous distribution of the organic within the treated cube.

III B: SAMPLE PREPARATION

III B-1 CONSTITUENTS

Based on the preliminary studies made at the Alberta Envi-
ronmental Centre, the following composition was used for the
stabilization:

Without clay: 62% foundry dust,   With clay: 60% foundry dust

                  14% coal fly ash,   14% fly ash

                  4.5% OPC type I,   4.5 OPC type I

                  19.5% tap water.   19.5% tap water

                                                        2.0% clay

III B-2 MIXNG

The mixing was done with three different methods, depending upon
the experiment:

    - For experiment I, and reference samples of the experiment
II; (involving fly ash, OPC, industrial dust and water only) .
The exact amount of foundry baghouse dust, fly ash and Ordinary
Portland Cement were first dry mixed in a Hobart mixer for 10
minutes. Water was then added to the dry mixture and the sludge
was mixed for an additional 15 minutes before it was ready to be
molded.

    - For experiment IV (involving fly ash, OPC, industrial
dust, water, clay and sodium salt PCP).

22

The equivalent of exactly 112.5 mg of PCP per gram of clay in the form of NaPCP was diluted into the exact amount of water required for the experiment. The amount of PCP was chosen according to the adsorption capacity of the treated clay. 2% of clay was then added to the solution and the suspension was mixed for one hour, at ambient temperature. Meanwhile, all the remaining dry constituents were mixed for 10 minutes. After proper mixing, the clay suspension was added to the dry mixture, and the sludge was mixed for an additional 15 minutes.

- For the reference samples in the experiment IV, and experiment III (involving fly ash, OPC, industrial dust, water and sodium salt PCP).

The amount of NaPCP added was calculated as 112.5 gram of PCP per gram of the mixture for 2% of the mixture. The NaPCP was solubilized in the amount of water required for the sample preparation. The exact quantity of fly ash was then added to the solution and the suspension was mixed for 1 hour. During this time all remaining dry components were mixed together. The remainder of the mixing was done as in the second case.

III B-3 SAMPLES MOLDING

Metal molds for 2" cubes were used. The interior surface of each mold was greased before the sludge was added.

A layer of the mixture was placed to fill half the mold and tamped to ensure a uniform filling. The remaining half of the mold was then completely filled, allowing the top of the sample to extend slightly above the top of the mold. The mixture was

tamped several times before cutting the top of the sample to ensure a flat top surface. Samples were removed from the molds after 24 hours at room temperature and cured at 22 C, 98% relative humidity in an environmental chamber. After 28 days of curing, specimens were ready for testing.

III C PHYSICAL TESTING OF SAMPLES

III C-1 UNCONFINED COMPRESSIVE STRENGTH

On the 28th day of curing, each sample was placed in a plastic
bag and tested according to ASTM C109-87 with a UCS tester,
recording the highest value on the scale, as the cube was break-
ing down.

III C-2 FREEZE/THAW TESTING

The weight of each control and testing cube (respectively W_{wc} and
W_{wt}) was recorded as the samples were removed from the environ-
mental chamber after 28 days of curing. Each specimen was placed
in a 500 ml beaker and went through a 12 cycles test. Test
specimens were placed in their beaker for 24 hours at 20 ^{o}C, then
24 hours at room temperature with 250 ml distilled water added to
the beaker. Then the samples were placed in a new beaker and the
process repeated 11 additional times. Control samples were run
at the same time, but were placed in the moisture chamber instead
of being frozen.

Dry residues for controls and test samples, respectively labeled
R_c and R_t, were obtained after evaporating the water in each
beaker at 120°C, and recorded as weight loss. All dry residues
were then kept for metal analysis in the first experiment.

Results are presented after calculating the % relative cumulative
corrected weight loss for each tested cube as function of the

number of cycles:

Calculation:

The dry weight , Wd, of the specimens was calculated as follows:

Wd(g) = Ww (g) * (1- water content)

$$\text{Relative weight loss after cycle } i = \frac{\text{Weight loss after cycle } i}{\text{Oven dry mass of specimen}}$$

The corrected relative weight loss of the test specimen was obtained by susbracting the relative weight loss of the control specimen from the relative weight loss of the test specimen. Results for each cycle are presented as the "relative cumulative corrected weight loss" for each sample and each cycle, up to the last cycle. The EPA guidance states that a maximum 10% relative cumulative weight loss should be recorded after 12 cycles in order for the method to be acceptable.

III C-3 WET/DRY TESTING

This weathering procedure was conducted in parallel with the freeze/thaw testing. Samples were tested in the same way except that the test specimens were placed in a vacuum oven with a nitrogen flow at a temperature of 60 C for 24 hours and then in the moisture chamber for 24 hours. The control samples were treated as were the ones for the freeze/thaw testing. All dry residue was kept for metal analysis in experiment I. Calculation for the relative corrected % weight loss is the same as for the freeze/thaw test.

III C-4 TRUE DENSITY

The true density was measured on dry broken samples which remained after the unconfined compressive strength testing. True density was measured with an helium pycnometer (Micromeritics, multivolume pycnometer model 1305).

III C-5 BULK DENSITY

The bulk density was measured as the sample were taken out of the environmental chamber. The weight of each mold was recorded (g) and divided by the volume of the mold (131.096 cc).

III C-6 POROSITY

The porosity was analyzed, using dry fragments remaining from the UCS test, with a mercury porosimeter capable of operating up to 33,000.0 psia, manufactured by Quantachrome (model Autoscan 33 Porosimeter).

III C-7 WATER CONTENT

Again, fragments remaining after UCS testing were used. The fragments were placed in a 120°C oven and their weight recorded after cooling the sample in a dessicator until stabilization. Water content was calculated on a wet weight basis as folow:

$$\text{Water content \%} = \frac{\text{wet weight} - \text{dry weight of the sample}}{\text{wet weight of the sample}} * 100$$

III D CHEMICAL TESTING:

III D-1 TOXIC CHARACTERISTIC LEACHING PROCEDURE (TCLP)

TCLP analysis was done according to the EPA method . The 2"
cubes were broken until they passed through a 9.5 mm sieve. S/S
samples, fly ashes and the industrial dust were each preliminari-
ly tested to establish the extraction solution which had to be
used . The dust and all S/S samples needed to be extracted with
extraction fluid #2, at pH = 2.88, using glacial acetic acid.
After extraction in Teflon bottles lasting approximately 18
hours, and filtration under pressure, the pH of the TCLP extract
was recorded. The solutions were acidified with nitric acid to
pH = 2 for metals analysis, and digested according to EPA method
30-50, using nitric acid, hydrochloric acid and hydrogen peroxide
(30%). Lead, chromium and cadmium were then analyzed by flame
emission atomic adsorption. It appears that metal composition
was the same with or without the digestion of the extract prior
to the analysis. It was then decided that the digestion was not
necessary in this study. Metals were analysed directly after the
TCLP exctract was acidified to pH = 2 and filtered through 0.45
um filter paper to eliminate any PCP precipitate that was formed
during the acidification procedure.

Pentachlorophenol was analysed after dilution of the TCLP extract
so that PCP concentration would be less than 10 ppm, and would
remain soluble in acidic conditions. HPLC was used for the
analysis, using a Supelco C18 column,15 mm, an adsorption wave-

lengh at 230 nm, and a gradient methanol/water containing 1%
acetic acid, as mobile phase.

III D-2 HEAVY METAL ANALYSIS ON RESIDUE FROM WEATHERING TESTING

Dry residues from the freeze/thaw and wet/dry tests were dis-
solved in 20 ml of digestion solution consisting of HNO_3: HCl :
H_2O with a 60 :10 : 40 ratio, to which was added 5 ml of 30%
H_2O_2. The digestion period lasted 15 minutes. After cooling,
the solution was filtered though a 45 um glass microfiber filter,
and sufficient distilled water was added to produce a 50 ml
sample; the metal analysis was then performed by atomic adsorp-
tion.

III D-3 COAL FLY ASH AND FOUNDRY BAGHOUSE DUST CHARACTERIZATION

Lead and chromium contents of both the coal fly ashes and the
foundry baghouse dust were determined by X-ray fluorescence
spectroscopy, using a KEVEX model 0700. All analyses were per-
formed using a coal fly ash standard obtained from the National
Institute of Standards and Technology (number 1633a) as a refer-
ence. Chromium was analyzed using an iron target, an excitation
of 20 KeV and 2.0 ma with an acquisition time of 100 seconds. A
specific analytical method had to be used because of the possible
interferences between iron and chromium. Calibration constants
were established, using the Exact program of the Kevex. This
program takes into account the complete element composition of
the standard, the pick intensity of elements of interest, the
exitation conditions, the fundamental parameters of this particu-

lar instrument. The metal oxides used for this analysis are iron, aluminum, potassium, silicate, calcium and chromium oxides. They represent 99% of the fly ash composition. A print out of the constants for the Ka1 emissions is given in Appendix III D-3. Fly ash and industrial dust samples were then run and their chromium concentration calculated using the calibration constants previously established.

Lead was analyzed using a silver target, an excitation of 30 KeV and 2.0 mA, with an acquisition time of 150 seconds. The Ka1 emission only was used for the analysis. Lead concentration in the fly ashes and the industrial dust was directly calculated using the linear relation between counts and concentration. The standard contained 72.4 ppm of Pb had a 18.0 Cts/sec in these conditions.

Cadmium could not be analysed by this method because its concentration in coal fly ash is about 1 to 5 ppm, and this is below the detection limit of the Kevex.

Cadmium, lead and chromium in the foundry dust were also analysed using the EPA method 30-50 acidic digestion.

CHAPTER III: RESULTS & DISCUSSION

IV A:EXPERIMENT #1:

EFFECT OF FLY ASH TYPE ON PHYSICAL /WEATHERING PROPERTIES

IV A-1 WATER CONTENT

The water content measurements of the treated samples are given in Table 1. All results are an average of three readings.

Table 1:

Water   Content   of   the   Treated   Samples

Fly Ash Number	Water Content %
1	14.9
2	15.5
3	15.2
4	15.3
5	15.5
6	14.9
7	15.5
8	14.8

The water content of all treated samples is very consistent. This parameter will not have any influence on the physical resistance or the density of the samples.

The bulk density measurement of the treated samples are summarized in Table 2. Each value represents a minimum of a ten-sample average, except for fly ash #8 which was calculated with four values only.

Table 2:

Bulk Density of Treated Samples

Fly ash #	true density g/cc	standard error %
1	2.33	4%
2	2.29	5%
3	2.39	2%
4	2.22	1%
5	1.98	2%
6	2.22	1%
7	2.21	1%
8	2.22	3%

The bulk density does not vary significantly between samples, except for the one using fly ash # 5, which is slightly lower than the others. This can not be related to a difference in the size distribution of this fly ash. A possible corresponding variation should be checked with the porosity measurements.

The data for bulk density vary from 1 to 5% among samples made with the same fly ash. Different reasons have to be considered in order to explain this variation. The porosity results will then be helpful to establish the cause of this variation.

The first hypothesis is that the observed differences are really due to a variation of the density within the matrix. This would suggest that the way the molds were done is not reproducible. This reason is possible considering the fact that the samples were tamped manually and this might be sufficient to influence the density. One way of reducing this error should be to use a vibration table. Also, this heterogeneity may be attributable to the time required to fill the molds. Each batch consisted of 15 molded cubes and required approximately one hour to prepare. During this time, the mixture begins to set, and this may affect the bulk density obtained. If this is the explanation to the variation, then corresponding variations should be observed for the porosity. Those parameters will be studied in the next chapter.

The second hypothesis can be simply based on a variation in the amount of sludge placed in each mold. The way samples were flattened can induce at least 0.3 cm variation in the cube height. A quick calculation using 2.3 as the average density of the treated samples, 6.45 cm^2 as the surface of the cube and 300 grams as the average weight of the cubes, it can be determined that 1.5% variation may be induced by the uncertainty in the flattening of the sample. The remaining variation may be attributable to the loss of small fragments when the cube was demolded after 24 hours. If it appears that variations are only due to the amount of sludge placed into the molds, the solution should be to weigh the sludge before filling the molds. Also, the use of teflon tape on the surface of the mold may reduce the

loss when the cubes wre remived from the molds.

IV A-3: TRUE DENSITY

The true density measurements on solidified samples are summarized in Table 3. The table gives the average true density resulting from a minimum of three readings on each mold, repeated on three or four molds done with the same fly ash. A complete table containing all data is presented in Appendix IV.A-3. All these measurements were done to estimate any possible variation at 3 different levels:

(1) Variation between fragments from the same mold,

(2) Variation between fragments from different molds made with the same fly ash

(3) Variation between fragments from molds made with different fly ashes.

<div align="center">

Table 3:

True Density of Treated Samples

</div>

Fly Ash Number	True Density g/cc
1	3.4
2	3.4
3	3.3
4	3.3
5	3.3
6	3.3
7	3.3
8	3.3

The interpretation of these results needs to be done considering

a margin of error of 0.05 g/cc on the true density due to analytical uncertainties. This represents about a 1.5% variation.

At 1.5% acceptable variation, there are no significant difference among fragments taken from the same cube. The maximum observed variation, as it can be seen in appndix IV.A-3, is 0.04 (fly ash #7, cube #3) which represents only 1.2% variation. Thus the true density may be considered uniform through each cube.

Considering the variation among the cubes made with the same fly ash, #1 and #2 show a significant variance (see appendix IV.A-3). The variation is a maximum of 4% in the case of sample #1. This variation does not appear in most cases, and does not correlate to a significant variation in the UCS test results or to the porosity.

Within 1.5% error, the true density does not vary between different fly ashes. The average is 3.30 g/cm^3. This is not too surprising as these coal fly ashes are rather similar in composition and particle size. Also, only 14.5% fly ash was added to the mixture which is quite a small proportion if the influence of fly ash is to be tested. In this case, the industrial dust is the element that most influences all the properties.

IV A-4: UNCONFINED COMPRESSIVE STRENGTH (U.C.S.)

The physical resistance of the treated samples to compression is

presented in Table 4. Each value is an average of three or four measurements.

Table 4:

Unconfined Compressive Strength of the Treated Samples

fly ash number	U.C.S, psi	Standard Error psi
1	425	25
2	412	17
3	725	39
4	260	7
5	258	15
6	325	6
7	384	9
8	334	15

The mixture formulation produces a UCS which is higher than the guidance level given by EPA (50 psi) for solids landfilling. There is a slight tendency towards higher UCS with larger particle size and lower-temperature firing conditions. However, the much stronger correlation is between the UCS and the bulk density, as is apparent by comparing Tables 2 and 5.

IV A-5: POROSITY

The porosity was first analyzed on pure fly ash samples as a reference. The pore size distribution, plotted as dV/dP vs

Radius, are presented in Figure 1. Only one graph is presented
as all fly ashes had similar distributions. The results such as
mean pore volume and mean pore surface area are summarized in
Table 5.

Table 5:

Pore Volume And Pore Surface of Fly Ashes

Fly ash	mean pore volume cc/g	mean pore surface area m^2/g
1	0.065	0.560
2	0.160	0.434
3	0.152	0.280
4	0.140	0.270
5	0.118	0.253
6	0.160	0.300
7	0.126	0.236
8	0.176	0.182
Dust	0.114	0.635

Fly ash #1 shows a significant smaller pore volume, with a corre-
sponding larger pore surface. Unfortunately, this variation can
not be related to any specific composition, or particle size, or
burning conditions of this fly ash. Conseuently, if any varia-
tions occur in the porosity measurements of various treated
samples, they will not be due to a difference in the porosities
of the corresponding fly ashes, except possibly for fly ash #1.
The pore size distribution of all the tested fly ashes are very
similar. Figure 1 shows that nearly all pores have a radius
larger than 4000 Angtroms.

A porosity analysis was done on the corresponding treated sam-
ples. The pore size distribution plotted as dV/dP vs Radius for

FIGURE 1 Pore Size Distribution of Coal Fly Ash

dV/dP vs. Radius
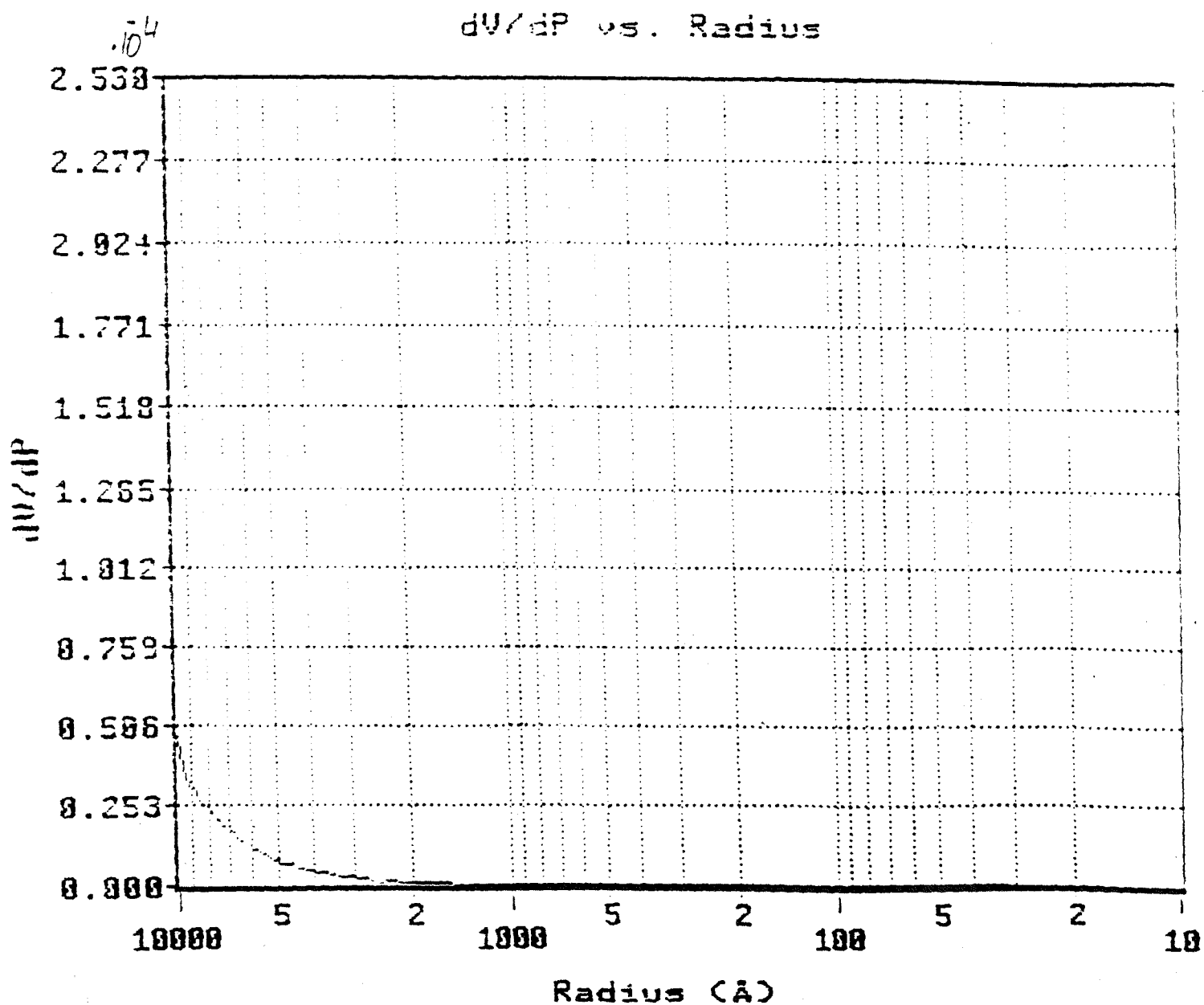
results are given in Table 6.

Table 6

Pore Volume And Pore surface of Treated Samples

Treated samples	mean pore volume cc/g	mean pore surface area m^2/g
1	0.078	4.6
2	0.094	4.8
3	0.064	5.4
4	0.086	1.2
5	0.090	4.2
6	0.077	0.8
7	0.058	0.7
8	0.052	2.7

The porosity measurements indicate a large variability in the readings. Each datum given above is an average of two or three measurements, and they vary by a factor of up to two for samples taken from the same cube. Meanwhile, the average of these gives very consistent reading for the pore volume in the treated samples. Pore volumes of the treated samples are smaller than those obtained for the fly ashes.

The lower bulk density observed for fly ash #5 does not correspond to a smaller pore volume as expected.

The results for the pore surface area are not consistent at all (Table 6), and can not be explained. However, the plot dV/dP vs Radius indicates that most pores in the treated samples have a

FIGURE 2

PORE SIZE DISTRIBUTION OF TREATED SAMPLE 3

dV/dP vs. Radius

Radius (A)
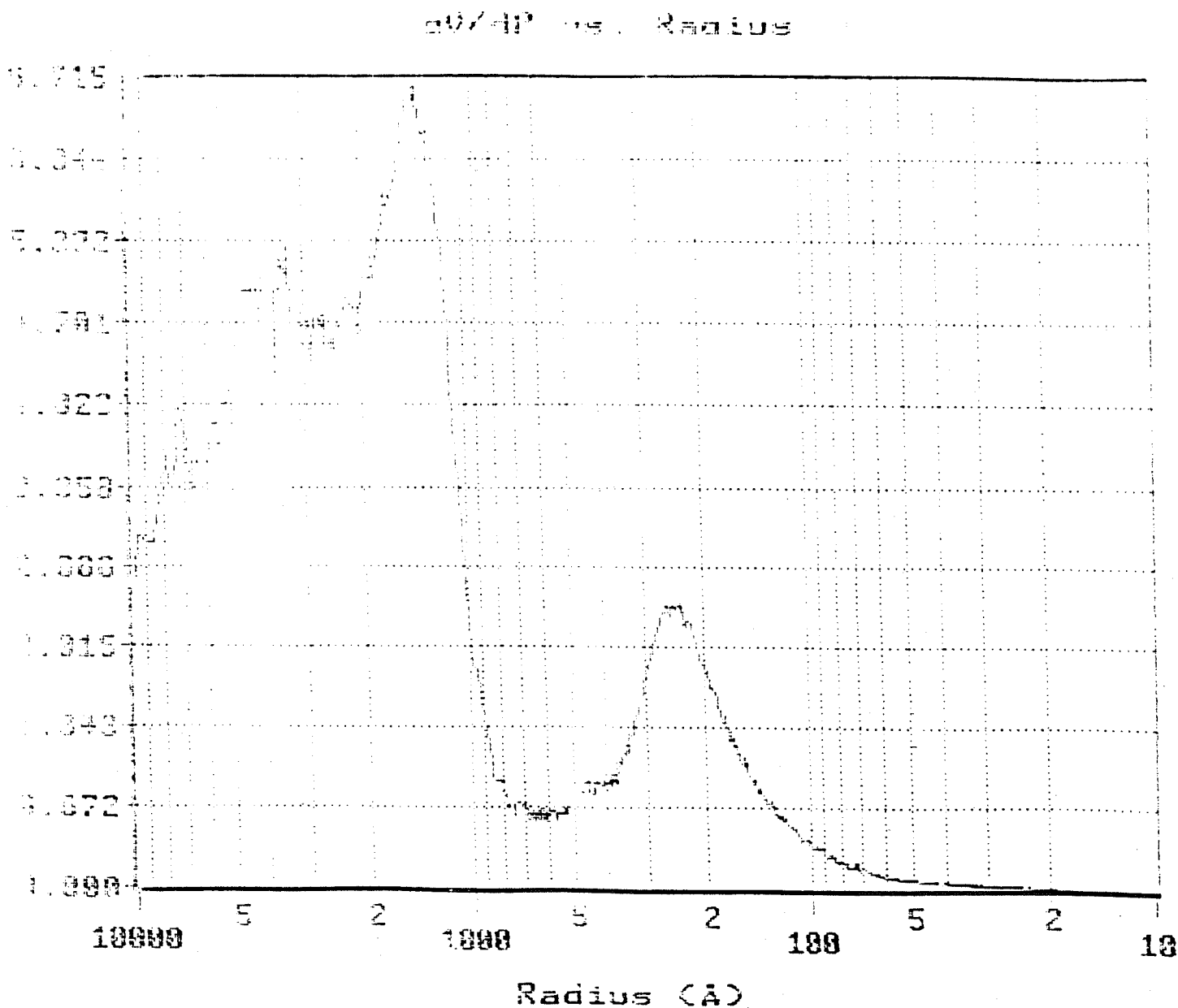
X axis scale units...
Y axis scale units... cc / (KPSIA)(g) x 1E-5

Range............... Intrusion

40

FIGURE 3

PO);E SIZE DISTRIBUTION OF TREATED SAMPLE 6

dV/dP vs. Radius

X axis scale units...
Y axis scale units... cc / (KPSIA)(g) x 1E-4

Range............... Intrusion

41
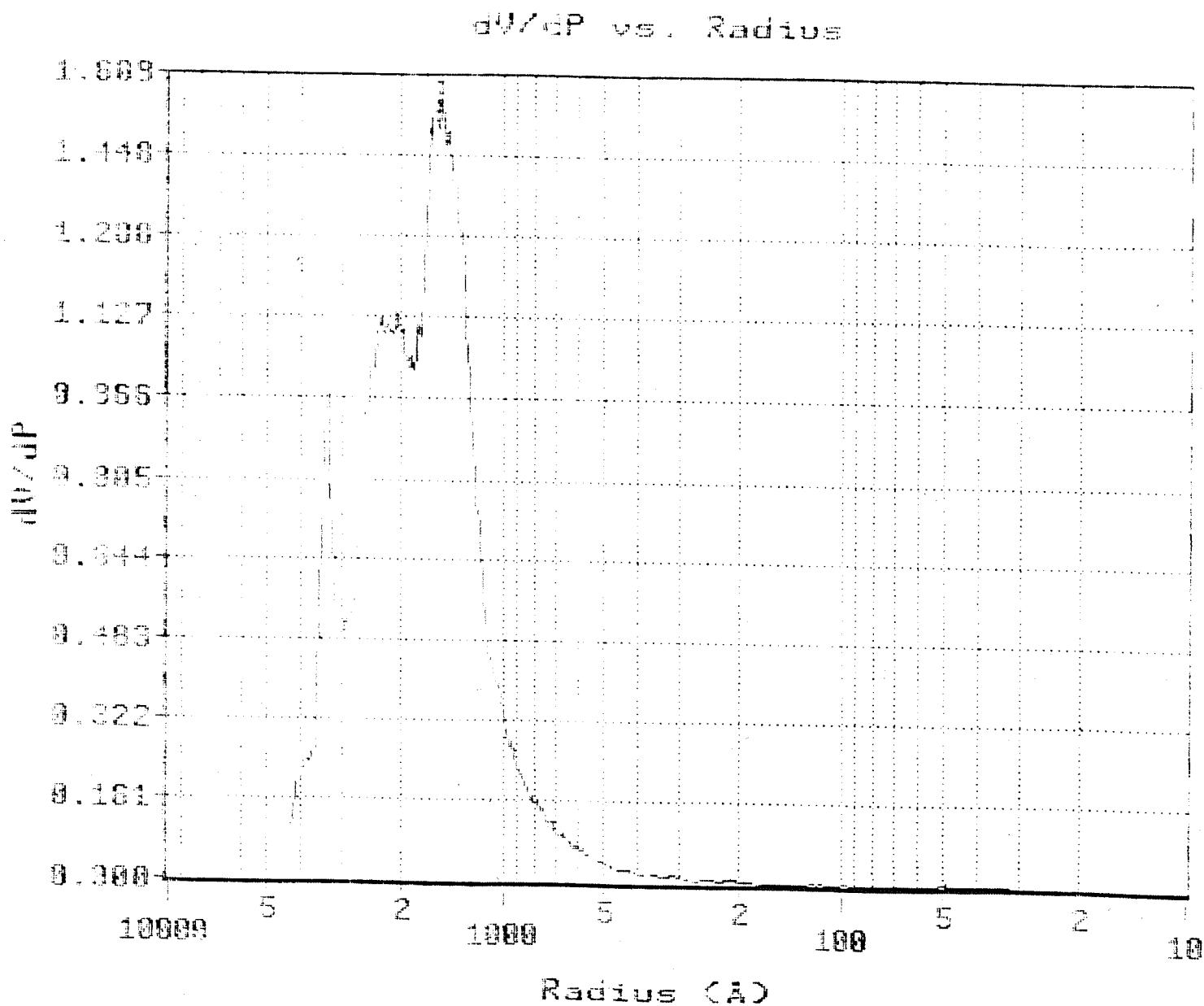
FIGURE 4

PORE SIZE DISTRIBUTION OF TREATED SAMPLE 8

dV/dP vs. Radius

X axis scale units...
Y axis scale units... cc / (KPSIA)(g) x 1E-4

Range............... Intrusion

42
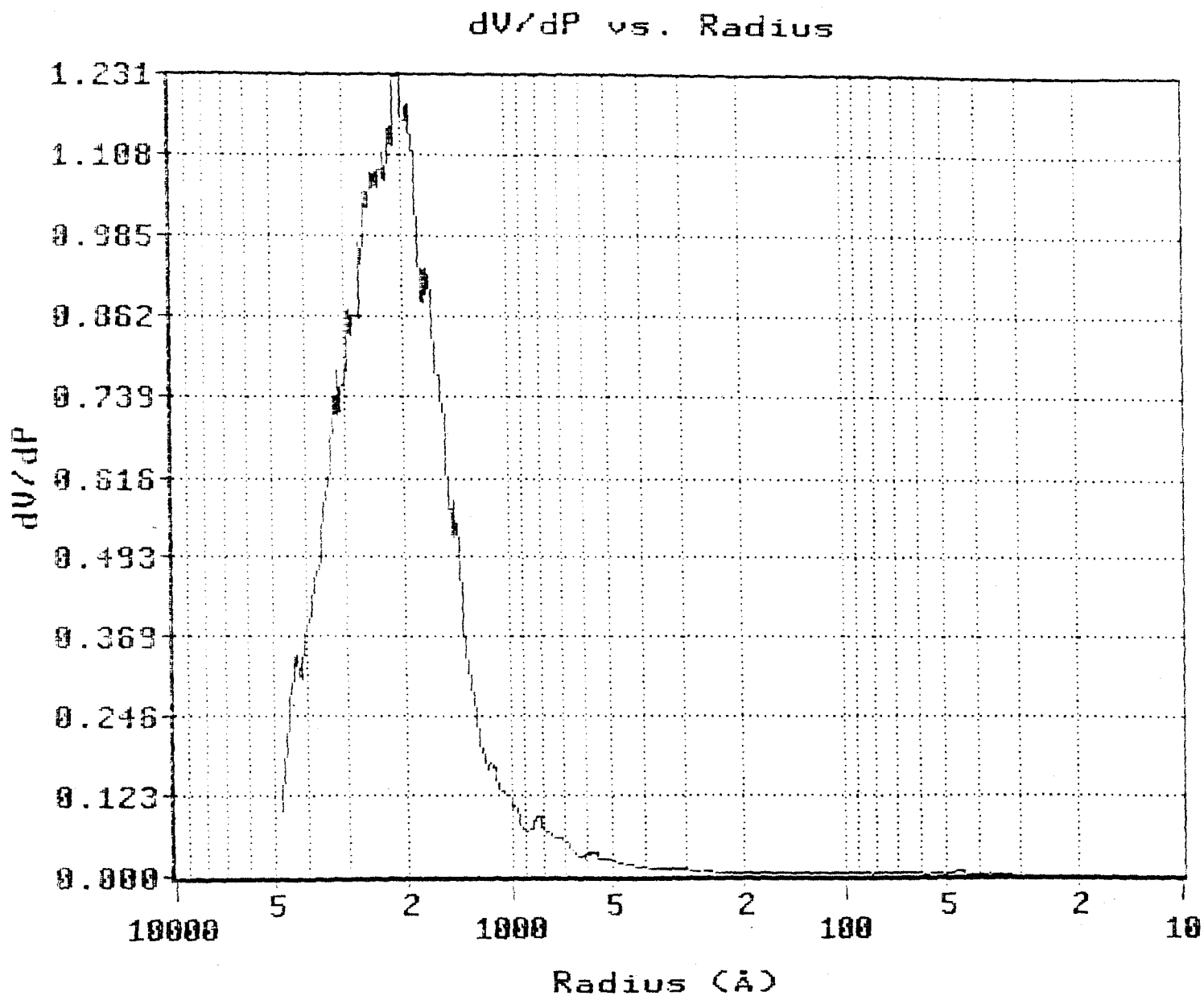
300 A and between 500 and 1000 A.

The average size of the pores are smaller for the treated samples than for either the fly ashes or the industrial dust. This indicates that additional smaller micro-pores are formed by the solidification of the waste. This explanation does not seems realistic as it suggests that micro-particles of the cement can close the pores of fly ash at a range lower than 1/10 micron. This result needs to be confirmed by complementary studies.

Because of the differences among data and the lack of any corresponding explanation, the results from the porosity analysis should be used only as an indication of the pore size distribution in a stabilized sample under these conditions. The results would have been a lot more helpful if the permeability analysis could have been done on the same samples. However, at the time of the analysis, the permeability cells were available. It may be possible, also, that the use of an heterogenous material such as the dust makes a specific analysis too difficult.

IV A-6: WEATHERING TESTING

This resistance of the treated samples was tested through wet/dry and freeze/thaw cycles. Nine cubes were made for each fly ash tested. They were separated between control samples, test samples for freeze/thaw and test samples for wet/ dry testing.

During the course of the freeze/thaw testing, most of the samples crumbled after three or four cycles. As an example, results obtained in the case of samples made with fly ashes #1 to #3, are presented in Figures 5, 6 and 7. But the corrected cumulative

FIGURE 5
Freeze/Thaw Testing on Treated Samples

% relative corr.cumul.Wt.loss

Number of cycles

Using Flyash #1
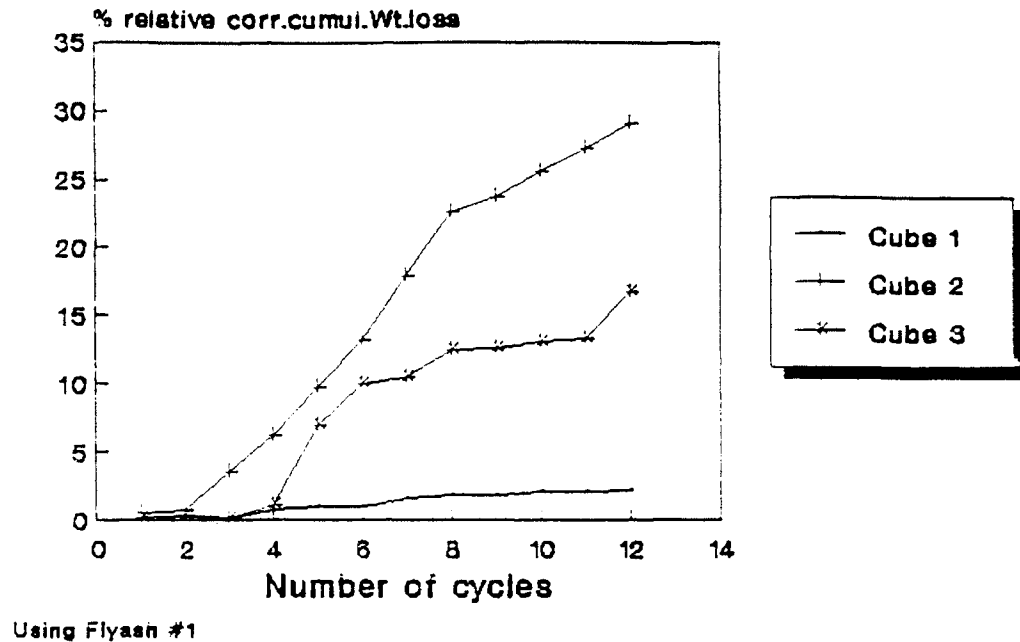
FIGURE 6
Freeze/Thaw testing of Treated Samples

% relative corr.cumul.Wt.loss

Number of cycles

Using Flyash #2
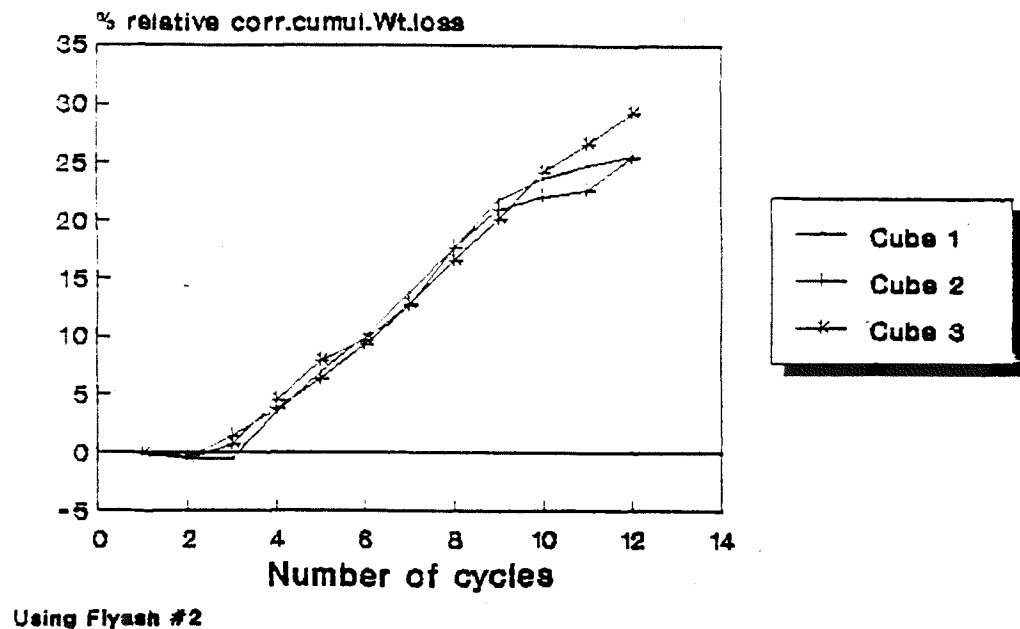
FIGURE 7
Freeze/Thaw Testing of Treated Samples

% relative corr.cumul.Wt.loss

Number of cycles

Cube 1
Cube 2
Cube 3

Using Flyash #3
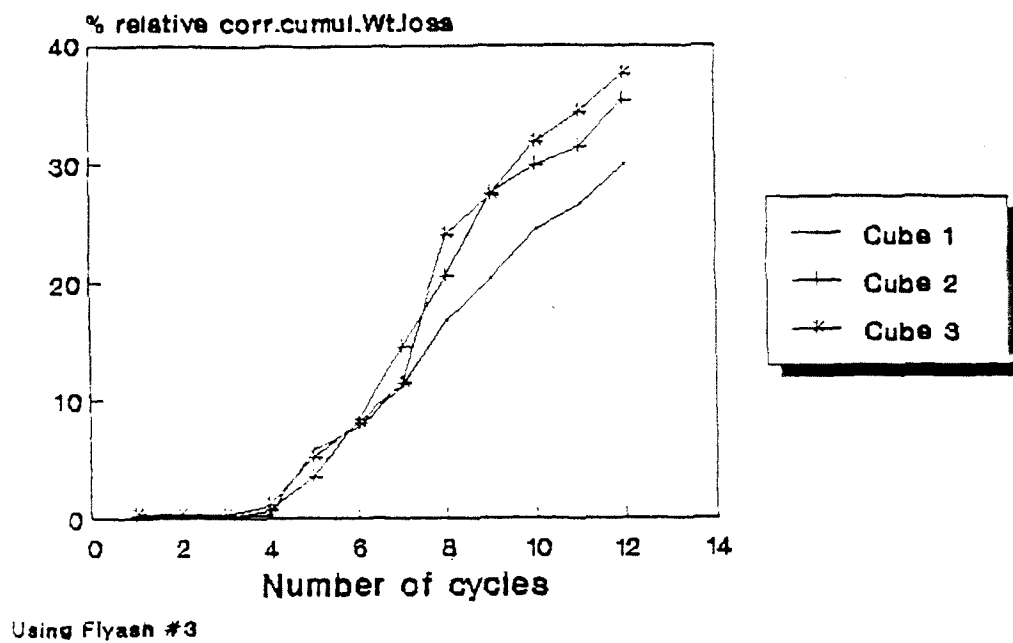
was not necessary to keep running the remaining samples. This poor resistance to freezing can be attributable to a nearly complete lack of entrained air in the cubes. While entrained air contributes to greater leachability by increasing porosity and permeability, nonetheless a small amount is necessary to permit the samples to survive freeze/thaw cycles. This phenomenom is frequently observed in civil engineering practice. This can be solved by adding a very small amount of an air entraining agent, in a proportion of a few drops per 100kg of cementitious material, in the mixture.

Wet/dry testing resulted uniformly in less than 1% corrected cumulative weight loss after 12 cycles. In fact, in several cases, the control samples suffered greater weight loss than the test samples. This likely results from the higher temperature at which the samples are dried. All graphs recording the weight loss for each cycle are presented in Figures 8 to 15.

The sample formulation provides good resistance to wet/dry testing, but an air entraining agent needs to be added in order to improve the resistance to freeze/thaw testing. Also, there is no discernible difference in wet/dry or freeze/thaw resistdance among made with different fly ashes.

IV A-7:METALS CONTENT OF THE WATER FROM THE WET/DRY TESTING

Lead, cadmium and chromium were analysed for samples made with fly ashes #4 through #7, during both wet/dry and freeze/thaw

FiGURE 8
Wet/Dry Testing of Treated Samples

Cube 1
Cube 2
Cube 3

Using Flyash #1
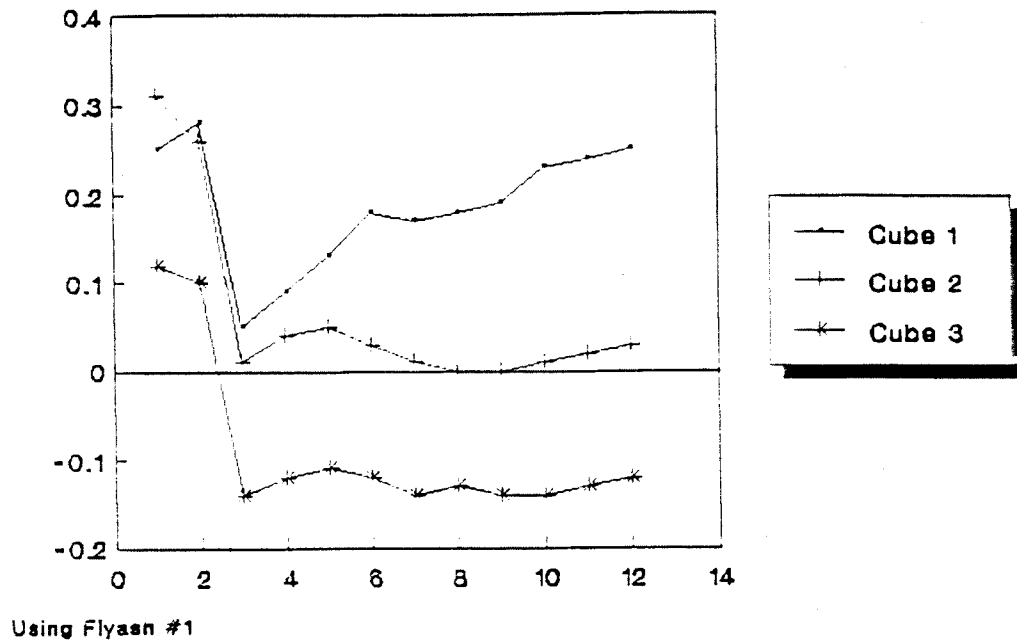
FiGURE 9
Wet/Dry Testing of Treated Samples

Cube 1
Cube 2
Cube 3

Using Flyash #2

47
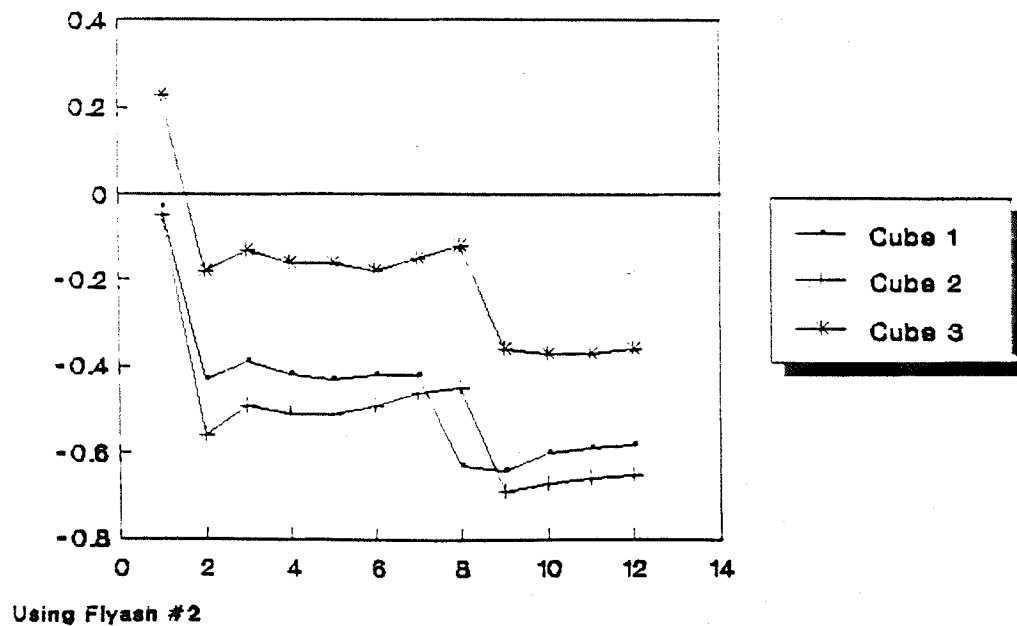
FIGURE 10
Wet/Dry Testing of Treated Samples
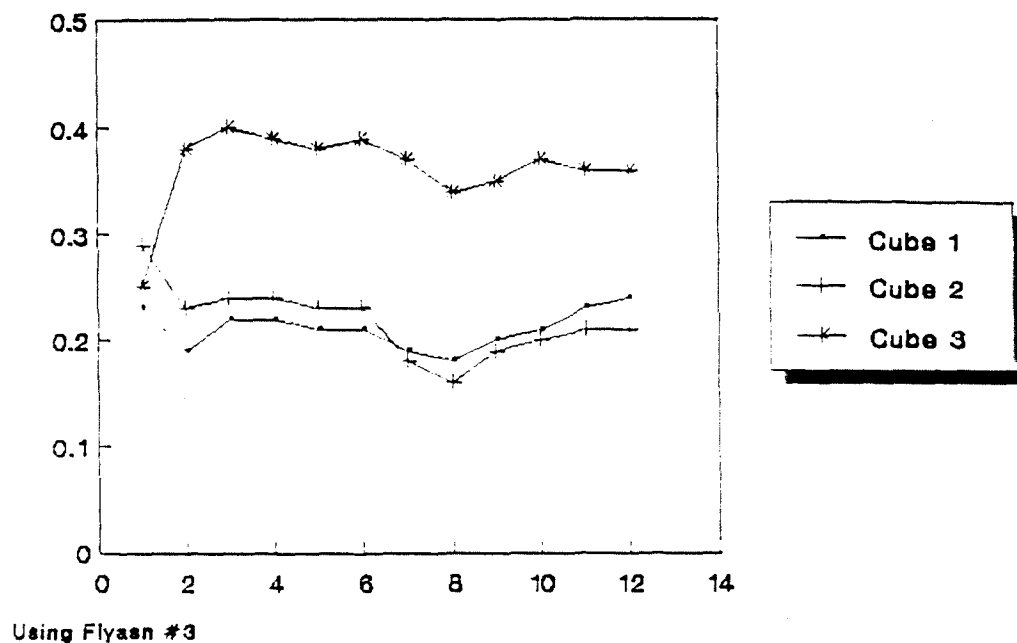
Using Flyash #3

FIGURE 11
Wet/Dry Testing of Treated Samples

Using Flyash #4

48
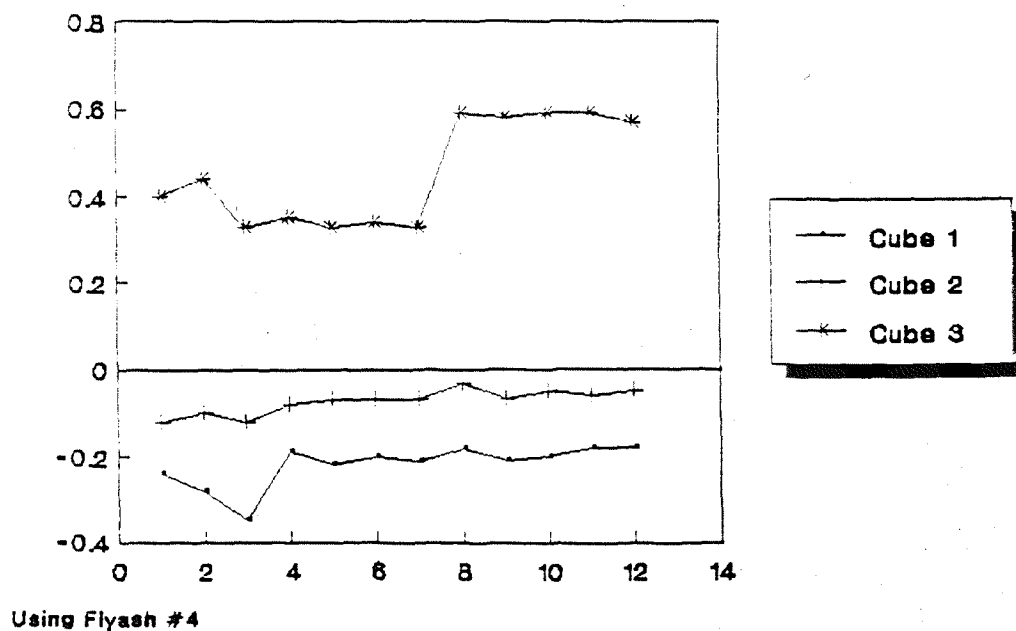
FIGURE 12
Wet/Dry Testing of Treated Samples

% relative corr.cumul.Wt. loss

Cube 1
Cube 2
Cube 3

Number of cycles
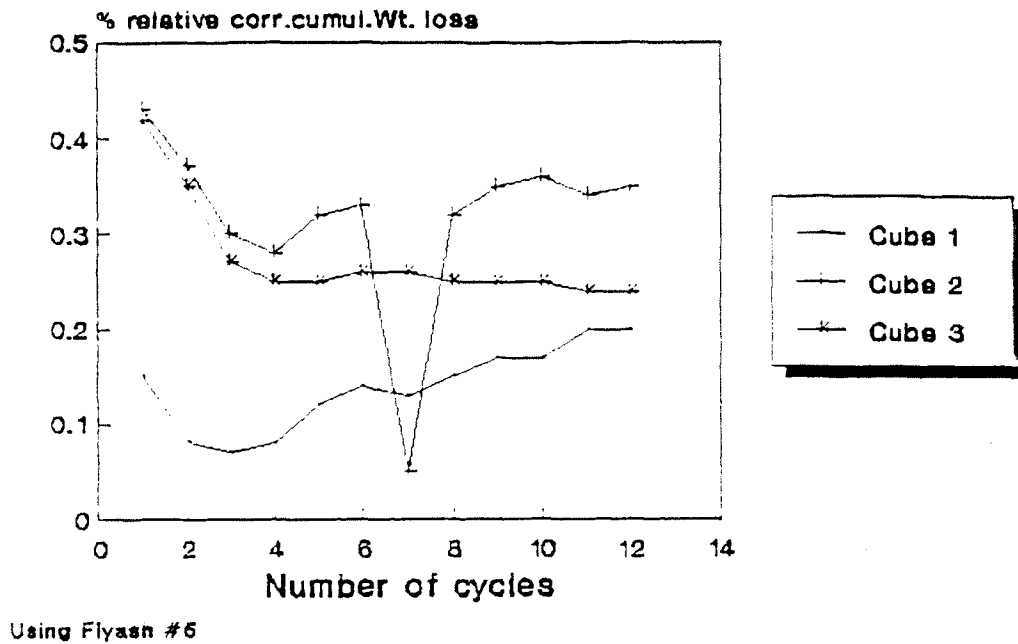
Using Flyash #6

FIGURE 13
Wet/Dry Testing of Treated Samples

% relative corr.cumul.Wt loss

Cube 1
Cube 2
Cube 3

Number of cycles
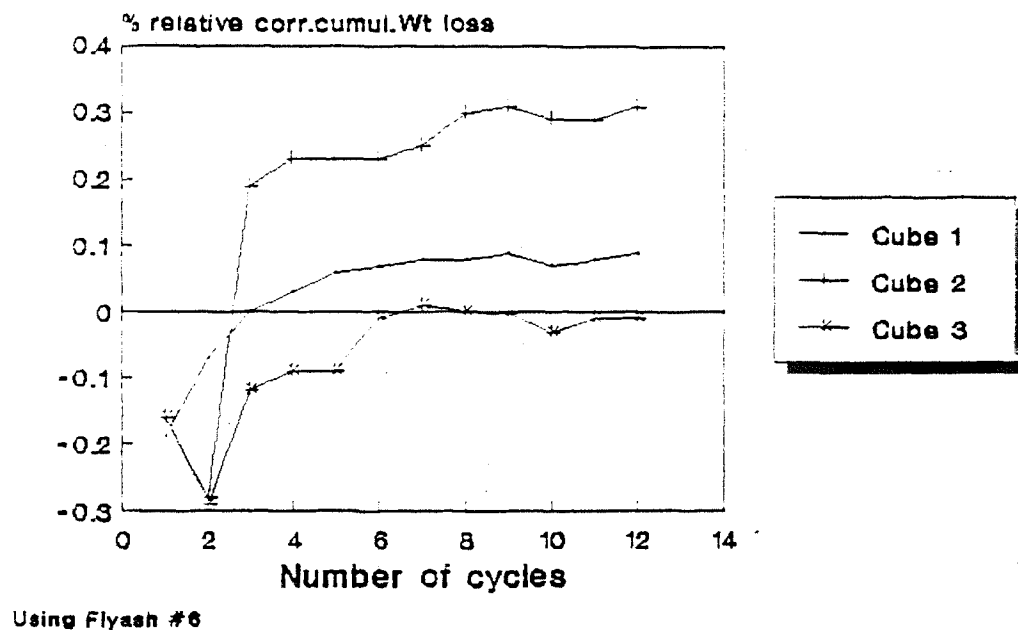
Using Flyash #6

FIGURE 14
Wet/Dry Testing of Treated Samples

% relative corr.cumul.Wt.loss

Cube 1
Cube 2
Cube 3

Number of cycles
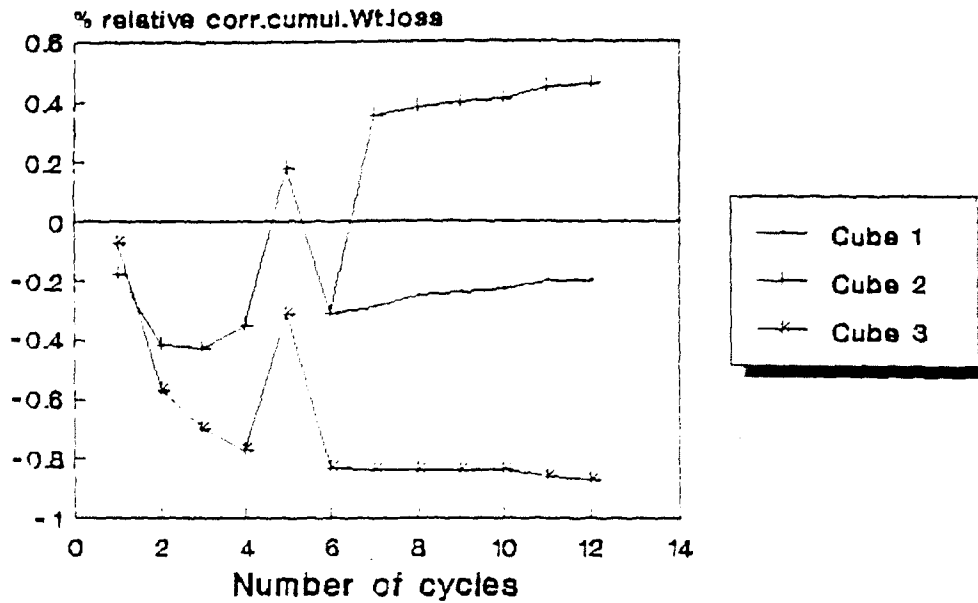
Using Flyash #7

FIGURE 15
Wet/Dry Testing of Treated Samples

% relative corr.cumul.Wt. loss

Cube 1

Number of cycles

Using Flyash #8

50
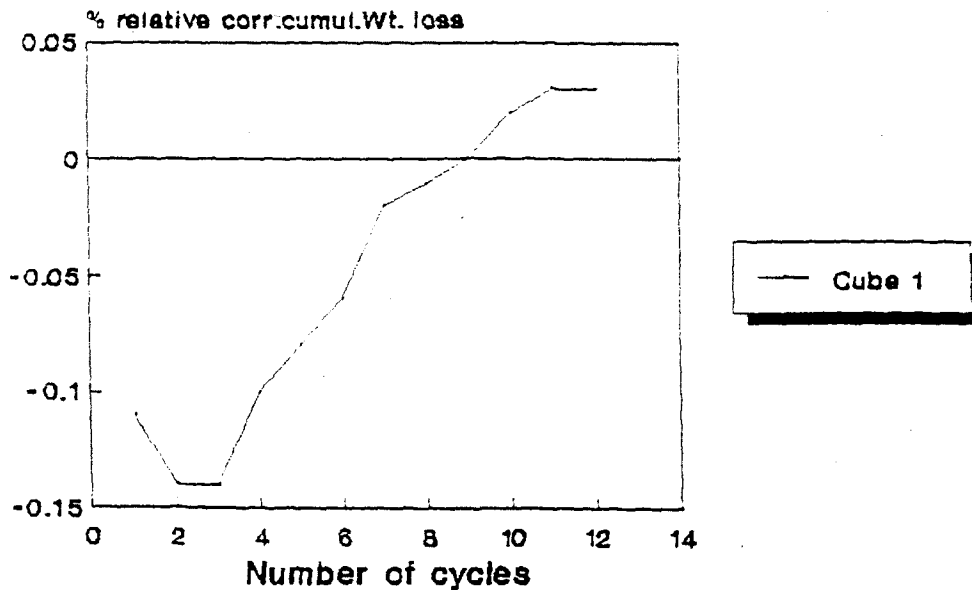
wet/dry and control specimens were analysed as the objective was to measure metals loss by dissolution while molds were immersed in distilled water. Cadmium content appears to be too low to be detected by flame ionization analysis. Total amount of chromium and lead in the water is plotted for each cycle in Figures 16 to 23. There are no significant differences for either lead or chromium, between control and test specimens. Also, no difference in the amount of heavy metals loss during the 12 cycles could be determined between the samples made with different fly ashes.

The pH of the leachate was recorded for each cycle, and in all cases it varied from approximately 12 (for the first cycle) to 10.5 for the 12th. The leachate solution consisted of sufficient amount of distilled water (pH 7.7) to give a solid/liquid ratio of 1.2. Following the protocol for the wet/dry test, the contact period was 24 hours. The observed leachability of Pb, Cd and Cr was very low. This can be explained by the alkaline pH of the leachate solution, at which metals are not soluble. The average amounts of lead and chromium loss during 12 cycles were less than 1.0 and 4.5 % respectively among the 20 samples analysed.

FIGURE 16
Chromium Leachate During Wet/Dry Cycles

Tot.amount in residue , fly ash #4
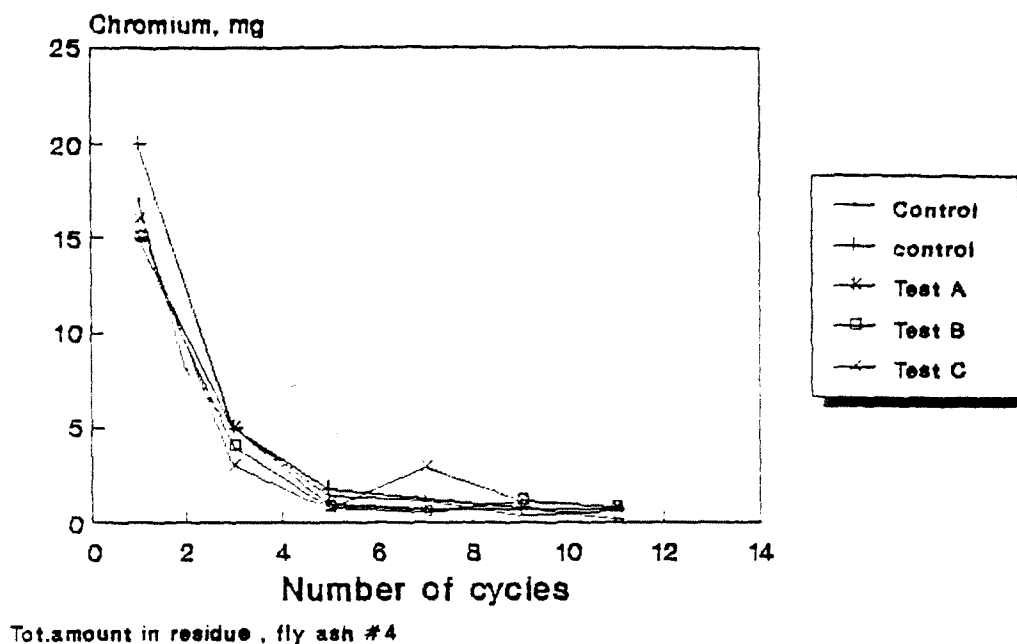
FIGURE 17
Chromium Leachate During Wet/Dry Cycles

Total in dry residue, Fly ash #5
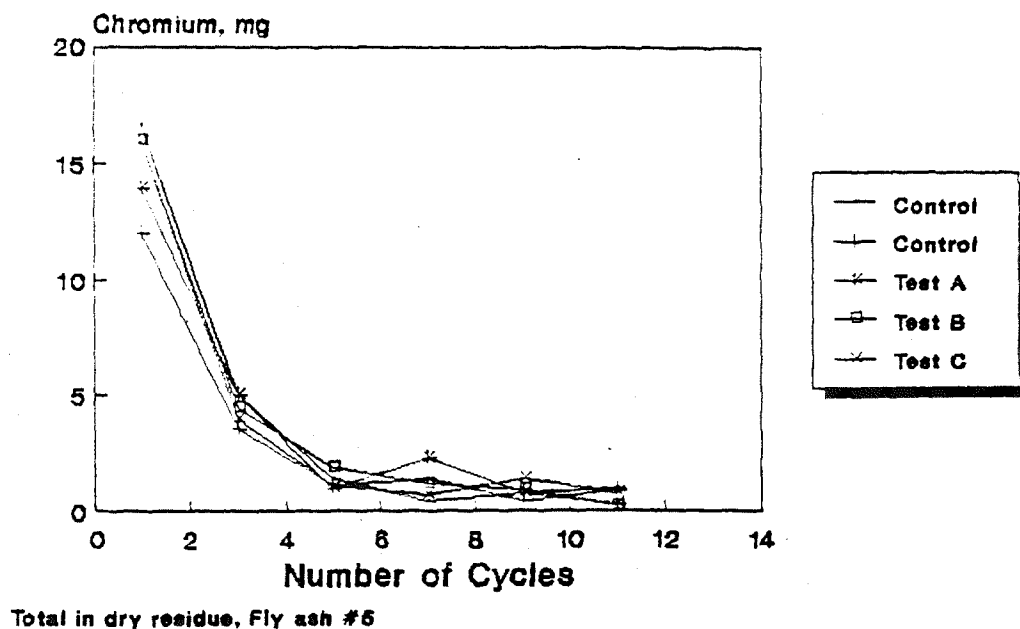
FIGURE 18
Chromium Leachate During Wet/Dry Cycles

Chromium, mg

Legend:
- Control
- Control
- Test A
- Test C
- Series 6

Number of Cycles

Total in dry residue, fly ash #6
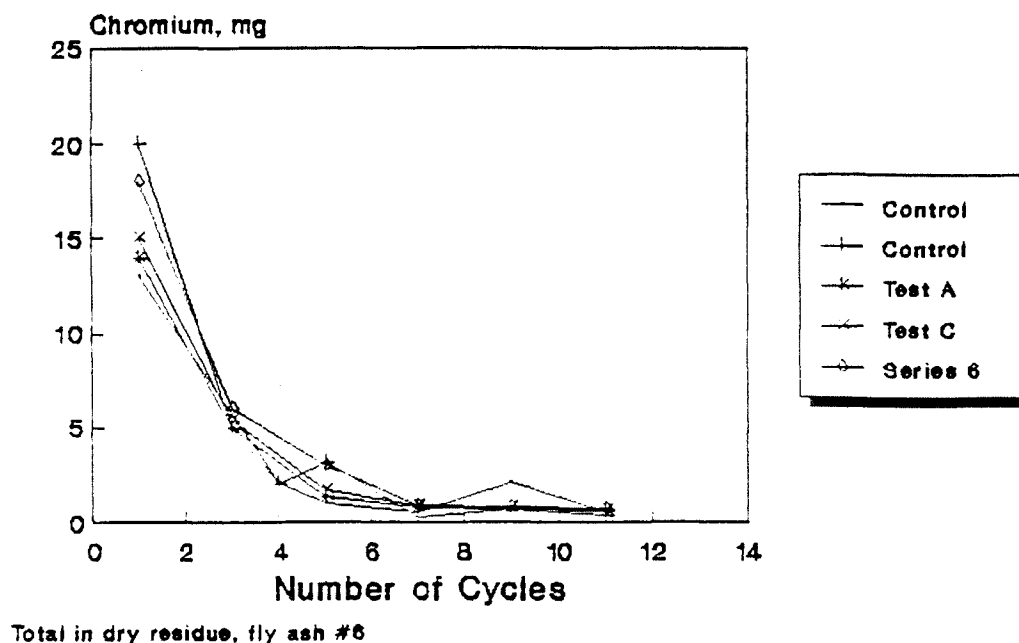
FIGURE 19
Chromium Leachate During Wet/Dry Cycles

Chromium, mg

Legend:
- Control
- Test A
- Test B
- Test C

Number of Cycles

Total in dry residue, fly ash #7
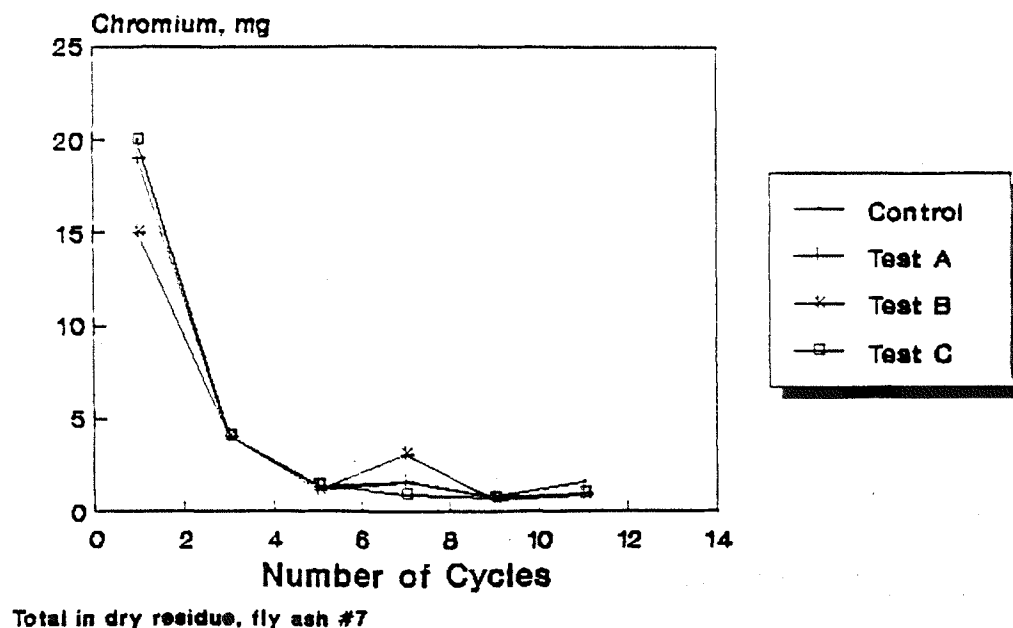
FIGURE 20
Lead Leachate During Wet/Dry Cycles

Total in dry residue, fly ash #4
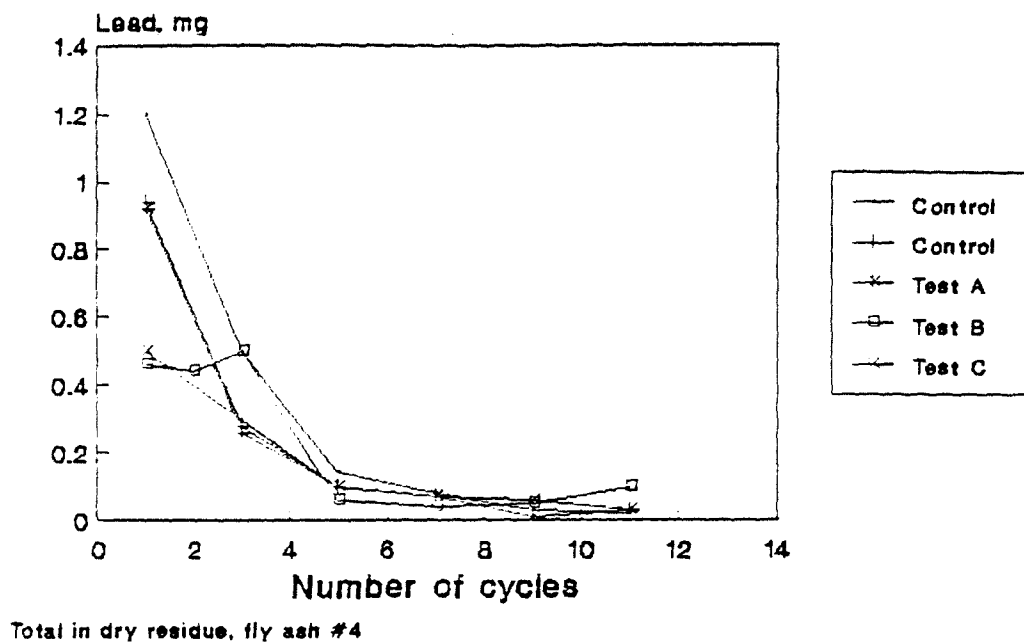
FIGURE 21
Lead Leachate During Wet/Dry Testing

Total in dry residue, fly ash #5
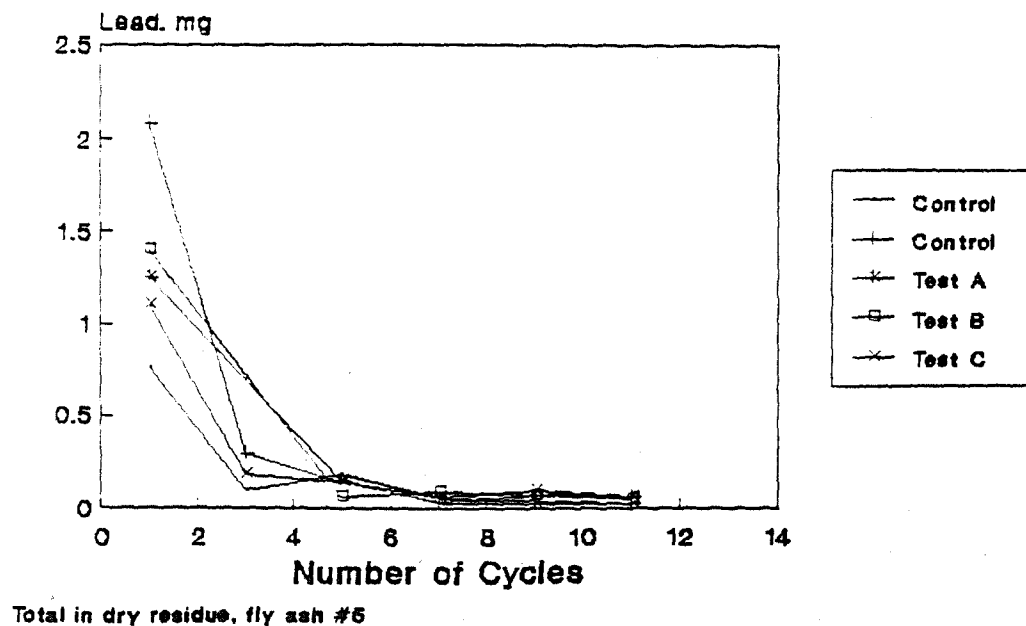
FIGURE 22
Lead Leachate During Wet/Dry Cycles

Lead, mg

Legend:
— Control
+ Control
✳ Test A
▢ Test B
✕ Test C

Number of cycles

Total in dry residue, fly ash 6
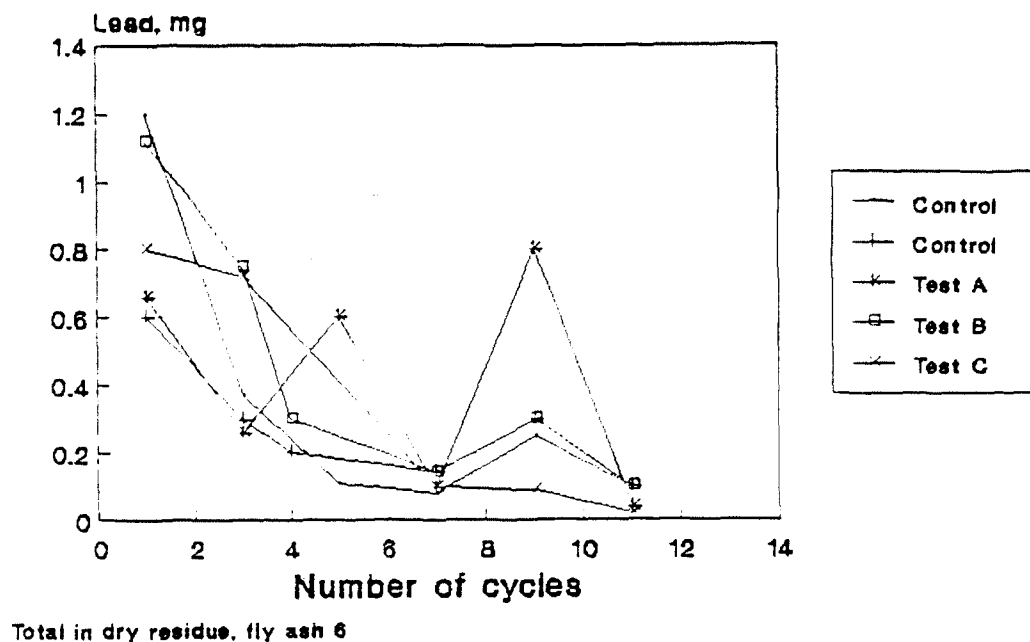
FIGURE 23
Lead Leachate During Wet/Dry Cycles

Lead, mg

Legend:
— Control
+ Test A
✕ Test B
▢ Test C

Number of cycles

Total in dru residue, fly ash #7
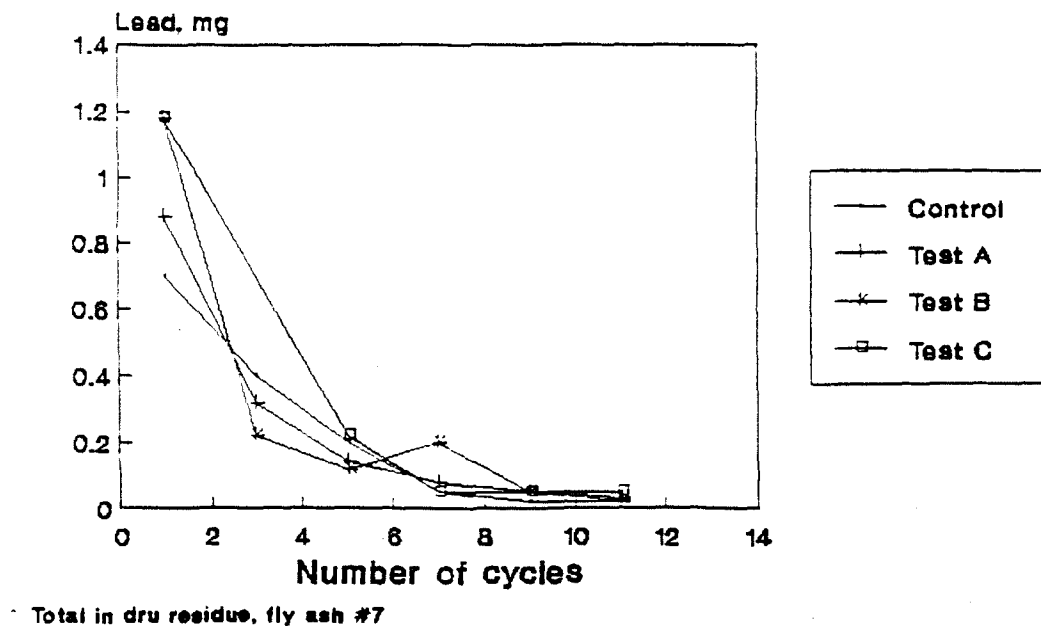
IV B: EXPERIMENT II :

EFFECT OF CLAY ON PHYSICAL/WEATHERING
PROPERTIES

The effect of including clay on the physical properties of the treated wastes was studied, using two different composition. The compositions for parts A and B are given in Table 7.

Table 7:

Sample Composition

Part A	Part B
60.08%ddast	
2.03% clay	2.0% clay
4.56 % OPC	4.5% OPC
18.45% water	19.5% water
14.40% fly ash #6	14.0% fly ash #6

The main difference between the two trials is basically the reduced amount of water in part A. This was done in order to investigate the influence of the water content on the physical testing of the samples. For both part A and part B, samples have been made using either no clay (NC), untreated clay (UC), or/and

treated clay (TC). For samples made without clay, the remaining percentage has been replaced by industrial dust to ensure a constant water, cement and fly ash composition.

IV B-1 WATER CONTENT

Water content (WC) measurements are given in Table 8. Each datumis an average of three measurements.

Table 8:

Water Content of Treated Samples

Sample	WC (part A) %	stan.dev. %	WC (part B) %	Stan. Dev. %
NC	14.5	0.1	16.7	0.4
UC	13.1	0.3	16.7	0.4
TC	12.6	0.4	16.2	0.2

In part A, samples made without clay have a higher water content. The added clay may use more water which is then not available for the cementation process of the sample. However, this observation is not confirmed by the other experiments, for which the results are all consistent. In this second case for which more water was added, the amount may have been sufficient to avoid any such limitation.

IV B-2 BULK DENSITY

Results for bulk density are summarized in Table 9, where each value is an average for 11 cubes.

57

Table 9:

Bulk Density of Treated Samples

Sample	Bulk Density(part A) g/cc + Std.Dev%	Bulk Density(part B) g/cc + Std.%
NC	2.41 + 3.6%	2.22 + 4%
UC	2.38 + 1.8%	2.23 + 4.6%
TC	2.31 + 4.5%	2.22 + 3%

The bulk density is slightly higher for the samples made without clay, and that the samples using the treated clay always have the lowest density. The average density on samples in part B, containing more water, is lower than that obtained in part A. This result should be confirmed by the porosity measurements.

IV B-3 TRUE DENSITY

Results for the true density are summarized in Table 10. Each value is an average of 9 measurements.

Table 10:

True Density of Treated Samples

Sample	true Density g/cc	standard deviation g/cc
Part A:		
NC	3.11	0.01
UC	2.81	0.02
TC	2.73	0.03
Part B:		
NC	3.10	0.03
UC	3.13	0.02
TC	3.14	0.02

There is no similar variation between NC, UT and TC samples when the comparison is made between part A and B. Also, it seems that samples made with more water (part B) have a higher true density than the others. However, it is known that increasing the water content in concrete will decrease its resistance and so should not have a higher density. Also, the bulk density readings show the opposite tendency.

IV B-4 UNCONFINED COMPRESSIVE STRENGTH

Results on the Unconfined Compressive Strength (U.C.S.) are given in Table 11. Each data is an average of three measurements.

Table 11:

U.C.S. of Treated Samples

Sample	UCS (part A) psi	stand.dev. psi	UCS (part B) psi	stand.dev. psi
NC	1058	32	304	21
UC	775	20	298	1
TC	1000	93	440	14

In case A, the addition of 2.03% treated clay does not affect the strength of the cubes. The UCS is similar to that obtained for the reference samples. The amount of untreated clay added to the samples significantly reduces their strength, by approximately 25%.

The results obtained in case B differ. In this case, the addition of treated clay seems to have a real beneficial effect on the UCS, as the resistance is increased by about 30%, compared to the

reference samples. Samples with no clay or non treated clay have a lower strength.

Further tests should be done to investigate on this.

Comparing part A and B indicates that a 5% decrease in the water content will increase the UCS by a factor of 2 or 3.

IV.B-5 POROSITY

Only samples made in part B of the experiment were tested for the porosity. Results are presented in Table 12.

Table 12:

Pore Volume and Pore Surface of Treated Samples

Treated Samples	Mean Pore Volume cc/g	Mean Pore Surface Area m^2/g
NC	0.09	1.7
UC	0.09	1.5
TC	0.09	1.6

All data represent a average of nine readings each. Variation in the pore volume and pore surface area is about 12% for each type of sample between different fragments. With this margin of error, all the results are similar. Each pore size distribution graph was similar, and each shows that the majority of the pores have a diameter between 1000 and 2500 Angstroms.

IV B-6 WEATHERING TESTING

IV B-6-1 Part A

Wet/dry testing of samples from part A resulted uniformly in less than 1% corrected cumulative weight loss after 12 cycles. Graphs for samples made with NC, UC and TC are presented in Figures 24, 25,and 26. Most of the samples have a negative value, about -0.5%, which means that the cycling at 60 C enhances the cementitious property for all samples relative to the control samples. No significant variation between NC, UC and TC samples can be observed.

Freeze/thaw testing of the treated samples did not give results as good as for the wet/dry testing. All results are presented in Figures 27, 28, and 29. Samples made with treated clay had about 16% corrected cumulative weight loss after 12 cycles. Samples done with untreated clay had an average of 25% corrected cumulative weight loss. The three reference samples that did not contain any clay had a corrected cumulative weigth loss that varied between 48 and 73%. Even if the treated samples are less resistant to the freeze/thaw cycles, it seems that the use of treated clay greatly enhances greatly the physical resistance of the cubes. The use of untreated clay is also beneficial to freeze/thaw resistance of the cubes, but to a lesser extent. Despite the advantage of adding treated clay in the sample, the result after 12 cycles still does not meet the level established by the EPA.

FIGURE 24
Wet/Dry Testing of Treated Samples

% relative corr.cumul. Wt loss

Test A
Test B
Test C

Number of cycles

Samples using treated clay, part A
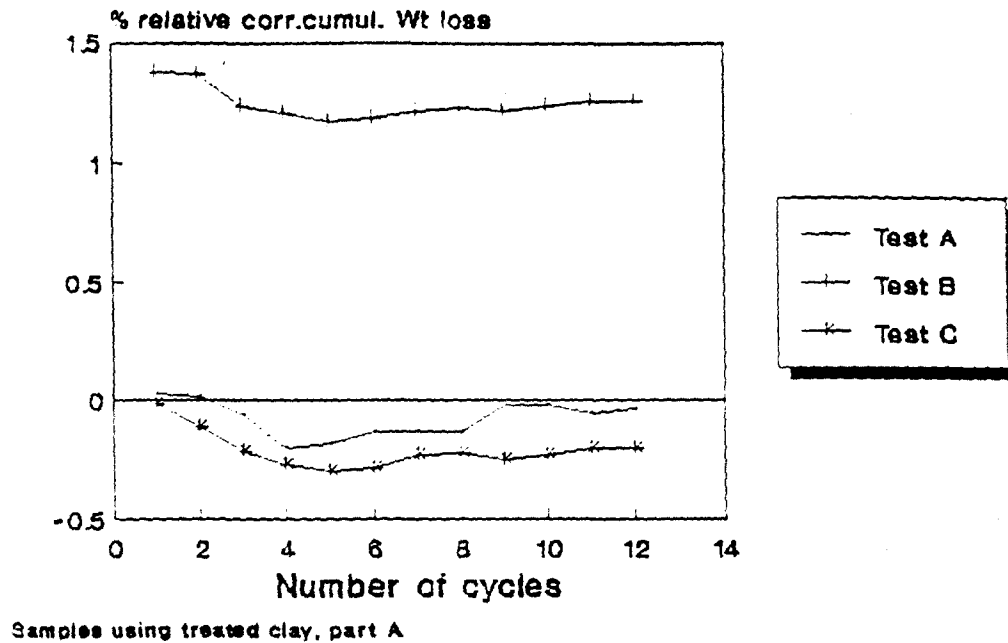
FIGURE 25
Wet/dry Testing of Treated Samples

% relative corr. cum.Wt loss

Cube A
Cube B
Cube C

Cycles

Samples made with no clay, part A
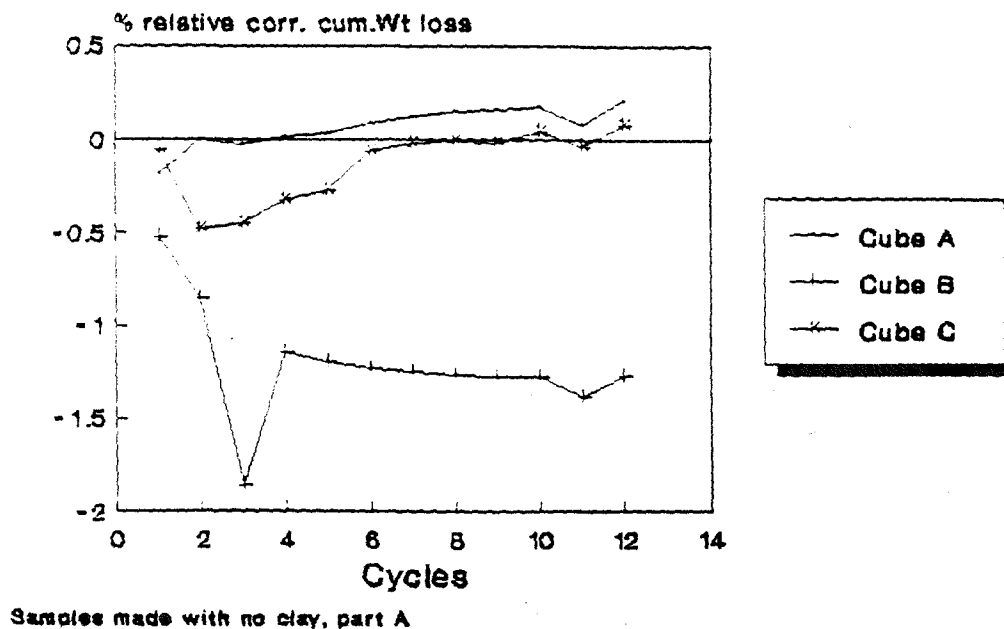
FIGURE 26
Wet/Dry Testing of Treated Samples

% relative corr.cumul. Wt loss

Number of Cycles

Cube 1
Cube 2
Cube 3

Samples using non treated clay, part A
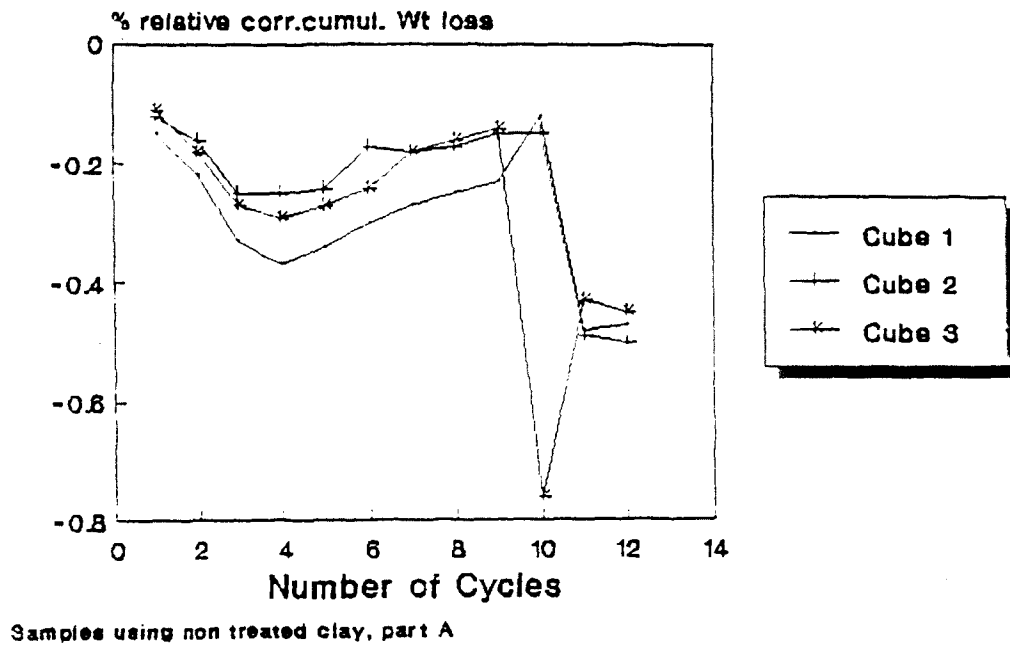
FIGURE 27
Freeze/Thaw Testing of Treated Samples

% Relative Corr.Cumul.Wt loss

Cycles

Cube 1
Cube 2
Cube 3

Samples made with Treated Clay, part A
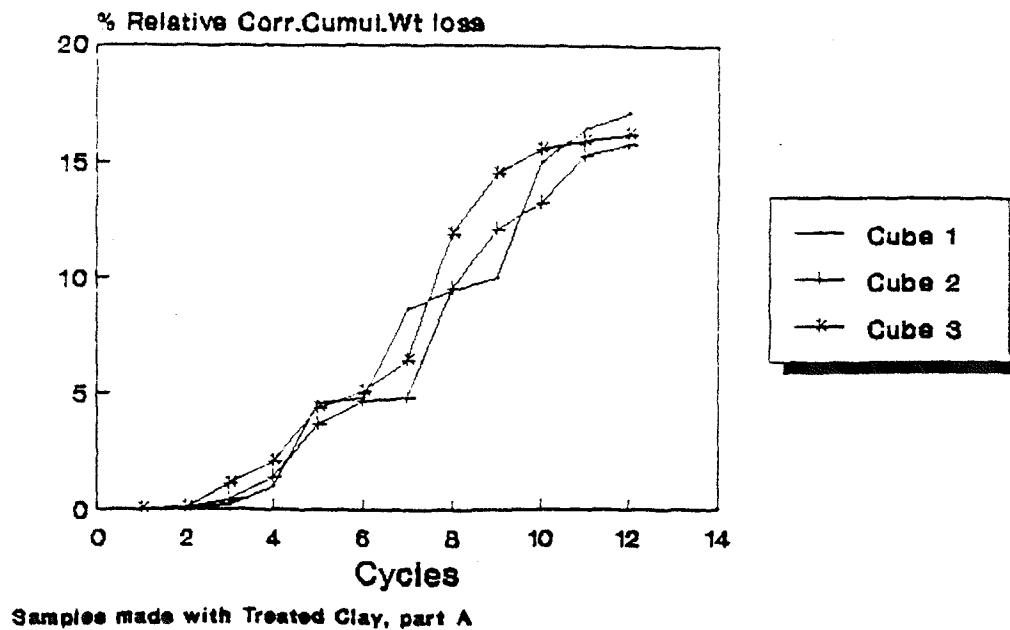
FIGURE 28
Freeze/Thaw Testing of Treated Samples

% relative corr.cumul. Wt loss

Legend:
— Cube A
+ Cube B
* Cube C
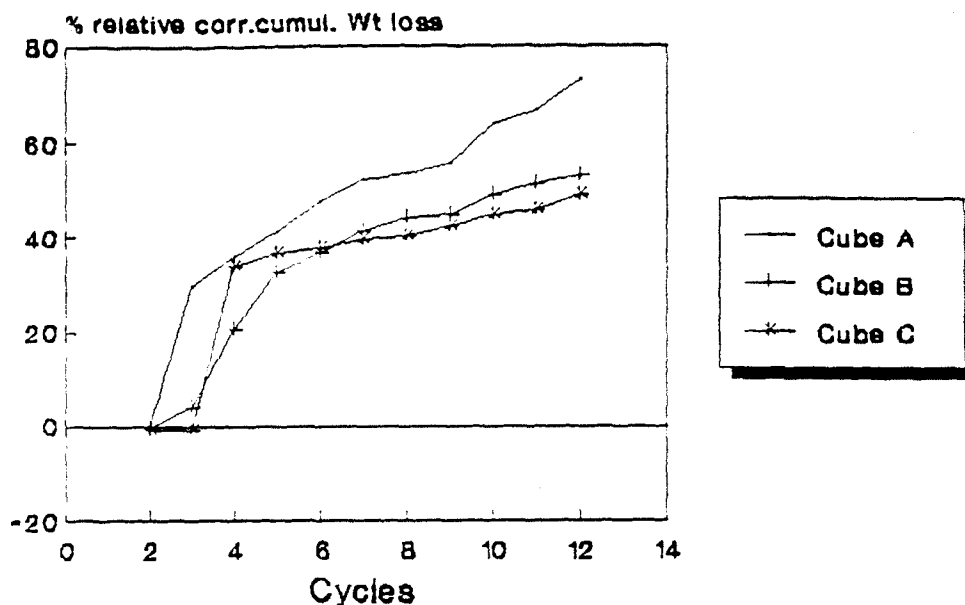
Samples made with no clay,part A

FIGURE 29
Freeze/Thaw Testing of Treated Samples

% Relative Cumul. Corr. Wt Loss

Legend:
— cube A
+ Cube B
* Cube C
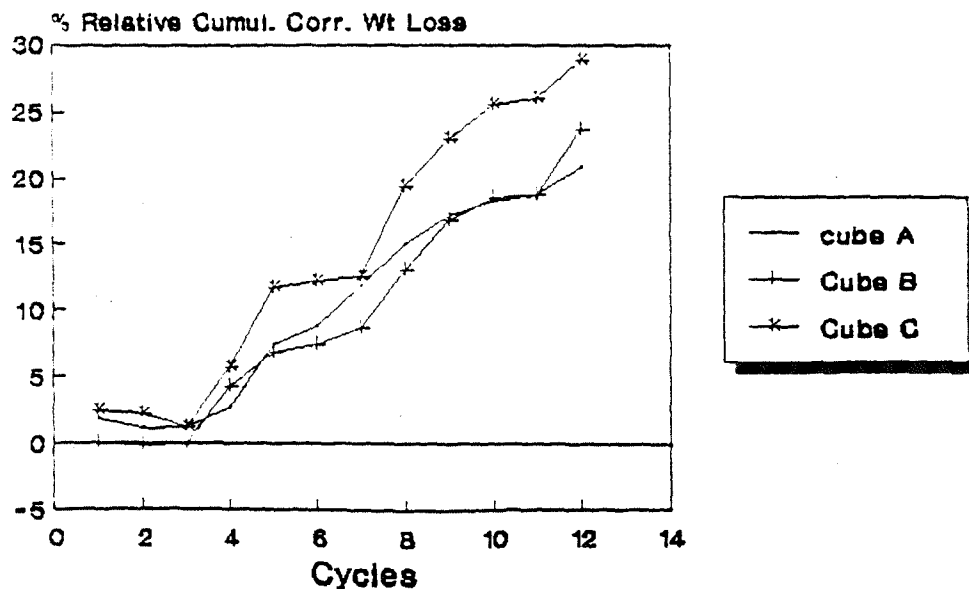
Samples using nontreated clay, part A

IV B-6-2 Part B

Wet/dry testing results on samples from part B are presented in Figures 30, 31 and 32. Again, no significant difference exists between NC, UC and TC samples. The relative cumulative weight loss after 12 cycles is always below 0.5%.

Results are given in FigureS 33, 34 AND 35 for the freeze/thaw cycles. It again appears that the physical resistance of the samples to freeze/thaw cycles is not sufficient. Samples made with untreated clay or treated clay have a better resistance. Their average corrected relative cumulative weight loss is about 30% after 12 cycles. Samples made with no clay had between 36 and 51% relative corrected cumulative weight loss after 12 cycles.

There is more variation between cubes in the same batches than there is in part A of the experiment.

The use of either treated clay or untreated clay in samples provides better resistance for freeze/thaw cycles. Samples made with a lower water content also have better resistance. But with the receipes used, the weight loss after 12 cycles is still higher than the limit provided by EPA. As was suggested in the first experiment, air entraining agent should be added to the samples in order to allow the samples to withstand freeze/thaw testing.

FIGURE 30
Wet/Dry Testing of Treated Samples

% relative cumul.corr.Wt.loss

Cube 1
Cube 2
Cube 3

Number of cycles

Samples made with treated clay, part B
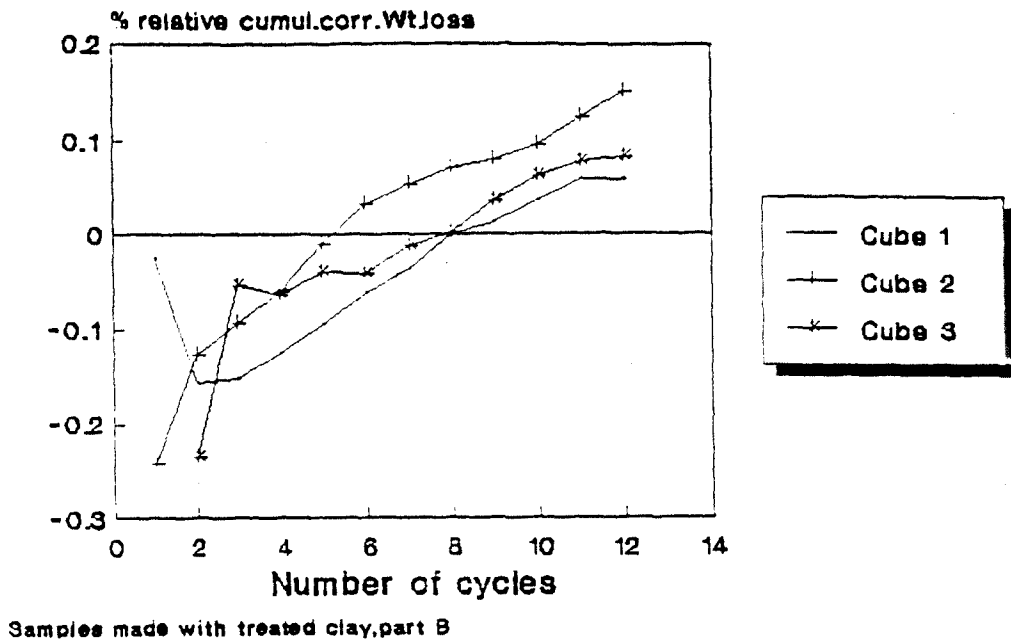
FIGURE 31
Wet/Dry Testing of Treated Samples

% relative cumul.corr.Wt.loss

Cube 1
Cube 2
Cube 3

Number of cycles

Samples using non treated clay, part B
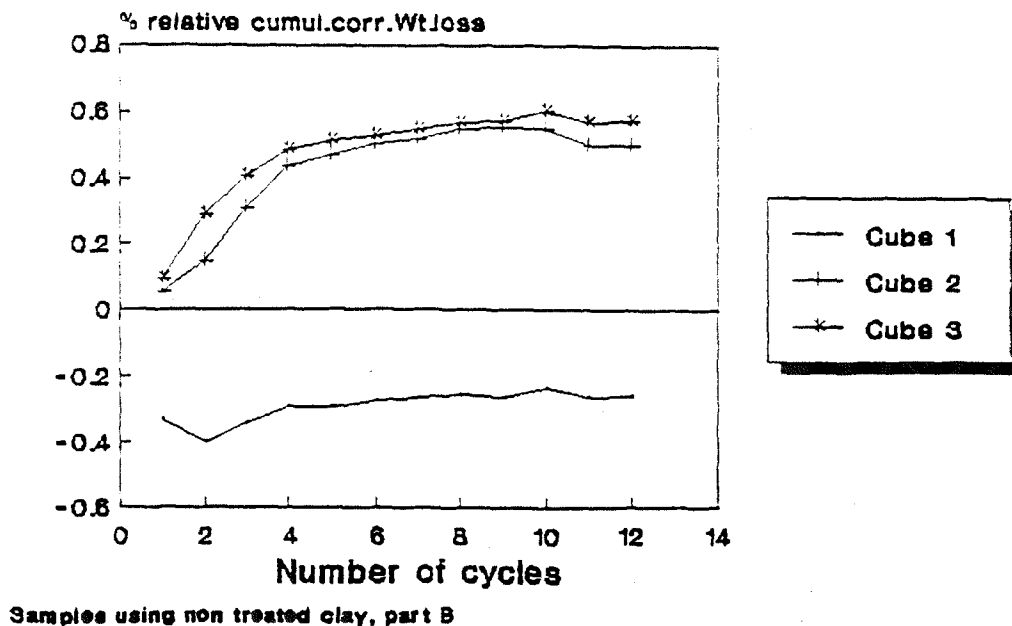
FIGURE 32
Wet/Dry Testing of Treated Samples

% relative cumul.corr.Wt loss

Number of cycles

Cube 1
Cube 2
Cube 3
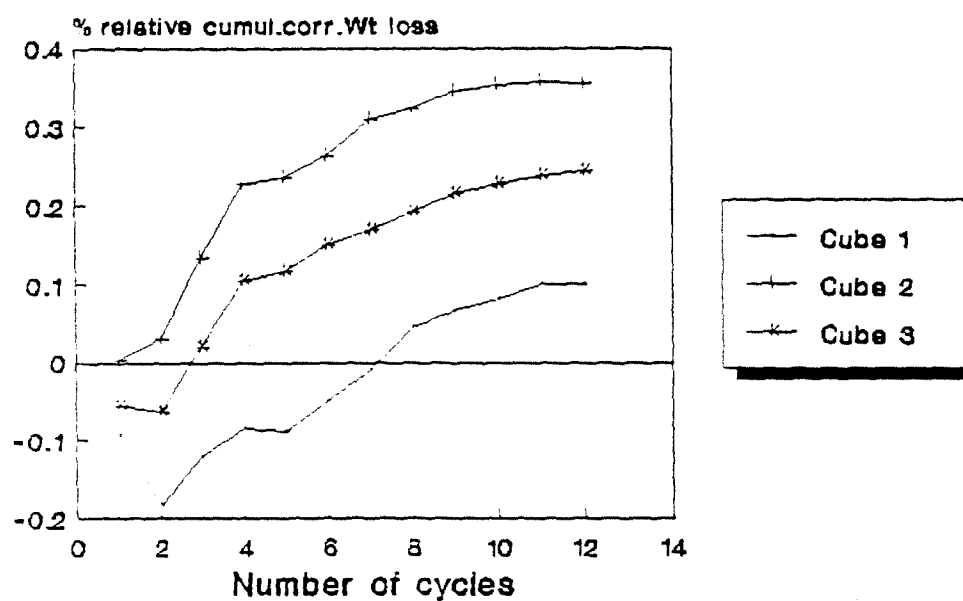
Samples made with no clay, part B

FIGURE 33
Freeze/Thaw Testing of Treated Samples

% relative cumul.corr.Wt loss

Cube 1
Cube 2
Cube 3

number of cycles

Samples made with treated clay, part B
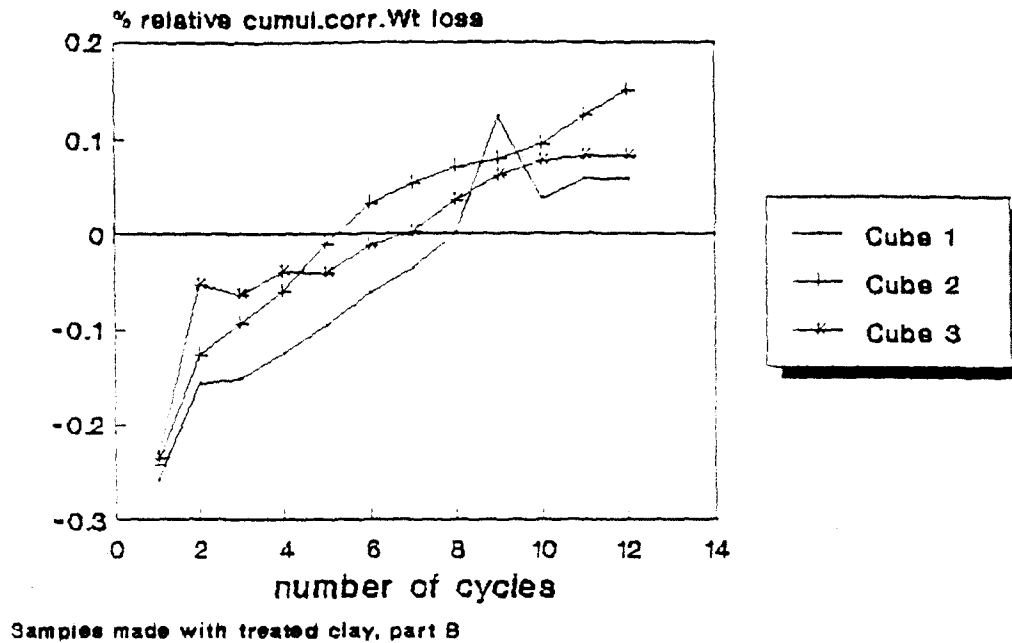
FIGURE 34
Freeze/Thaw Testing of Treated Samples

% relative cumul.corr.Wt loss

Cube 1
Cube 2
Cube 3

Number of cycles

Samples Using non treated clay, part B
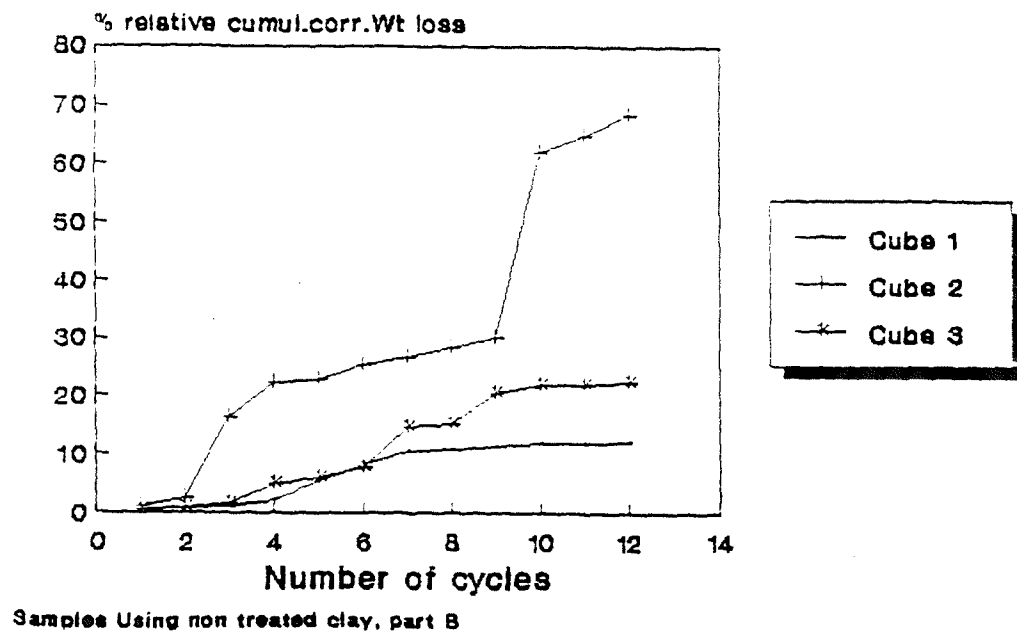
FIGURE 35
Freeze/Thaw Testing of Treated Samples

% relative cumul.corr.Wt.loss

Number of cycles

Cube 1
Cube 2
Cube 3

Samples made without clay, part B
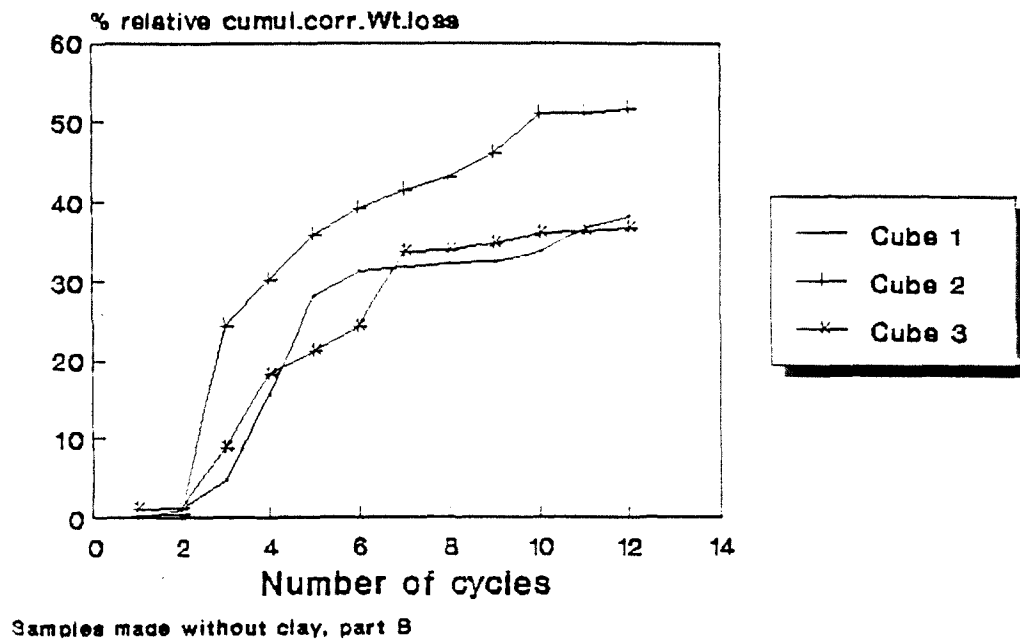
IV C: EXPERIMENT # III:

INFLUENCE OF FLY ASH TYPE ON LEACHING PROPERTIES

The influence of fly ash type on containment of pentachlorophenol (PCP) and metals was evaluated using the nine different fly ashes already used for the first experiment.

The same formulation was used, however, 3.75 mg of PCP per gram of the mixture was added.

The first part of this experiment consisted of the analysis of the chromium and lead content of the fly ash and the industrial dust using Kevex 700. These results are presented in Table 13.

Table 13:

Chromium and Lead Content in the Fly Ash and Industrial Dust

	Lead ppm	Chromium ppm
F.A.#1	95 ±3%	230 ±7%
F.A.#2	85 ±3%	220 ±6%
F.A.#3	120 ±3%	239 ±7%
F.A.#4	89 ±7%	243 ±7%
F.A.#5	95 ±9%	247 ±7%
F.A.#6	72 ±6%	221 ±6%
F.A.#7	95 ±3%	218 ±6%
F.A.#8	64 ±4%	219 ±6%
F.A.#9	170 ±4%	305 ±9%
Ind.Dust	805 ±9%	1170 ±9%

Lead and chromium concentrations in the fly ashes are very consistents. Only fly ashes #3 and #9 have a higher lead concentration. Fly ash #9 contains also more chromium than the other fly ashes. The industrial dust has approximately 6 times more lead and chromium that the other fly ashes.

To be used as a second reference, a TCLP extraction was conducted on all fly ashes and the industrial dust, using the same extraction solution. Chromium, cadmium and lead were analyzed to evaluate the extract of metal leaching. Results are presented in Table 14.

Table 14:

TCLP extract of fly ash & dust Analysis:

Fly Ash Number	pH	Chromium ppm	Lead ppm	Cadmium ppm
1	4.23	0.1	0.0	0.0
2	4.12	0.0	0.0	0.0
3	4.23	0.0	0.0	0.0
4	3.83	0.0	0.0	0.0
5	3.78	0.1	0.0	0.0
6	3.90	0.7	0.0	0.0
7	3.84	0.4	0.0	0.0
8	3.91	0.8	0.0	0.0
9	3.84	0.1	0.0	0.0
Ind. dust	11.9	1.6	26.4	0.0

All fly ashes leach very small amount of metals. Only from fly ashes #6 #7 and #8 does a small amount of chromium leach. Only lead is released in a larger quantity from the industrial dust,

Although the industrial dust is known to contain much more metals than fly ashes. Chromium concentration in the leachate is only 1.6 ppm. Cadmium could not be detected by atomic adsorption analysis. The release of cadmium from the industrial dust may have been inhibited by the high pH value of the extract, at which cadmium is essentially insoluble.

Table 15 shows the average of the analytical results after TCLP extraction was done on stabilized samples. The detailed data are given in Appendix IV C-1. A second extraction was done for the sample made with fly ash #9. The three filter cakes were kept and dried at 60°C. Some of the dry residues were used for a second extraction at the same conditions. This was done to determine whether any PCP left in the stabilized cube could leach after a second extraction.

Table 15:

Effect of Coal Fly Ash on the Composition

of TCLP extract of Treated Samples:

Fly Ash Used	Lead ppm	Chromium ppm	Cadmium ppm	PCP ppm	Final pH
1	0.4	0.2	0.9	66.5	7.5
2	0.4	0.2	1.1	63.2	7.6
3	0.4	0.3	1.4	64.8	7.7
4	0.2	0.1	1.5	65.5	7.5
5	0.4	0.1	0.6	66.3	7.7
6	0.4	0.2	1.1	66.5	7.7
7	0.4	0.3	1.1	70.0	7.8
8	0.6	0.4	1.7	66.6	7.6
9	0.9	0.1	2.1	70.0	7.5
9(2nd ex.)	6.2	0.0	8.8	7.2	6.6

All results are promising as none of the stabilized sample re-
leases a large amount of heavy metals. All concentration are
below the EPA standard. Lead releases are always below 0.6 ppm,
except for fly ash #9. This can be related to its higher lead
content compared to the others. Results show that lead release
is very pH dependant: for a slight increase of pH, the concentra-
tion of lead in leachate will decrease. Results for the chromium
are very consistant between all fly ashes. The cadmium concen-
trations found for all fly ashes suggest that the lower pH in the
stabilized samples is responsible for the leachate of cadmium,
which should come from the industrial dust. In this case, the
cadmium release is enhanced by the treatment.

These results demonstrate that the PCP is not well adsorbed by
the fly ashes in the treated samples. Approximately 60% of the
PCP added leaches during the first extraction, and 7% during the
second one.

An example of a chromatogram from TCLP extract, obtained at 230
nm is given in Appendix IV C-2. A small peak appears at a small-
er retention time than the PCP peak (3.65 mn). This compound has
not yet been identified. In any case, the amount is very small.
In order to control the presence of any other by products, an
U.V.spectra was run on each the extrat. One of those spectra is
presented in appendix IV C-3. No additional peak was found
between 220 nm and 300 nm. This demonstrates that the remaining
amount of PCP was not changed into a non-volatile by-product,
suggesting that the remaining 33% are fixed in the matrix. With
3% error in concentration, there is no variation in the adsorp-
tion capacity with the ash type.

IV D: EXPERIMENT IV:

EFFECT OF CLAY ON CONTAINMENT OF ORGANIC AND METALS

The effect of clay on containment of organic and metals was
studied by comparing results between samples made without clay
(NC), containing 2% untreated clay (UC), or 2% treated clay.
Three extractions were obtained for each cube. Lead, chromium,
cadmium and PCP were analyzed and the pH recorded. TCLP extrac-
tions were also run on the industrial dust, as the waste refer-
ence. All data are in Appendix IV D. Table 16 gives the average
results for the three trials as well as the corresponding stand-
ard deviations.

Table 16:

Analysis of TCLP Leachate of Waste and Treated Samples

Waste treated	Lead ppm ±%Sd	Chromium ppm ±%Sd	Cadmium ppm ±%Sd	PCP ppm ±Sd	pH
Baghouse Dust	26.4±28%	1.6±6%	0.0± 0%	0.0±0%	11.9±2%
Treat.sam. No clay	0.3±30%	0.1±60%	0.5±26%	71.4±6%	7.5±4%
Treat.sam. clay	0.3±30%	0.1±130%	0.5±20%	72.2±8%	7.3±2%
Treat.sam. treat.clay	0.4±18%	0.1±150%	0.5±21%	7.2±4%	7.3±2%

Clay effect on PCP adsorption:

To asses the effective retention of PCP within the treated wastes, a calculation of the maximum possible PCP concentration is necessary.

TCLP extraction was conducted with 50 grams of treated sample diluted into one liter extraction solution. Based upon the amount of PCP added to the waste, the one liter of TCLP extract can contain a maximum of:

$$50g \text{ of treated sample} * \frac{2.1824g \text{ of PCP added}}{970 \text{ g of total components}} = 0.112 \text{ g.}$$

This shows that in the worst case, in which all the PCP would leach, the TCLP extract should contained 112 ppm of PCP.

Samples containing no clay and untreated clay show similar results. PCP release is about 72 ppm, with 8% variation between results . This clearly indicates that samples containing either untreated clay or no clay are not efficient preventing PCP from leaching. In these tests, 64% of the initial amount of PCP is found in the leachate. The release may be limited by the solubility of PCP in water. The solubility is about 70 ppm, and will decrease with a lower the pH. Although a second consecutive extraction was not done on the treated samples, the results found in the experiment III showed that only an additional 7 ppm leach in a second extraction for samples containing no clay. This would mean that the remaining 30% is adsorbed by the matrix. Again in this case again, an U.V. spectra from 220 nm to 300 nm was conducted on the leachate. No other peak was found, assuring

that the remaining 30% of PCP not found in the leachate was not converted into non-volatile by-products. Possible degradation of PCP into by-products and losses during the 28 days of containment should be study.

This table shows that treated clay is necessary to retain organic contaminant, as only 6% of the PCP leach in TCLP extract. Samples made with treated clay thus reduce the leachate concentration by an order of magnitude.

Clay effect on metals adsorption

The lead, cadmium and chromium composition of the industrial dust were determined using the EPA method 30-50. Their concentration were respectively 1200 ppm, 200 ppm and 1400 ppm. Since the composition was not confirmed by any separated method, these results should be used as an estimate and not as an exact composition. Noneless, the results still offer a basis for comparison. A good indication of the efficiency of the S/S treatment is a comparison of the results obtained for the waste and the treated samples.

It should first be noticed, that the solubility of lead and cadmium is strongly influenced by the pH of the TCLP extract. The average pH for the waste was 12, while the pH for the treated samples was about 7.4. At this pH, most metals are more soluble. No cadmium could be detected in the TCLP extract of waste. According to the concentration determined by the digestion analysis, if all of it were to leach, about 6 ppm of cadmium would be found in TCLP extract. It is known that at pH=12, cadmium is essentially insoluble, explaining the absence of this metal from

the TCLP extract of waste. The TCLP extract of all treated samples has a pH close to 7, at which cadmium is slightly more soluble. This explains the 0.5 ppm found in the extract of the treated sample. This level is below EPA standard.
As expected, no difference can be detected between samples containing untreated clay, treated clay or no clay.

Lead is the heavy metal which leaches the most from the industrial dust. The average concentration found was about 25 ppm, which is higher than the EPA standard. According to the amount of lead in both fly ash and the dust, all lead leaches by the TCLP test.

As was the case for cadmium, there is no difference between treated samples using treated clay, untreated clay or no clay. The average lead concentration is about 0.3 ppm, which is about 70 times lower than the concentration obtained for the waste itself.
Again, chromium concentration in TCLP extract does not vary among samples. The average concentration is 0.1 ppm, which is below EPA standard, and 16 times lower than the concentration obtained for the waste.

The use of an adapted treated clay is very efficient for adsorption of the PCP in the matrix. The use of a untreated clay does not offer any advantage, as results are similar for the samples that did not contain clay. The PCP adsorption was very poor. The use of untreated clay or treated clay does not influence the pH of the extract, the lead, chromium or cadmium release.

CHAPTER IV: CONCLUSIONS

The goal of this research was to demonstrate the feasibility of using a stabilization/solidification process to treat an organic-containing waste. The experiments done show that the use of treated clay promises an effective treatment for hazardous wastes containing a small amount of pentachlorophenol.

Treatment of the heavy metal contamination in the foundry bag-house dust is very efficient: all metal concentrations are below the EPA level after running the TCLP test. Results are specifically good for lead for which the concentration in the leachate is reduced by a factor of 70. The required strength is also achieved as the U.C.S. is always more than 250 psi.

The source and type of coal fly ash used in such processes does not appear to have a significant effect on the physical properties of the waste form produced. The U.C.S., true density, bulk density, porosity and water content were similar for all samples. The U.C.S. was between 250 and 400 psi. Variations among samples made with the same fly ashes were in the same range as those between samples made with different fly ashes. Physical properties were much more sensitive to such factors as the overall

treatment recipe and how the mixing and molding processes were carried out. The fly ash type does not seem to have any influence on the metal and PCP concentrations in the TCLP leachate. Concentrations werer respectively 0.4 ppm, 0.3 ppm, and 1.5 ppm for lead, chromium and cadmium, and 68 ppm for PCP.

The inclusion of 2% HDTMA-treated clay in the sample reduces the PCP concentration in the leachate by an order of magnitude. The final concentration is 7 ppm. Results show that clay inclusion in the mixture does not reduce the physical resistance but can even enhance it. The use of 2% untreated clay in the mixture does not have any influence on PCP adsorption: the concentration in the leachate is 70 ppm, as it is for samples made without clay. This demonstrates the need to select a good clay additive adapted to the organic that has to be treated.

Results on weathering testing are very consistent between all samples. The relative corrected cumulative weight loss after 12 cycles was lower than 1% for wet/dry testing. Freeze/thaw cycles did not give good results, as more than 40% relative corrected cumulative weight loss was recorded after 12 cycles for all samples.

Although the overall success of this project is evident, some additional fundamental research can be suggested.

The efficiency of this S/S method on PCP adsorption should be studied by using the same waste spiked with an larger amount of PCP. A comparative study should also be done with different

organic compounds. Tetrachloroethylene was first suggested for this project, but could not be included because of analytical difficulties and lack of time. This compound, or other similar volatile organics, should be studied . This would require protection, as losses by volatilization would occur easily, and by-products will certainly be created. The confined air in the environmental chamber will have to be monitored, and U.V. spectra will need to be run to determine all by-products.

All experiments done to assess the effect of fly ash type on the physical/chemical properties of the final waste form did not end up with any significant conclusion. Part of the reason is that fly ash only constituted 14.5% of the mixture. This was done to test the feasibility of the method by adding a minimum of additives in order to minimize the cost. Future work should focus on this aspect. Similar treatments using the same waste should be carried out, but comparative studies should be done by adding various amounts of fly ashes. Also a study should include the effect of washing the ash before its use in stabilization/solidification processes. Doing so may well improve the characteristics of the waste form produced; moreover, many facilities store their ashes in ponds and thus commercially available ash may already be "washed".

Experiments should also be done using an air entraining agent in the mixture, in order to increase the resistance of the samples to the freeze/thaw cycles.

CHAPTER 6: REFERENCES

[1]   ABBASCHIAN,G.J.,"Solidification processing: challenges and achievements", in Journal of Metals, p.35, 1985.

[2]   ARNIELLA, E.F., BLYTHE, L.J., "Solidifying traps hazardous wastes", in Chemical Engineering, Feb 1990, pp.92-102.

[3]   BANERJEE, K., D.Eng.Sc. Thesis, New Jersey Institute of Technology, Newark, NJ, December 1988.

[4]   BARTH, E.F., "An overview of the history, present status, and futur direction of solidification technologies for hazardous waste treatment", presented in the 2nd annual symposium on hazardous substances, Beaumont, Feb. 15-16, 1990.

[5]   BARTH, E.P., "Summary of solidification/stabilization SITE demonstrations at uncontrolled hazardous waste sites", presented in the 2nd ASTM International Symposium on S/S of hazardous wastes, May 29-June 01 1990.

[6]   BECKWITH, P.M.; MULLINS, R.L., " Analysis of eastern coal fly ash using separated sampling and exitation atomic emission spectrometry", in Analytical Chemistry, Vol.59, pp.163-167, 1987.

[7]   BENTUR, A.; GRINBERG, T., "Modification of the cementing properties of oil shale ash", in Ceramic Bulletin, Vol.63,

No2, pp.290-300, 1984.

[8] BISHOP, P.L., "Leaching of inorganic in hazardous constitu-
     ents from stabilized/solidified hazardous wastes", in Haz-
     ardous Wastes and Hazardous Materials, Vol 5, No2, 1988.

[9] CERVASSI, J.R., "The quantitative determination of elemental
     composition of coal fly ash samples via X-Ray fluorescence",
     Thesis for Ms of Science, NJIT, 1983.

[10] COCKE, D.L.,"The binding chemistry and leaching mechanisms
     of hazardous substances in cementitious solidification/stabi
     lization systems", presented at the 2nd annual Symposium on
     Hazardous Wastes in Beaumont, February 15-16, 1990.

[11] CONNER, J.R., "Fixation and solidification of wastes", in
     Chemical Engineering, pp.79-85, Nov.1986

[12] CONNER, J.R.,"Chemical fixation and solidification of haz
     ardous wastes", published in Van Nostrand Reinhold, New
     York, 1990, 692 pages.

[13] CUIU, C.; HALMAN, R.; LI,K.; THOMAS, R.S.;LAO, R.C., "Analy-
     ical procedure to assay environmental samples for PCDD/PCDF,
     PAH, PCB, Chlorobenzenes (CB), and Chlorophenols (CP), in
     Chemosphere, Vol.15, pp.1091-1096, 1986.

[14] DE GROOT, G.J.; WIJKSTRA, J.; HOEDE, D.; VAN DER SLOOT,
     H.A., "Leaching characteristics of hazardous elements from
     coal fly ash as a function of the acidity of the contact
     solution and the liquid/solid ratio", May 1987.

[15] DINCHAK, W.G., "Solidification of hazardous wastes using
     portland cement", in Concrete Construction, pp.781-783,
     Sept 1985.

[16] DROZ, P.O.; KREBS, Y.; NICOLE, B.; GUILLEMIN, M., "A direct reading method for chlorinated hydrocarbons in breath", in American Industrial Hygiene Association, J.49(7), pp.319-24, 1988.

[17] ESTES, T.J.; SHAH, R.V.; VILKER, V.L.,"Adsorption of low molecular weight halocarbons by montmorillonite", in Environment Science Technology, Vol.22, No4, pp.377-381, 1988.

[18] FUNSTON, J.J.; KRELL, W.C.; ZIMMER, F.V., "Flowable fly ash: a new cement stabilized backfill", in Civil Engineering , pp.48-51, March 1984.

[19] FURUYA, K.; MIYAJIMA, Y.; CHIBA, T.; KIKUCHI, T., "Elemental characterization of particle size-density separated coal fly ash by spectrophotometry, inductively coupled plasma emission spectrometry, and scanning electron microscopy-Energy dispersive X-Ray analysis", in Environmental Science and Technology, Vol.21, No9, 1987.

[20] GIBBONS, J.J.; SOUNDARAJAN, R., "The nature of chemical bonding between modified clay minerals and organic waste materials", in American Laboratory, July 1988.

[21] GRIEST, W.; TOMKINS, B.A.; "Influence of carbonaceous particles on the interaction of coal combustion stack ash with organic matter", in Environmental Science and Technology, Vol.20, No3, pp.291-295, 1986.

[22] HAGENMALER, H.; KRAFT, M.; BRUNNER, H.; HAAG, R., "Catalytic effects of fly ash from waste incinerator facilities on the formation and decomposition of polychlorinated dibenzo-p-

dioxins and polychlorinated dibenzofurans", in Environmental Science and Technology, Vol.21, No11, 1987.

[23] HANNAK, P.; LIEM, J.,"Stabilization options, selection considerations, in APCA technical meeting, May 5-7 1987, Edmonton, Alberta.

[24] HAQUE, M.N.; LANGAN, B.N.; WARD, M.A., "High fly ash concretes", in Journal of American Concrete Institute, pp.54-60, 1984.

[25] JENKINS, R., "X-Ray fluorescence spectrometry", published in the American Chemical Society, 200 p., 1978.

[26] JENKINS, R.; GOULD, R.W.; GEDCKE, D.A., "Quantitative X-Ray spectrometry, published in Decker, New york, chp.11, 1978.

[27] KARASEK, F.W.; CHARBONNEAU, G.M.; REUEL, G.J.; TONG, H.Y., "Determination of organic compounds leached from municipal incinerator fly ash by water at different pH levels", in Analytical Chemistry, Vol.59, pp.1027-1031, 1987.

[28] KUANG YE CHENG; BISHOP,P.L., "Developing a kinetic leaching model for solidified/stabilized hazardous wastes, presented at the 2nd annual Symposium on Hazardous Wastes, Beaumont, February 14-15, 1990.

[29] LAGOUTTE, E., HANNACK, P., KNOX, D., CONRAD, D.,"Stabiliza tion/solidification of organic containing wastes using organophilic clay and coal fly ash", presented in the 2nd ASTM International Symposium on S/S at Williamsburgh, May 29-June 01, 1990.

[30] LICHMAN, D.; MC OCZKOWSKI, S., "Scanning electron microscopy and energy dispersive X-Ray spectroscopy analysis of submi-

crometer coal fly ash particules", in Environmental Sciences and Technology, Vol.19, pp.274-277, 1985.

[31] LISKOWITZ, J.W.; GROW, J.; SHEIH, M.; TRATTNER, R., "Sorbate characteristiques of fly ash", technical report to USDEP, coal research program, Pittsburgh, PA, August 1983.

[32] MARKOWSKI, G.R.; FILBY, R., "Trace element concentration as a function of particle size in fly ash from a pulverized coal utility boiler", in Environmental Science and Technology, Vol.19, No9, 1985.

[33] MC BRIDE, M.B., MORTLAND, M.M., Faraday Society Transaction, Vol.1, 1955, pp.323-329.

[34] MONTGOMERY, D.M.; SOLLARS, C.J.; PERRY, R., "Cement based solidification for the safe disposal of heavy metal contaminated sewage sludge", in Waste Management & Research, Vol.6, pp.217-226, 1988.

[35] MONTGOMERY, D.M.; SOLLARS, C.J.; SHERIFF, T.S.; PERRY, R., "Organophilic clays for the successful stabilization/solidification of problematic industrial wastes", in Environmental Technology Letters, Vol.9, pp.1403-1412, 1988.

[36] MORTLAND, M.M., SHAOBAI, S., BOYS, S.A., "Clays and clay minerals", Vol.34, No5, 1986, pp.581-585.

[37] MURPHY, T.E.; CHRISTENSEN, P.A., "Fly ash analysis by complementary atomic absorption spectrometry and energy dipersive X-Ray spectrometry". in Analytical Chemistry, Vol.56, pp.2534-2537, 1984.

[38] NORTON, A.; MALABY, K.L.; DEKALB, E.L.,"Analytical characterisation of ash produced during combustion of refuse-derived fuel with coal", in Environemtal Science and Tech

nology, Vol.22, No11, 1988.

[39] PANDAY, K.K.; PRASAD, G.; SINGH, V.N.;, "Copper (II) removal from aqueous solutions by fly ash", in Water Research, Vol.19, No7, pp.869-873, 1985.

[40] PARKASH, S.; CHAKRABARTTY, S.K.; DU PLESSIS, M.P., "Porosity in Alberta subbituminous coals", report for the coal research dpt, Alberta research council, Edmonton, Alberta, Canada, 1984.

[41] PLATBROOD, G.; BARTEN, H., "Infrared analysis of low temperature ashed coal fly ashes and their classification by application of clustering theory", in Analytical Chemistry, Vol.57, pp.2504-2510, 1985.

[42] POON,C.; CLARK, A.I.; PERRY, R., "Atomic structure analysis of stabilized toxic wastes", in Environmental Technology Letters, Vol.7, pp.461-468, 1986.

[43] POON, C.S.; CLARK, A.I.; PERRY, R., "Permeability study on the cement based solidification process for the disposal of hazardous wastes", in Cement and Concrete Research, Vol.16, pp.161-172, 1986.

[44] POON, C.S.; CLARK, A.I.; PETERS, C.J.; PERRY, R., "Mechanisms of metal fixation and leaching by cement based on fixation processes:, in Waste Management Research, Vol.3, pp.127-142, 1985.

[45] RICHARDSON, G.L., "The phantom dissolution leach model", in Nuclear and Chemical Waste Management, Vol.2, pp.237-241,

[46] SHEFFIELD, A.; MAKENA, S.; TITTLEBAUM, M.; EATON, H.; CARTLEDGE, F., "The effect of three organics on selected

physical properties of type I portland cement", in Hazardous Waste & Hazardous Materials, Vol.4, No3, 1987.

[47] SHERIFF, T.S., SOLLARS, C.J., MONTGOMMERY, D., PERRY, R., in Environmental Technology Letters, Vol.8, 1987, pp 301-514.

[48] SOUNDARAJAN, R.,"An overview of existing leach tests for treated waste", report for RMC Environmental & Analytical Laboratories, Missouri, April 1989.

[49] SUSSMAN, D.B., "Municipal waste combustion ash: testing methods, constituents and potential uses", report for Ogden Martin Systems, Alexandria, VA, pp.1041-1053, 1988.

[50] SWAMY. R.N.; ALI, S.A.R.; THEODORAKOPOULOS, D.D., "Early strength fly ash concrete for structural applications", in Journal of American Concrete Institute, pp.414-422, September 1983.

[51] TITTLEBAUM, M.E.; SEALS, R.K.; CARTLEDGE, F.K.; ENGELS, S., "State of the art on stabilization of hazardous organic liquid wastes and sludges", in Critical Review in Environmental Control, Vol.15, Issue 2, pp.179-211, 1983.

[52] TITTLEBAUM, M.E.; EATON, H.C.; CARTLEDGE, F.K.; WALSH, M.B.; ROY, A., " Procedure for characterizing effects of organics on solidification/stabilization of hazardous wastes", in Industrial and Hazardous Waste, pp.308-318, 1987.

[53] THOMAS, N,L.; JAMESON, D.A.; DOUBLE, D.D., Cement and Concrete research, Vol No11, pp .143, 1981.

[54] WALSH, M.B.; EATON, H.C.,; TITLLEBAUM, M.E.;CARTLEDGE, F.K.; CHALASANI,D.,"The effect of two organic compounds on a port-

land cement-based stabilization matrix", in Hazardous Waste and Hazardous Materials ,pp.111-128, 1986 .

[55] VAN DER SLOOT,H.;COTE, P., "Modelling chemical interactions at a waste/waste interface", in Environmental Technology Letter, Vol.10, pp.969-976, 1989.

[56] VAN DER SLOOT; DE GROOT, G.J.; WIJKSTRA, J., "Leaching characteristics of residues and potential for modification of leaching", report, ECN-89-045, 1989.

[57] VIPULANANDAN, C., KRISHNA, S., "Solidification/stabilization of phenolic waste with cementitious and polymeric material", presented in the 2nd Annual Symposium of the Gulf coast, Beaumont, feb.15-16, 1990.

[58] WARREN, D.S.; CLARK, A.I.; PERRY, R., "A review of clay-aromatic interactions with a view to their use in hazardous waste disposal", in The Science of the Total Environment, Vol.54, pp.157-172, 1986.

[59] WILES, C., "Perspectives on solidification/stabilization technology for treating hazardous waste", report for USEPA, Cincinnati, OH, Jan.1987.

[60] WOLFE, T.A., DEMIRELL, T., BAUMANN, E.A., in Journal of Water Poluution Control Federation, Vol.8, No1, 1986, pp.58-76.

PCP/Clay Isotherms at 23°C

PCP Adsorbed, mg/g

PCP Solution, mg/L

— Untreated   — TMA   — HDTMA   — CP

FIGURE II.D-2-4

Effect of Clay on UCS

Chart: "Effect of Clay on UCS" — X-axis: Clay, %; Y-axis: UCS, GPa; Legend: 1, 3.1, 5.2 % OPC
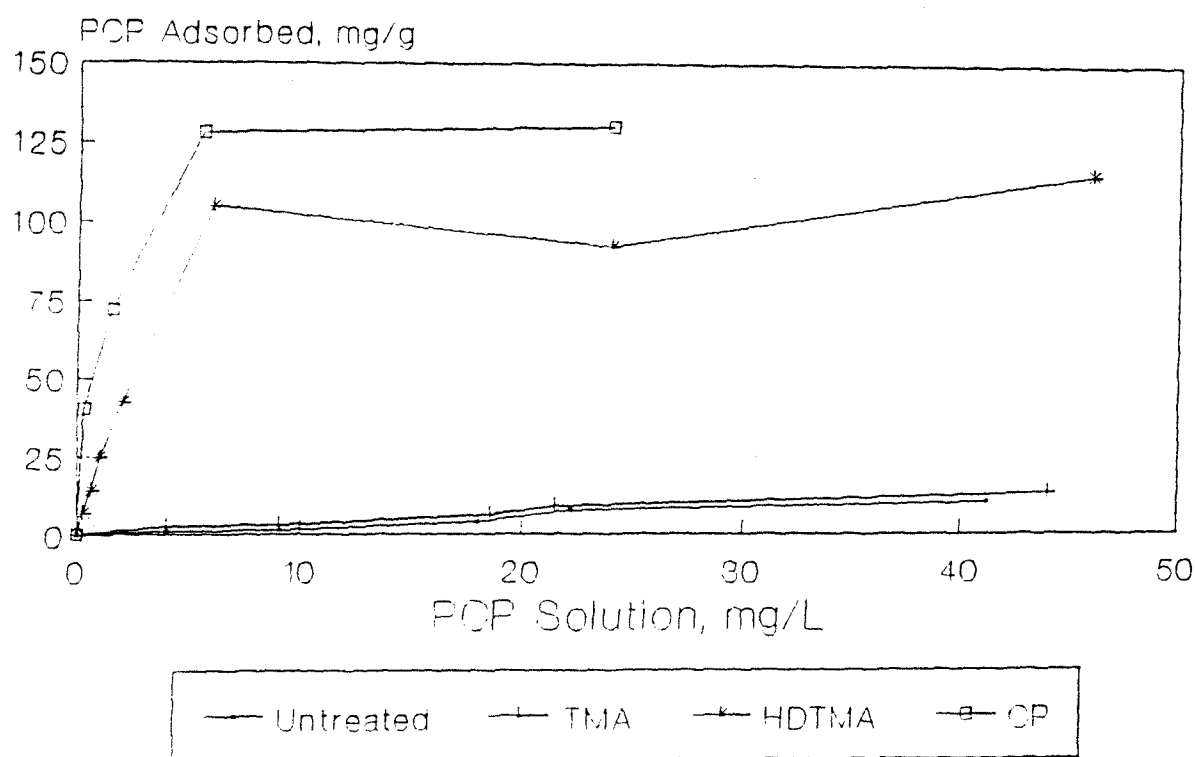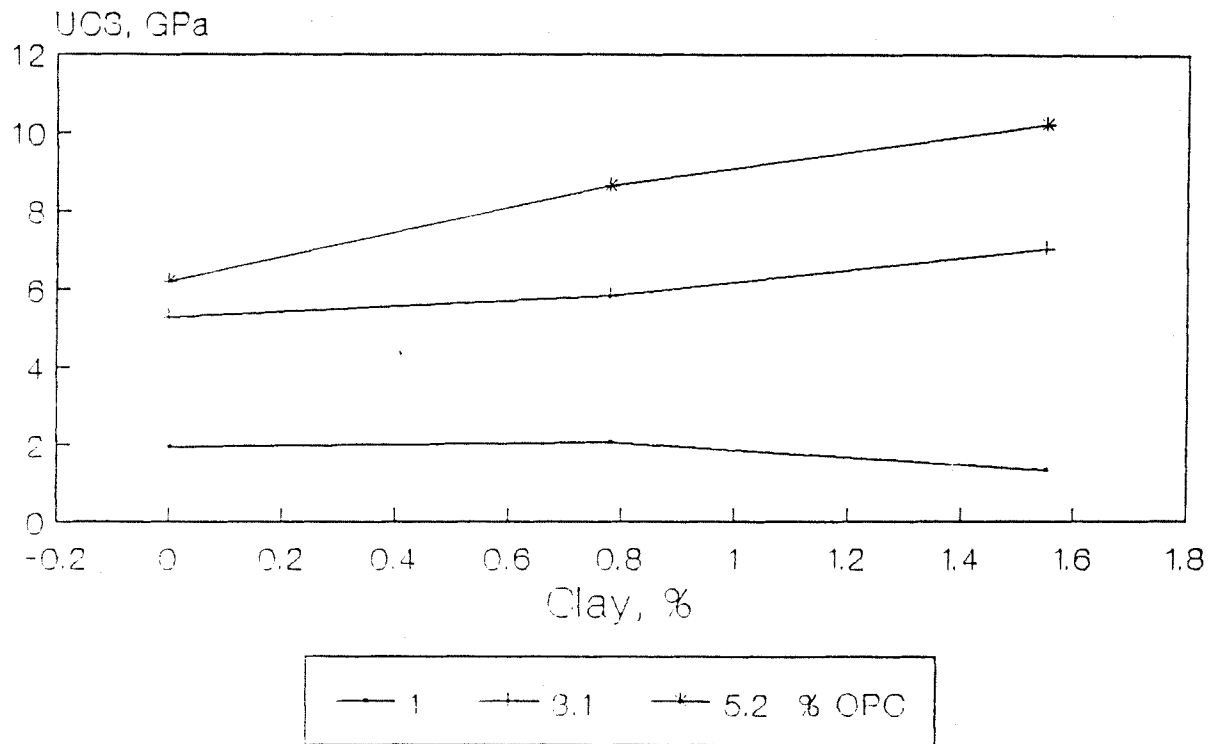
APPENDIX III.A: Fly Ash Analysis: Essential Elements

Fly ash #	SiO2 %	Al2O3 %	Fe2O3 %	CaO %	K2O %	Na2O %	MgO %
1	49.6	25.8	13.8	3.0	3.45	1.0	1.45
2	49.8	27.0	11.8	3.15	3.0	1.05	1.4
3	46.0	27.2	16.1	2.3	3.43	0.92	1.08
4	49.7	29.3	13.8	1.78	2.62	-	0.76
5	47.4	31.9	12.9	1.48	2.67	-	0.66
6	50.1	28.8	13.5	1.47	2.48	-	0.64
7	49.6	30.0	13.2	1.31	2.58	0.70	-
8	50.5	29.1	12.4	1.55	2.69	-	0.70
9							

Fly Ash Analysis: Trace Elements

Fly ash #	c %	Cd ppm	pb ppm	Cr ppm	Ti ppm	Sn ppm	Ni ppm	Mo ppm	Zn ppm
1	1.63	2.1	405	225	7893	1514	231	178	159
2	3.73	7.2	377	222	9073	257	241	113	280
3	1.29	0.34	922	254	10065	64	231	131	242
4	1.52	3.0	482	245	9510	776	262	134	331
5	1.17	5.0	379	325	12933	342	268	157	264
6	1.02	4.8	378	265	12604	376	263	131	258
7	-	5.8	413	278	13205	348	257	162	307
8	-		501		13832	-	289	164	396
9									

SPECTRUM - 025
----

    10 EV/CH
    100. SEC. ACQ. TIME
     TARGET # 5-FE   1000.00 REF.   CTS.

                         UNKNOWN ANALYSIS RESULTS

				CALIB. ENERGY	MEAS. ENERGY	CTS/SEC	PERCENT ERROR
				......	......	....	....
1	AL	(Z=13)	K-ALPHA 1	1.486	1.486	8.195	7.4
2	AL	(Z=13)	K-ALPHA 2	1.485	1.485	4.118	15.1
	AL	(Z=13)				12.31	4.6
3	SI	(Z=14)	K-ALPHA 1	1.741	1.741	55.73	2.1
4	SI	(Z=14)	K-ALPHA 2	1.739	1.739	28.03	4.6
	SI	(Z=14)				83.76	1.2
5	SI	(Z=14)	K- BETA 1	1.829	1.829	2.437	48.0
6	K	(Z=19)	K-ALPHA 1	3.313	3.313	254.0	0.9
7	K	(Z=19)	K-ALPHA 2	3.310	3.310	128.4	2.0
	K	(Z=19)				382.3	0.5
8	K	(Z=19)	K- BETA 1	3.588	3.588	0.1854	340.5
9	K	(Z=19)	K- BETA 3	3.589	3.589	0.6522E-01	3126.4
	K	(Z=19)				0.2506	313.4
10	CA	(Z=20)	K-ALPHA 1	3.691	3.691	299.1	0.8
11	CA	(Z=20)	K-ALPHA 2	3.687	3.687	151.3	1.8
	CA	(Z=20)				450.4	0.4
12	CA	(Z=20)	K- BETA 1	4.012	4.012	46.84	2.3
13	CA	(Z=20)	K- BETA 3	4.013	4.013	17.33	7.1
	CA	(Z=20)				64.17	1.6
14	CR	(Z=24)	K-ALPHA 1	5.414	5.414	34.55	3.0
15	CR	(Z=24)	K-ALPHA 2	5.405	5.405	17.57	6.3
	CR	(Z=24)				52.13	1.8
16	CR	(Z=24)	K- BETA 1	5.946	5.946	34.52	2.6
17	CR	(Z=24)	K- BETA 3	5.947	5.947	14.20	6.6
	CR	(Z=24)				48.72	1.8
18	FE	(Z=26)	K-ALPHA 1	6.403	6.403	1097.	0.4
19	FE	(Z=26)	K-ALPHA 2	6.390	6.390	559.6	0.9
	FE	(Z=26)				1656.	0.2
20	FE	(Z=26)	K- BETA 1	7.057	7.057	150.2	1.1
21	FE	(Z=26)	K- BETA 3	7.058	7.058	63.78	3.0
	FE	(Z=26)				214.0	0.7

MAY 4, 1990

CALIBRATION   025

LINE TARGET	WT. %	OXIDE	%	SEC	REF.CTS.	CPS
CR KA 5 FE	0.029	CR2O3	0.042	100	1000.00	52.12
O	44.706					
AL	21.055	AL2O3	39.783			
FE	13.840	FE2O3	19.788			
K	2.758	K2O	3.334			
SI	16.785	SIO2	35.909			
CA	0.817	CAO	1.143			

CALIBRATION CONSTANT:
CR KA, TARGET 5 = 6.748E+06
               (6.739E+06

MAY 4, 1990

CALIBRATION   025

LINE TARGET	WT. %	OXIDE	%	SEC	REF.CTS.	CPS
FE KA 5 FE	13.840	FE2O3	19.788	100	1000.00	1656.
O	44.706					
AL	21.055	AL2O3	39.783			
K	2.758	K2O	3.334			
SI	16.785	SIO2	35.909			
CA	0.817	CAO	1.143			
CR	288 PPM	CR2O3	422 PPM			

CALIBRATION CONSTANT:
FE KA, TARGET 5 = 2.340E+06
               (2.385E+06)

MAY 4, 1990

CALIBRATION   025

LINE	TARGET		WT. %	OXIDE	%	SEC	REF.CTS.	CPS
AL KA	5 FE		31.055	AL2O3	39.783	100	1000.00	12.31
O			44.706					
FE			13.840	FE2O3	19.788			
K			2.768	K2O	3.334			
SI			16.735	SIO2	35.909			
CA			0.817	CAO	1.143			
CR			288 PPM	CR2O3	422 PPM			

CALIBRATION CONSTANT:
AL KA, TARGET 5 = 3.060E+04
                 (3.124E+04)

MAY 4, 1990

CALIBRATION   025

LINE	TARGET		WT. %	OXIDE	%	SEC	REF.CTS.	CPS
SI KA	5 FE		16.735	SIO2	35.909	100	1000.00	83.76
O			44.706					
AL			31.055	AL2O3	39.783			
FE			13.840	FE2O3	19.788			
K			2.768	K2O	3.334			
CA			0.817	CAO	1.143			
CR			288 PPM	CR2O3	422 PPM			

CALIBRATION CONSTANT:
SI KA, TARGET 5 = 7.037E+05
                 (7.053E+05)

MAY 4, 1990

CALIBRATION 025

LINE	TARGET	WT. %	OXIDE	%	SEC	REF. CTS.	CPS
K KA	5 FE	3.768	K2O	3.334	100	1000.00	382.3
O		44.706					
AL		21.055	AL2O3	39.783			
FE		13.840	FE2O3	19.788			
SI		16.785	SIO2	35.909			
CA		0.817	CAO	1.143			
CR		298 PPM	CR2O3	422 PPM			

CALIBRATION CONSTANT:
K KA, TARGET 5 = 2.362E+06
         (2.388E+06)

MAY 4, 1990

CALIBRATION 025

LINE	TARGET	WT. %	OXIDE	%	SEC	REF. CTS.	CPS
CA KA	5 FE	0.817	CAO	1.143	100	1000.00	450.+
O		44.706					
AL		21.055	AL2O3	39.783			
FE		13.840	FE2O3	19.788			
K		3.768	K2O	3.334			
SI		16.785	SIO2	35.909			
CR		298 PPM	CR2O3	422 PPM			

CALIBRATION CONSTANT:
CA KA, TARGET 5 = 6.394E+06
         (4.591E+06)

95

APPENDIX IV.A-3:True Density of Treated Samples

Fly ash number	true density g/cc	Average g/cc
Fly ash 1		
cube 1	3.32	
2	3.39	3.4
3	3.47	
4	3.46	
Fly ash 2		
cube 1	3.46	
2	3.39	3.4
3	3.42	
4	3.30	
Fly ash 3		
cube 1	3.33	
2	3.34	3.3
3	3.35	
Fly ash 4		
cube 1	3.31	
2	3.32	3.3
3	3.32	
Fly ash 5		
cube 1	3.26	
2	3.35	3.3
3	3.33	
Fly ash 6		
cube 1	3.31	
2	3.34	3.3
3	3.23	
Fly ash 7		
cube 1	3.32	
2	3.28	3.3
3	3.25	
Fly ash 8		
cube 1	3.266	
2	3.263	3.3
3	3.27	

APPENDIX IV C-1: TCLP Test on Treated Samples

| Sample	pH	chromium ppm	cadmium ppm	lead ppm	PCP ppm
Fly ash #1					
cube 1	7.58	0.2	0.9	0.4	70.2
cube 1	7.45	0.2	1.1	0.5	66.7
cube 2	7.55	0.2	0.9	0.4	66.0
cube 2	7.61	0.2	0.8	0.4	64.6
cube 3	7.58	0.2	0.8	0.3	64.3
cube 3	7.48	0.2	1.0	0.4	67.0
Fly ash #2					
cube 1	7.67	0.2	0.8	0.3	59.9
cube 2	7.50	0.2	1.3	0.5	63.5
cube 3	7.63	0.2	1.2	0.4	66.3
Fly ash #3					
cube 1	7.9	0.3	0.8	0.1	67.5
cube 2	7.59	0.3	1.7	0.5	59.2
cube 3	7.6	0.3	1.7	0.5	67.8
Fly ash #4					
cube 1	7.54	0.2	1.4	0.2	69.8
cube 2	7.54	0.1	1.6	0.3	63.1
cube 3	7.54	0.1	1.4	0.2	63.5
Fly ash #5					
cube 1	7.72	0.2	0.5	0.4	64.2
cube 2	7.61	0.1	0.9	0.5	64.8
cube 3	7.74	0.1	0.5	0.4	70.0
Fly ash #6					
cube 1	7.72	0.2	1.1	0.4	65.8
cube 2	7.72	0.2	1.2	0.4	65.2
cube 3	7.72	0.2	1.1	0.4	68.6
Fly ash #7					
cube 1	7.68	0.3	1.5	0.5	65.1
cube 2	7.82	0.3	0.8	0.3	74.3
cube 3	7.79	0.3	1.0	0.3	70.7
Fly ash #8					
cube 1	7.59	0.2	1.7	0.6	64.6
cube 2	7.70	0.2	1.4	0.5	70.4
cube 3	7.56	0.2	1.9	0.7	64.9
Fly ash #9					
cube 1	7.45	0.1	2.2	0.9	74.0
cube 2	7.45	0.1	2.1	0.9	70.4
cube 3	7.48	0.2	2.1	0.8	64.9
Fly ash #9, 2nd extraction.					
cube 1	6.74	0.0	6.0	8.0	8.0
cube 2	6.51	0.0	6.0	7.0	6.0
cube 3	6.70	0.0	6.5	11.5	7.6

APPENDIX IV-C-2:

Chromatogramme of the TCLP extract of
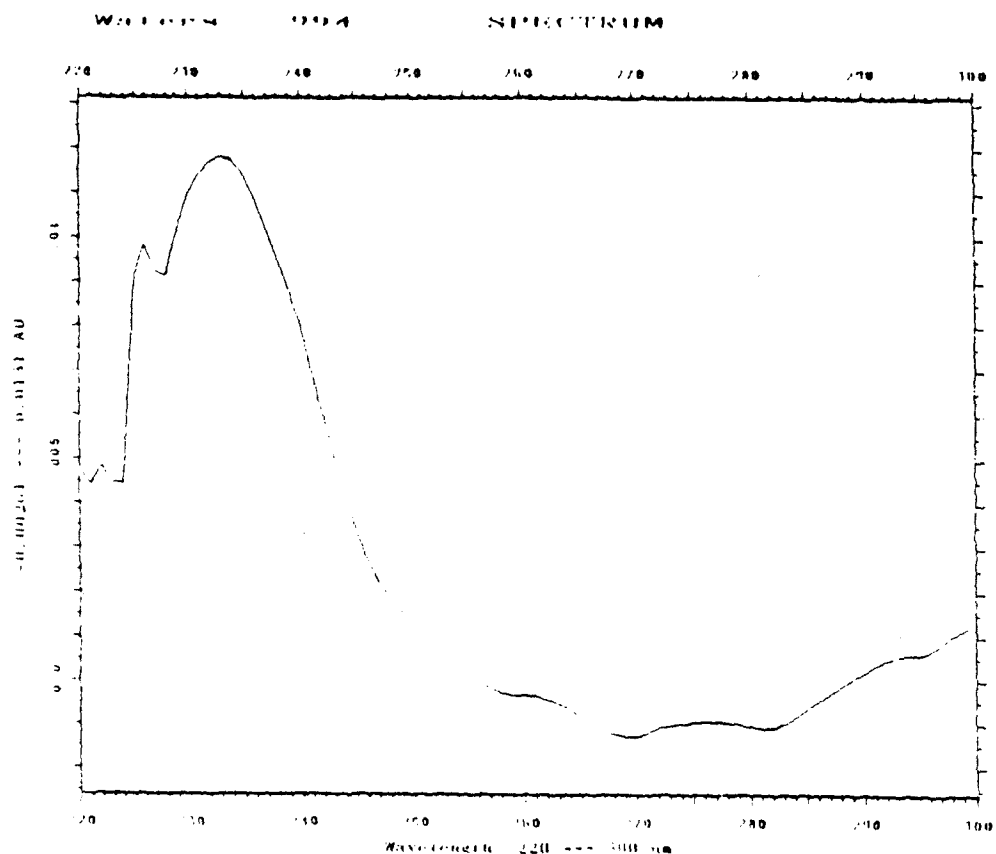treated sample using FA#10   Reading at 230 nm.
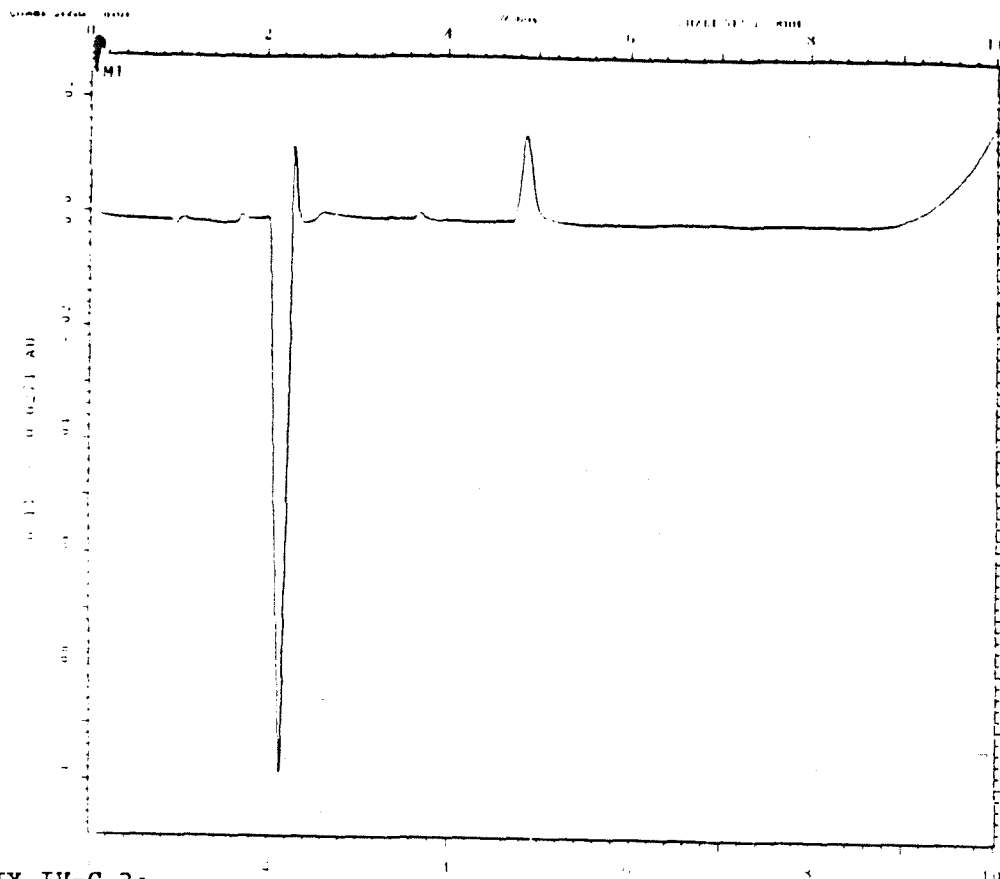
APPENDIX IV-C-3:

Chromatogramme of PCP standard solution.
Concentration 10 ppm. Reading at 230 nm.
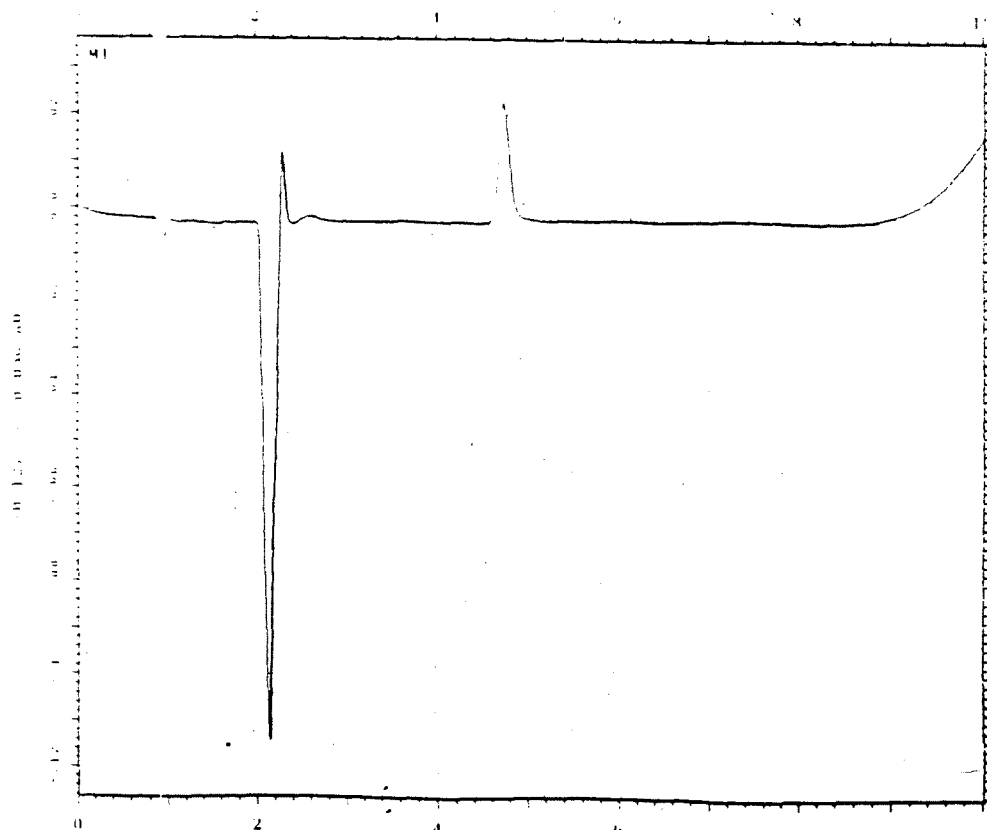
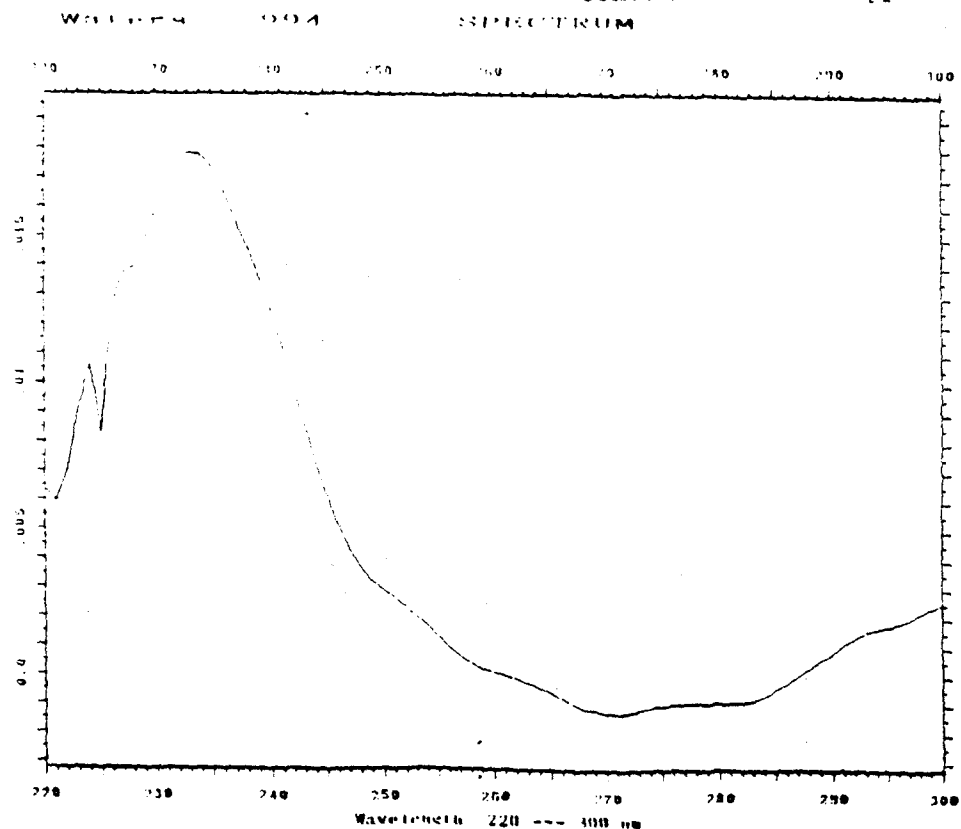# Spectra of the TCLP extract of treated sample using FA#10

APPENDIX IV-C-5:

Spectra of PCP standard solution,

Concentration: 10 ppm

APPENDIX IV.D-1: TCLP on Treated Samples, Experiment IV.

Sample	pH	Cr (ppm)	Pb (ppm)	Cd (ppm)	PCP (ppm)
Ind. Dust	11.43	1.6	14.0	0	0
Ind. dust	11.59	1.6	16.8	0	0
Ind. dust	11.62	1.5	24.0	0	0
"	12.0	1.6	33.2	0	nd
"	12.1	1.7	36.4	0	nd
"	12.0	1.65	33.6	0	nd
"	12.02	1.8	25.8	0	nd
"	12.1	1.5	27.0	0	nd
"	12.0	1.7	26.4	0	nd
no clay(1)	7.26	0.1	0.4	0.55	nd
"	7.43	0.0	0.4	0.6	74.0
"	7.74	0.4	0.1	0.3	71.0
no clay(2)	7.07	0.1	0.4	0.60	63.8
"	7.39	0.05	nd	0.5	72.0
"	8.02	0.0	0.2	0.5	71.0
no clay(3)	7.33	0.0	0.4	0.60	66.7
"	7.65	0.0	0.3	0.3	76.5
"	7.47	0.4	0.3	0.3	76.4
clay(1)	7.02	0.1	0.4	0.65	nd
"	7.3	0.0	0.4	0.6	65.2
"	7.42	0.3	0.3	0.6	71.0
clay(2)	7.10	0.05	0.35	0.6	63.9
"	7.42	0.0	0.5	0.5	74.3
"	7.62	0.3	0.2	0.4	76.0
clay(3)	7.41	0.0	0.3	0.5	76.2
"	7.41	0.0	nd	0.4	nd
"	7.39	0.3	0.3	0.4	79.0
treat.clay(1)	7.18	0.1	0.4	0.6	nd
"	7.46	0.0	0.3	0.5	7.0
"	7.3	0.2	0.3	0.6	7.0
treat,clay(2)	7.12	0.0	0.4	0.5	7.0
"	7.38	0.0	0.5	0.4	7.1
"	7.43	0.3	0.3	0.3	7.0
treat.clay(3)	7.32	0.0	0.4	0.6	7.1
"	7.45	0.0	0.3	0.4	7.5
"	7.33	0.4	0.4	0.4	7.8