INVESTIGATION OF THE CONVERSION OF THE SLUDGE OF HIGH ORGANIC CONTENT INTO ECONOMICALLY VALUABLE PRODUCTS

by

Albert Levi

B.Sc. in Materials Science and Engineering, Sabancı University, 2006

Submitted to the Institute of Environmental Sciences in partial fulfillment of the requirements for the degree of

Master of Science

in

Environmental Sciences

Boğaziçi University

2009

Yollar uzun, dikenli, taşlı olsa da,

Bastığın yer üzüntülerle dolsa da,

Sel, çığ, ateş, önünde her ne olsa da,

İzci gülerek yürür.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my thesis supervisor Prof. Dr. Günay Kocasoy for her teachings, guidance and support throughout my studies and research.

I would like to extend my thanks to my jury members Prof. Dr. Ahmet Demir and Prof. Dr. Ayşen Erdinçler.

I would like to extend my gratitude to Prof. Dr. Yusuf Z. Menceloğlu, Assoc. Prof. Mehmet Ali Gülgün, Asst. Prof. Alpay Taralp, Prof. Dr. Yuda Yürüm and Dr. Burak Birkan from Sabancı University for their teachings and insights on life.

I would like to thank my colleagues and friends Aylin Z. Alagöz, Dr. Merih Ö. Uslu, Savaş Sarıoğlu, Asu Ziylan, Başak B. Daylan, Altuğ Saygılı, Hakkı O. Özhan, Yusuf Eşidir, Gülden Baydar and Ertuğrul Tiryaki for their support throughout my stay in Boğaziçi University.

I also would like to thank Boğaziçi University Research Fund (Project No: 06HY104) for the realization of the research and İncal Mineral Company, Kemerköy Thermoelectric Powerplant, Paşaköy Wastewater Treatment Facility and Persan Perlit for supplying zeolite, fly ash, sludge and perlite used in the research.

I would like to thank my friends Lisya, Nedim, Esti, İzel and all others for their support on helping achieve my greater dreams.

Finally, I would like to thank my family for supporting me with their love and patience through the three years I have spent at Boğaziçi University.

ABSTRACT

Sludge generated from domestic wastewater treatment is used for different purposes such as fertilizer, land reclamation, solid waste stabilization, energy production, composting etc. On the other hand, new areas for sludge utilization are favored for alternative solutions. Solidification/stabilization technique has been investigated widely for final disposal of industrial wastewater treatment plant sludge. Whereas, studies on solidification/stabilization of domestic wastewater treatment plant sludge is limited. Proposed technique in this study not only aimed for the solidification and stabilization of domestic wastewater treatment plant sludge, but also utilization of the product in various construction applications. In order to achieve this goal, solidification/stabilization technique was applied to domestic wastewater treatment plant sludge to obtain products with high unconfined compressive strength and low metal leaching.

Different additives were used in the research in order to achieve the solidification of domestic wastewater treatment plant sludge. Clinoptilolite, a type of zeolite, was preferred for its high cation exchange capacity preventing metal leaching from the solidified samples, and its low price. Class C fly ash, waste of thermoelectric power plant, was used for its self-cementing property. Lime was added in order to enhance the solidification and sludge stabilization. Perlite was used in latter studies in order to benefit from its light weight and thermal insulation property. Sludge was mixed with the additives in varying ratios and cured at different media for different periods.

Objective of the study is to investigate a new area for domestic wastewater treatment plant sludge utilization, such as construction applications. For this purpose, solidification/stabilization of domestic wastewater treatment plant sludge with high organic content, which is not a widely studied process, was achieved with zeolite, fly ash, lime and perlite. The products obtained have high unconfined compressive strength values and low metal leaching which indicates the applicability of the products in construction applications.

ÖZET

Evsel atıksuların arıtılması sonucu oluşan çamurlar, gübre, toprak iyileştirmesi, katı atık stabilizasyonu, enerji üretimi, kompost gibi çeşitli alanlarda kullanılmaktadır. Öte yandan, arıtma çamurlarının kullanımı için alternatif yöntemler de araştırılmaktadır. Endüstriyel atıksulardan elde edilen arıtma çamurlarının solidifikasyon/stabilizasyonu geniş bir şekilde incelenmiş olmasına rağmen, evsel atıksuların arıtılmasından oluşan yüksek organik içerikli arıtma çamurlarının solidifkasyon/stabilizasyon çalışmaları oldukça sınırlıdır. Bu çalışmada önerilen yöntem, sadece evsel arıtma çamurlarının solidifikasyon ve stabilizasyonu değil, aynı zamanda elde edilen ürünün inşaat sektöründe kullanımını sağlamaktır. Bu amaç doğrulutusunda, evsel arıtma çamurları yüksek serbest basınç dayanımına ve düşük metal sızıntısına sahip ürünler elde etmek için solidifikasyon/stabilizasyon yöntemine tabi tutulmuştur.

Arıtma çamurlarının solidifikasyon ve stabilizasyonunu sağlamak için farklı maddeler kullanılmaktadır. Yüksek katyon değişim kapasitesine sahip doğal bir madde olan -zeolit-klinoptilolit, termoelektrik santralin atıklarından olan C tipi uçucu kül ile kireç ve perlit, evsel arıtma çamurlarıyla değişik oranlarda karıştırıldıktan sonra farklı ortamlarda ve sürelerde bekletilerek çamurların katılaştırılması sağlanmıştır.

Bu çalışmanın amacı, evsel arıtma çamurları için inşaat sektörü gibi yeni bir kullanım alanı araştırmaktır. Bu amaçla, katılaştırılarak elde edilen ürünlerin yüksek serbest basınç mukavemeti ve düşük metal sızdırma değerleri, ürünlerin inşaat uygulamalarında kullanılabileceğinin göstergesidir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS/ABBREVIATIONS

Symbol	Explanation
AQ	Aquarium
FA1	Fly ash whose characteristics are given at Table 3.4
FA2	Fly ash whose characteristics are given at Table 3.5
FA3	Fly ash whose characteristics are given at Table 3.5
FA4	Weight equivalent mixture of FA2 and FA3 whose characterisics are given at Table 3.5
HR	Humid room
RT	Room temperature
TCLP	Toxicity Characteristic Leaching Procedure
UCS	Unconfined compressive strength
Weight Stab.	Weight stabilization

1. INTRODUCTION

Domestic wastewater treatment systems, which are aiming the prevention of environmental pollution from contaminants of wastewater, are causing humanity to face another environmental pollutant, sludge. The high amount of sludge generated having high concentration of pollutants cause significant environmental pollution. Solutions must be found in order to eliminate/prevent the pollution problems caused by the sludge generated at wastewater treatment plants (Epstein, 2003).

Domestic wastewater is treated in several steps both physically and chemically in wastewater treatment plants. In preliminary treatment large objects are removed. Then in the primary treatment unit, floating and settled solids are removed from wastewater. In some cases, advanced primary treatment is applied, which is a chemical process, in order to enhance the suspended solid removal. In the secondary treatment, chemical and biological processes are applied in order to remove suspended solids and organic matter. Finally in advanced treatment dissolved solids in addition to suspended materials that are left over are removed (Tchobanoglous et al., 2003).

Sludge generated at the domestic wastewater treatment plants may contain different types of contaminants in different concentrations. The content of the sludge of primary treatment accumulated at the sedimentation tank is mainly organic solid material. The sludge generated at the secondary treatment which settles after aeration contains microscopic biological material. The sludge generated at the advance treatment consists of various nutrients such as nitrogen and phosphorus. The sludge generated at different processes/units of wastewater treatment are collected together for treatment or stabilization prior to disposal (FAO, 1992).

Domestic wastewater treatment plant sludge is composed of water and various solids. As being the by-product of domestic wastewater treatment, sludge contains pathogens and heavy metals, in addition to nutrients and organic materials. Presence of these components creates a significant threat to the environment. If not treated or stabilized properly before disposal, microbial activity or heavy metal settling may continue at the disposed areas

causing environmental problems such as odor, metal leaching, groundwater pollution (Morisson, 1981; Rubin et al., 1991; Rodger et al, 1992; Filibeli and Ayol, 2008).

Alternative uses for sludge utilization can be listed as raw material for fertilizers, land reclamation, stabilization of solid waste, energy production by incineration and methane production by anaerobic treatment process (Sopper, 1993; Güleç, 1999; Çınar, 2001; Sangwan et al., 2008). In addition to these available systems, sludge can be used as an additive in construction applications after stabilization/solidification (S/S) process. Thus, the amount of the sludge to be disposed will be reduced. This can be achieved by solidification/stabilization techniques (Spence and Shi, 2005).

S/S techniques are used as pre-landfilling waste treatment technology. S/S processes consist of mixing wastes such as sludge, contaminated soil, etc. with binder materials for the enhancement of physical properties and immobilization of contaminants. This way, the sludge can be disposed safely. In S/S processes, different organic or inorganic binder materials can be used according to the needs of the waste and S/S process. Some of the binders may be listed as Portland cement, gypsum, polymers, lime, etc. Most common S/S process is the cement-based process. Even though, it is the most common process, the costs of additives such as cement causes researches investigating for alternative additives and methods. S/S techniques can also generate new research areas such as investigation of the beneficial usage rather than disposal of the solidified/stabilized sludge (Balkan, 1999; Spence and Shi, 2005; Tiryaki, 2005).

Researches about the S/S processes of sludge generally deal with industrial sludge. S/S studies conducted with domestic wastewater treatment sludge are limited. Therefore, it is significant to conduct researches on S/S of domestic wastewater treatment sludge for alternative usages of sludge, such as construction applications.

In this research, different natural materials were investigated for their efficiency in the treatment of domestic wastewater treatment plant sludge. Moreover, the applicability of producing products that can be used in construction applications was investigated by mixing different ratios of different natural pozzolanic materials with domestic wastewater treatment plant sludge.

Pozzolanic materials are those which show cementitious properties when they react with calcium hydroxide. They are usually used to strengthen cement. Pozzolanic materials are vitreous siliceous materials which form calcium silicates in addition to other cementitious materials such as calcium aluminate, calcium ferrite, etc. Fly ash, silica fume, blast furnace slag, zeolite are some of the widely used pozzolanic materials (Mehta, 1983).

Within the scope of the research, the pozzolanic materials such as zeolite and fly ash were mixed with domestic wastewater sludge and lime in order to solidify/stabilize the sludge. Natural product clinoptilolite, a kind of natural zeolite, was used in order to benefit from its porous structure and for its high cation exchange capacity. Usage of fly ash in construction applications and waste management makes it a good choice as a binder (Biernacki et al 2008; Erol et al, 2008).

Perlite, which is an amorphous volcanic rock, is mixed with other additives in order to decrease the weight as well as increasing the thermal properties of the solidified product. Due to its porous structure upon heating, perlite is also used in construction applications for insulation purposes (Demirboğa and Gül, 2003; Demir and Başpınar, 2008).

Prepared samples were tested for their unconfined compressive strength (UCS) and leaching potential. Optimum mixture of domestic wastewater treatment sludge, zeolite, fly ash, perlite and lime ratios were determined accordingly.

Following the determination of the optimum ratios of mixtures yielding high UCS values, Toxicity Characteristic Leaching Procedure (TCLP) test was applied to evaluate the performance of the S/S process towards metal leaching. Finally, potential areas of usage for the S/S processed domestic wastewater treatment sludge were investigated.

2. LITERATURE REVIEW

2.1. Sewage Sludge

Domestic wastewater, generated from residences, commercial properties and agricultural areas, contains a wide range of pollutants. In order to minimize the impact of wastewater on environment domestic wastewater treatment systems are set up. Wastewater treatment is applied both physically and chemically in several units in treatment plants. In preliminary treatment of wastewater large objects that may damage the system are removed. In primary treatment, some of the floating and settled solids are removed from wastewater. In some cases, advanced primary treatment is applied by addition of chemicals in order to enhance the suspended solid removal. In the secondary treatment, chemical and biological processes are applied in order to remove suspended solids and dissolved organic matter. Finally in advanced treatment dissolved solids in addition to suspended materials that are left over are removed (Tchobanoglous et al., 2003).

Materials that are removed during the treatment of domestic wastewater are called sludge. Sludge, by-product of domestic wastewater treatment, contains contaminants which are generally hazardous. Sludge is generated in various stages of the wastewater treatment. In the primary treatment, sludge, containing mainly organic solid material, is accumulated at the sedimentation basin. In the secondary treatment, settled sludge contains microscopic biological material while the sludge generated in advanced treatment is rich in nutrients such as nitrogen and phosphorous. Sludge generated in different units of the treatment plant is not handled separately but collected together for their treatment/disposal (Tchobanoglous et al., 2003; Filibeli and Ayol, 2008).

After treatment, sludge can either be disposed by landfilling, lagooning, incineration, or it can be reused. These disposal options may cause soil or air pollution. There are several reuse options for sewage sludge such as usage as fertilizers in agricultural activities, composting and in land reclamation (Tchobanoglous et al., 2003; Filibeli and Ayol, 2008; Jamali et al., 2008; Carbonell et al., 2009; Hermann et al., 2009).

2.1.1. Characteristics of Sewage Sludge

Characteristics of sewage sludge are significantly affected by factors such as:

- source and quality of the wastewater,
- types of treatment,
- extent of treatment processes,
- process modes – use of chemicals and
- methods of stabilization (Epstein, 2003).

Sewage sludge contains different kinds of pesticides, chemicals, high concentrations of minerals, especially phosphates and nitrates, and human waste. It is also high in organic content, due to food waste. Industrial pollutants and some heavy metals are also present, which can be a health risk if not kept within the limits (Dean and Suess, 1985; FAO, 1992).

Usage of sewage sludge as fertilizers in land applications brings both advantages and risks for the soil. Presence of nitrogen and phosphorous ions in addition to potassium, calcium, magnesium and iron ions in sewage sludge makes it a good alternative as a fertilizer (Logan et al., 1997; Filibeli and Ayol, 2008). On the other hand, pathogenic bacteria, viruses and protozoa content of sewage sludge may cause health hazards to humans, animals and plants. Therefore, the hazardous content of sludge should be reduced prior to its application at agricultural activities (FAO, 1992; Baveye et al., 1999).

Sludge also contains trace amount of heavy metals such as arsenic, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, selenium and zinc. Most of these heavy metals have health risks to animals, plants and humans at high concentrations and some are toxic even at low concentrations (Rubin et al., 1991; Epstein, 2003). According to a research conducted to compare the heavy metal content of different materials used as fertilizer, it was found out that rock phosphate has the highest concentration of heavy metals. Sewage sludge is the next one in the ranking. The ranking of heavy metal concentration of materials used in the research was found as: rock phosphate > sewage sludge > commercial phosphate fertilizer > organic amendments and liming material > commercial K fertilizer > commercial N fertilizer (Raven and Loeppert, 1997).

According to the EU Directive "on the protection of environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC)" states that the data about the sludge parameters enlisted below should be recorded systematically:

- dry matter (%), organic matter (% dry solids),
- pH,
- total and ammoniacal nitrogen, total phosphorus (% dry solids),
- copper, nickel, zinc, cadmium, lead, mercury and chromium (mg/kg dry solids) (Council of the European Communities, 1986).

Limit values for the parameters listed above are determined by national environmental agencies.

For sludge to be used in agricultural activities heavy metal concentration limits have been set by Council of the European Communities Directive 86/278/EEC (Table 2.1). Limit values for only the metals listed in the Table 2.1 are given for sludge to be used in agricultural activities. Limit values for other metals are not presented in the Directive.

Table 2.1. Limit values for heavy metal concentrations in sludge for use in agriculture (Council of the European Communities, 1986).

Parameter	Limit Value (mg/kg of dry matter)
Cadmium	20-40
Copper	1000-1750
Nickel	300-400
Lead	750-1200
Zinc	2500-4000
Mercury	16-25

2.1.2. Sludge Treatment and Disposal

Taking the hazardous and toxic characteristics of sludge into consideration, several techniques for sludge treatment have been developed. These techniques aim to reduce the toxicity and health hazard risks, as well as providing long term storage possibility.

Different sludge treatment techniques used in the UK in order to reduce health hazards of sludge to be used in agricultural activities are as follows:

- Sludge Pasteurization: Minimum of 30 minutes at 70°C or minimum of four hours at 55°C (or appropriate intermediate conditions), followed in all cases by primary mesophilic anaerobic digestion.
- Mesophilic Anaerobic Digestion: Mean retention period of at least 12 days primary digestion in temperature at the range of 35 ± 3°C or at least 20 days primary digestion at the temperature range of 25 ± 3°C followed in each case by a secondary stage of a mean retention period of at least 14 days.
- Thermophilic Aerobic Digestion: Mean retention period of at least seven days digestion. All sludge should be subject to a minimum of 55°C for a period of at least four hours.
- Composting (Windrows or Aerated Piles): The compost must be maintained at 40°C for at least five days and for four hours during this period at a minimum temperature of 55°C within the body of the pile followed by a period of maturation adequate to ensure that the compost reaction is substantially complete.
- Lime Stabilization of Liquid Sludge: Addition of lime to raise pH to a value greater than 12.0 and sufficient to ensure that the pH is not less than 12.0 for a minimum period of two hours. The sludge can then be used directly.
- Liquid Storage: Storage of untreated liquid sludge for a minimum period of three months.
- Dewatering and Storage: Conditioning of untreated sludge with lime or other coagulants followed by dewatering and storage of the cake for a minimum period of three months. If sludge has been subject to primary mesophilic anaerobic digestion, storage should be for a minimum period of 14 days (Department of Environment-UK, 1989).

Sludge can be used in agricultural applications or disposed according to the treatment process it undergoes. Due to different preferences/priorities in waste minimization in different countries, disposal methods show differences. For example, in Greece 97% of sewage sludge is landfilled, whereas only 8% of sludge is landfilled in the USA. Sewage sludge generation rates in the European Union member countries and the United States and the different disposal techniques applied are given in Table 2.2 (USEPA, 1999).

Table 2.2. Sewage sludge generation rates and disposal methods (USEPA, 1999).

Country	Amount (million tons dry solids/year)	Disposal Method (%)			
		Application to land	Landfilling	Incineration	Other
Austria	320	13	56	31	0
Belgium	75	31	56	9	4
Denmark	130	37	33	28	2
France	700	50	50	0	0
Germany	2500	25	63	12	0
Greece	15	3	97	0	0
Ireland	24	28	18	0	54
Italy	800	34	55	11	0
Luxembourg	15	81	18	0	1
Holland	282	44	53	3	0
Portugal	200	80	13	0	7
Spain	280	10	50	10	30
Sweden	180	45	55	0	0
Switzerland	215	50	30	20	0
UK, 1991	1107	55	8	7	30
United States	6900	41	17	22	20

2.1.3. Sewage Sludge in Turkey

When the amount of sludge generation in Turkey is investigated, it is observed that there is not much reliable data about the amount, composition and the disposal methods of sludge. The limited data was just obtained from the Turkish Statistical Institute (TÜİK). According to the Environmental Statistics Report in 2007, the amount of the treated wastewater is 2141 Mm^3/year. It is also mentioned that the ratio of the population served by wastewater treatment plants is only 42% of the total population. Table 2.3 shows the amount of the treated wastewater and the generated sludge (TÜİK, 2007; Filibeli and Ayol, 2008; TÜİK, 2008). In addition, the increase in population causes increase in wastewater generation, consequently the number of the wastewater treatment plants and the amount of the sludge generated will increase.

The characteristics of sewage sludge vary according to the source and the wastewater treatment processes applied. Table 2.4 shows that the metal concentrations of sewage

Table 2.3. Amount of sludge production in different treatment processes in Turkey (TÜİK, 2007).

Wastewater Treatment Process	Treated Wastewater (Mm^3/year)	Sludge Production (25% dry matter, m^3/year)
Physical	714	0.051
Biological	927	0.086
Advanced	500	0.129
TOTAL	2141	0.266

Table 2.4. Metal concentrations of sewage sludge from different wastewater treatment plants in Turkey.

	Concentration (mg/kg dry matter)				
Treatment Plant / Parameter	İzmir (IZSU, 2007)	Kayseri, (KASKI, 2005)	Malatya, (MASKI, 2007)	Ankara, (ASKI, 2007)	Limit Values (ÇOB, 2005a)
Pb	85.96	201	28.6	82.7	1200
Cd	3.41	6.5	1	2.6	40
Cr^{+3}	200.96	732	90	216	1200
Cu	305.64	521	106	185.5	1750
Ni	73.26	309.5	41	93.5	400
Hg	<1	1.2	0.66	3.8	25
Zn	1017.4	1552	448	1887	4000

sludge of different wastewater treatment plants around Turkey. When Table 2.4 is evaluated, it is observed that the metal concentrations of the wastewater treatment plant sludges show significant variations. In some cases, metal concentrations from different treatment plants may differ 7-8 times. Nevertheless, all metal concentrations are within the limits of Soil Pollution Control Regulation of Turkey (ÇOB, 2005b).

Sludge generated from domestic wastewater treatment plants remains as a significant environmental issue worldwide. Different treatment methods such as pasteurization, aerobic or anaerobic digestion, stabilization, dewatering and storage as final disposal are temporary solutions to this problem. Use options such as composting are used worldwide, but public prejudice on health concerns remains as a problem. Therefore, alternative use options for domestic wastewater treatment plant sludges should be investigated.

2.2. Solidification/Stabilization

Solidification/stabilization (S/S), or stabilization/solidification which are used interchangeably, is a process that involves mixing of sludge with binder materials in order to reduce leachability of the pollutants both physically and chemically and to convert the hazardous waste into environmentally acceptable form, which may be disposed or used as construction material (PCA, 2008). Most important strategies for S/S technologies are;

1. to treat waste or contaminating pollutants of the sites to the possible extent,
2. to obtain chemically inert and non-leachable solidified products to the possible extent,
3. to be economical (Spence and Shi, 2005).

Stabilization is the techniques used chemically to reduce the potential hazards of waste by converting them into less soluble, mobile or toxic forms. Whereas, solidification is encapsulating the waste, possibly forming solid material such as clay-like material, granular particulate or some other forms of solid. It does not involve any chemical reaction (Conner and Hoeffner, 1998).

S/S technologies have been used since 1950s starting with the treatment of radioactive wastes. On the other hand, regulations on S/S were passed only at 1970s, after Chemfix Inc. patented S/S system using sodium silicate and Portland cement for mine drainage sludge. In the same years, similar studies were conducted by Conversion System Inc., Dravo Corporation, etc. (Spence and Shi, 2005). After Resource Conservation and Recovery Act (RCRA) was published in the USA in 1976, researches on S/S increased tremendously. Primary goals of RCRA are as to;

- protect human health and the environment from the potential hazards of waste disposal,
- conserve energy and natural resources,
- reduce waste,
- ensure that wastes are managed in an environmentally-sound manner (USEPA, 2007).

In addition, S/S is considered as the best treatment technology for 57 hazardous wastes by US EPA (1993).

2.2.1. Solidification/Stabilization Processes

2.2.1.1. Inorganic Processes. Inorganic processes are classified as cement-based and pozzolanic processes. They are explained in the following section.

In cement-based S/S processes the main ingredients are Portland cement and industrial sludge with various additives. The main target of the process is the stabilization and solidification of sludge containing heavy metals. During the process, high pH of the cement mixture either keeps metals as insoluble hydroxides and carbonate salts or causes metals to mix with the cement matrix as metal ions. Solidified products are usually landfilled (Liu et al., 1997).

Clay, vermiculite (a type of zeolite) and soluble silicate may be used as additives in order to improve the physical characteristics and decrease of the leaching properties of the solidified sludge (Liu et al., 1997).

Advantages of cement-based processes can be summarized as:

- readily available mixing equipment,
- relatively simple process and
- suitable for sludge containing metals (USEPA, 1980).

Disadvantages of the process are:

- suspension of solids, but not chemically bounding, therefore subject to leaching,
- expensive additives,
- increase in waste volume,
- requirement of secondary containment of solidified product and
- incompatibility with many wastes (USEPA, 1980).

The efficiency of pozzolanic process depends on the reaction of lime with siliceous material and water in order to solidify the sludge. Most common materials for the process

are fly ash, ground blast furnace slag and cement kiln dust. All these materials are by-products of other processes which are also considered as waste and have to be disposed or reused. Mixture of these additives with sludge, which is to be stabilized/solidified, also strengthen the final product and help reducing the leaching of contaminants (Liu et al., 1997).

Advantages of pozzolanic S/S processes are:

- its low cost,
- having readily available mixing equipment and
- suitability for the wastes such as metals, oil and solvents of power plants and industries (USEPA, 1980).

Disadvantages of pozzolanic S/S processes are:

- the increase in waste volume,
- possibility of leaching and
- requirement of secondary containment for final disposal (USEPA, 1980).

2.2.1.2. Organic Processes. Organic processes are classified as thermoplastic and organic polymer processes. They are explained in the following section.

Thermoplastic stabilization techniques are initially used for the stabilization of radioactive wastes and for handling industrial wastes. In this process (generally called as bitumen process), dried waste is mixed with bitumen, paraffin or polyethylene at temperatures above 100°C. During cooling, the mixture solidifies as well. Prior to disposal, the solidified mixture is placed in a steel drum or a thermoplastic coating (Liu et al., 1997).

A variation of bitumen process, mixing asphalt emulsion with wet sludge, is conducted at lower temperatures than bitumen process. But, the emulsion-waste mixture must be dried prior to disposal (Liu et al., 1997).

Advantages of thermoplastic S/S processes can be summarized as:

- causing less increase in volume of product produced with respect to inorganic processes,

- reduced leaching with respect to inorganic processes and
- suitability for radioactive and some industrial wastes (USEPA, 1980).

On the other hand, disadvantages of thermoplastic processes are:

- necessity to dry the wastes before S/S processes,
- high equipment cost,
- high energy cost,
- necessity of trained personnel,
- incompatibility with oxidizers, grease and chelating/complexing agents and
- requirement of secondary containment (USEPA, 1980; Liu et al., 1997).

In the organic polymer process, waste or sludge is mixed with the monomers prior to the addition of catalyst. The solution is mixed until catalyst disperses. By the time, the mixture starts to harden, and consequently a spongy polymer mass forms. This mass physically entraps the waste. After the S/S process, the polymer may be dried and disposed. Several polymers such as urea formaldehyde, polybutadiene, polyester, epoxy and polyethylene may be chosen for organic polymer S/S processes. Among these, urea formaldehyde is the most commonly used polymer.

Advantages of organic polymers in the S/S processes are:

- suitability for insoluble solids due to entrapment in polymer matrix and
- high rate of success in limited applications (USEPA, 1980).

Whereas, disadvantages of the process are:

- probability of leaching due to physical entrapment of wastes instead of chemical bounding,
- risk of production of strong acidic leach water,
- necessity for special equipment and operators,
- corrosivity of some of the catalysts used,
- risk of production of harmful gases,
- incompatibility with oxidizers and some organics and

- probability of decomposition of some of the S/S agents, such as resins, by time (USEPA, 1980).

Some of the studied binding materials for S/S systems are listed in Table 2.5.

Table 2.5. List of binders used for S/S (Spence and Shi, 2005).

Inorganic Binders	Organic Binders
Portland cement	Bitumen
Portland slag cement	Urea formaldehyde
Portland pozzolan cement	Polybutadiene
Portland cement - silicate system	Polyester
Polymer modified cemet	Epoxy
Masonary cement	Polyethylene
Lime-pozzolan cement	
Calcium aluminate cement	
Alkali-activated slag cement	
Alkali-activated pozzolan cement	
Phosphates	
Gypsum	
Sulfur polymer cement	
Alkali silicate minerals	

2.2.2. Testing for Solidification/Stabilization Processes

The products of S/S processes can be evaluated with different tests, both physically and chemically. In general, these tests determine the characteristics such as compressive strength, permeability, durability, density and leachability of the S/S products.

2.2.2.1. Physical Tests. Physical tests are conducted to characterize the materials used in S/S processes, such as fly ash, zeolite, etc. as well as the specifications of the products. These tests are classified in five groups such as;

- Index property testing,
- Density testing,

- Permeability testing,
- Strength testing,
- Durability testing (USEPA, 1980; USEPA, 1989).

Index property tests are applied to raw sludge and other additives of the S/S process in order to determine the feasibility of the S/S processes. These tests are conducted in order to understand the physical properties of the materials, both waste and additives, used in the processes (USEPA, 1989).

Particle size analysis (ASTM D422-63) determines the texture and the uniformity of the particles. Quantitative analysis helps to classify the materials and make predictions on various characteristics as permeability, compressibility, etc. of the product (USEPA, 1989).

Atterberg limits (ASTM D4318-84) are used to characterize and classify the clay used in ceramics. The results of the technique are used to estimate compressibility, strength and swelling characteristics as well as the behavior of the clay under stress (USEPA, 1989).

Moisture content (ASTM D2216-80) determines the amount of free fluid in a given material. The results indicate the necessity of pretreatment of the waste, such as drying, dewatering or consolidation of sludge (USEPA, 1989).

Suspended solids (USEPA Method 208C) indicate the quality of the wastewater to be processed. Thus, the method/process to be applied for handling the wastewater would be determined (USEPA, 1989; Tchobanoglous et al., 2003).

Paint filter tests (USEPA Method 9095-SW846), which is a requirement of RCRA, are used to determine the release of free liquids. This test is important to control if any free liquid would escape under compressive force (USEPA, 1989).

Density testing is applied in order to determine the bulk density of the materials. Bulk density in addition to moisture content and specific gravity can be used to calculate

material porosity. It is also important for the comparison of the unstabilized and stabilized waste, in order to determine the porosity of the solidified product (USEPA, 1989).

Permeability testing, also known as hydraulic conductivity, is a measure of resistance of the product against the passage of water. It is an estimation of quantity and flow rate of water from the saturated waste or product. Two different types of permeability tests are available: falling-head permeability and constant-head permeability (EPA Method 9100-SW846). In falling head permeability method, specimens are placed in a pressurized water chamber. In constant-head permeability method, specimens are placed in a water bath and connected to water in an air-free glass tube, in which water flows by gravity (USEPA, 1989).

Strength testing evaluates how a material will respond to mechanical stress created by overload. There are different strength testing methods such as unconfined compressive strength of cohesive soils (ASTM D2166-85), unconfined compressive strength of cylindrical cement specimens (ASTM D1633-84), flexural strength (ASTM 1635-87) and cone index (ASTM D3441-79). Use of different tests changes according to the type of the material used in the solidification process (USEPA, 1989).

Unconfined compressive strength (UCS) of cylindrical cement specimens' test which was used in this research is conducted for stabilized cement-like wastes. The results of the tests give information about the ability to withstand overload. The optimum water to binder ratios (in this research sludge to binder ratios) may be determined according to results of the tests, as well. Cylindrical specimens prepared should be cured for different durations (generally 1, 7, 14 and 28 days) in an environment with 100% humidity. UCS test is conducted by compression testing machine which can control the rate of the stress applied (USEPA, 1989).

Durability tests evaluate the resistance of stabilized/solidified material to external environmental stresses, such as temperature and moisture. Freeze and thaw test (ASTM D4842) is applied to observe the effects of change in temperature, while wetting and drying test (ASTM D4843) is applied to determine the effect of moisture on the solidified waste. These tests indicate the mechanical property of the solidified waste material. Other

physical tests explained above may be used after cycles of durability tests in order to examine the effects of the durability tests on the solidified products (USEPA, 1989).

2.2.2.2. Chemical Tests. Chemical tests conducted in order to evaluate the performance of stabilized/solidified waste are called the leaching tests. There are different leaching tests according to the applied process as well as the characteristics of the waste. The most common leaching test methods are listed below:

- Toxicity characteristic leaching procedure (TLCP)
- Extraction procedure toxicity test
- California waste extraction procedure
- Multiple extraction procedure
- Monofill waste extraction procedure
- Equilibrium leach test
- Acid neutralization capacity
- Sequential extraction test
- Sequential chemical extraction test
- Materials characterization center static leach test
- American Nuclear Society leach test
- Dynamic leach test (USEPA, 1989).

Among the listed methods, TLCP was used in the research. In this method, waste is pulverized into grain size of 9.5 mm or less. According to the buffering capacity and the alkalinity of the waste, two different acetate buffer solutions may be used, one having a pH of 5 and the other having a pH of 3. The buffer solutions are mixed with the pulverized waste with a liquid:solid ratio of 20:1. The mixture is agitated with a rotary tumbler at 30 rpm for 18 hours. Then the leaching solution is filtered for analysis (USEPA, 1989).

2.3. Zeolites

Zeolites are microporous crystalline, hydrated aluminosilicates containing exchangeable cations of Group IA and Group IIA elements, which are also referred as extraframework cations. Zeolites are in tetrahedral structure, TO_4. T represents aluminum and silicon cations. As Al^{+3} are introduced into the system, the structure becomes

negatively charged. To neutralize the structure, extraframework cations, such as sodium, potassium, magnesium, calcium, strontium, barium, are introduced to the zeolite structure. The empirical formula of a zeolite can be represented as follows (Barrer, 1978; Şahin, 1996; Tiryaki, 2005):

$$M_{2/n}O \cdot Al_2O_3 \cdot x\ SiO_2 \cdot y\ H_2O$$

where;
M: extraframework cation
n: valance of extraframework cation
x and y: mole fractions

The ion exchangable property of the extraframework cations gives rise to high ion exchange capacity of zeolites.

Even though Si/Al ratio can vary from one to infinity, ratios below two are not favored due to the electrostatic repulsion between two adjacent AlO_4^- tetrahedra. In addition, as the Si/Al ratio of the structure increases, the hydrothermal stability and hydrophobicity of zeolites increase (Barrer, 1978).

The structure of zeolites has channels and interconnected voids which are occupied by extraframework cations and water molecules. The sorbed water in zeolites may be removed by thermal treatment applications, which create intercrystalline voids. This application increases the ion exchange capacity of the zeolites.

2.3.1. History of Zeolites

Zeolites are naturally occurring minerals that are formed when ash from the volcano eruptions settled in lakes million years ago. The saline/alkaline characteristics of the lakes caused variations in the composition of zeolites.

Even though, it is believed that zeolites were first used by Romans before Common Era for water purification, the modern discovery of zeolites dates back to 1756 when Swedish mineralogist Freiherr Axel Fredrick Cronstedt examined a kind of zeolite, stilbite,

and found out that gas bubbles were released when the mineral was heated. Thus, the name zeolite, “zeo” meaning “to boil” and “lithos” meaning “stone”, was given to the mineral (Mumpton, 1977; ZEO-TECH Corp., 2008).

Studies on zeolites have been conducted for more than 250 years now. The zeolite types that have been discovered are presented in Table 2.6. On the other hand, studies on zeolites just go back to 1950s, right after Richard Maling Barrer conducted the preliminary research on zeolites in 1940s (Magic Mineral, 2008).

Table 2.6. Dates of discovery of some zeolites (Barrer, 1978).

Zeolite	Date	Zeolite	Date
Stilbite	1756	Mordenite	1864
Natrolite	1758	Clinoptilolite	1890
Chabazite	1772	Offretite	1890
Harmotome	1775	Erionite	1890
Analcime	1784	Kehoeite	1893
Laumontite	1785	Gonnardite	1896
Thomsonite	1801	Dachiardite	1905
Scolecite	1801	Stellerite	1909
Heulandite	1801	Ferierite	1918
Gmelinite	1807	Viselite	1942
Mesolite	1813	Yugawaralite	1952
Gismondine	1816	Wairakite	1955
Brewsterite	1822	Bikitaite	1957
Epilstilbite	1823	Paulingite	1960
Phililipsite	1824	Garronite	1962
Levynite	1825	Mazzite	1972
Herschelite	1825	Barreite	1974
Edingtonite	1825	Merlinoite	1976
Faujasite	1842		

2.3.2. Classification and Structure of Zeolites

The classification of zeolites is based on subunits in their aluminosilicate structure that is called secondary building units (SBU). SBUs are formed by different configurations of $(Al,Si)O_4$ tetrahedra within the structure, which leads to seven different groups/classifications of zeolites (Table 2.7). Different SBU structures are presented in Figure 2.1 and some of the polyhedral structures formed by these units are presented in Figure 2.2. The differences in SBU structures affect the properties of zeolites such as, void volume, density, degree of hydration, cation exchange capacity, catalytic activity, adsorption properties, electrical conductivity and stability after dehydration.

Table 2.7. Classification of natural zeolites according to SBU (Breck, 1974).

Group	Secondary Building Unit (SBU)
1	Single 4-ring, S4R
2	Single 6-ring, S6R
3	Double 4-ring, D4R
4	Double 6-ring, D6R
5	Complex 4-1, T_5O_{10} unit
6	Complex 5-1, T_8O_{16} unit
7	Complex 4-4-1, $T_{10}O_{20}$ unit

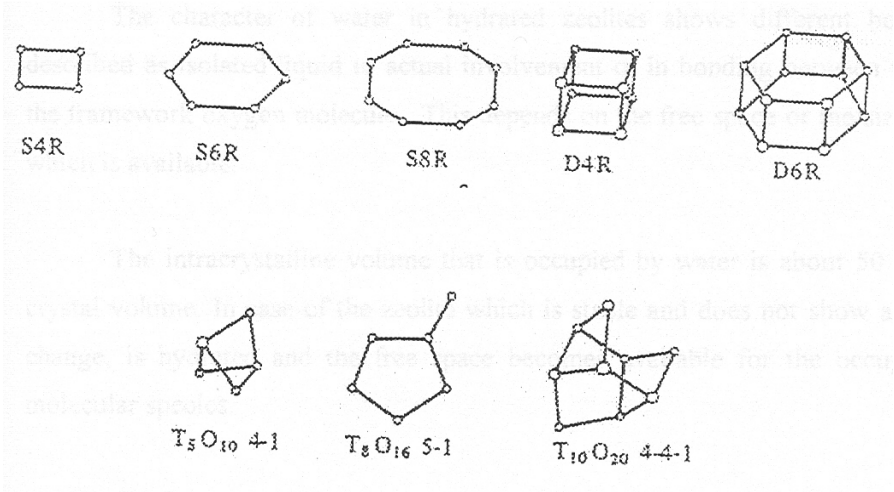

Figure 2.1. Secondary building units in different zeolite structures (Meier, 1968).

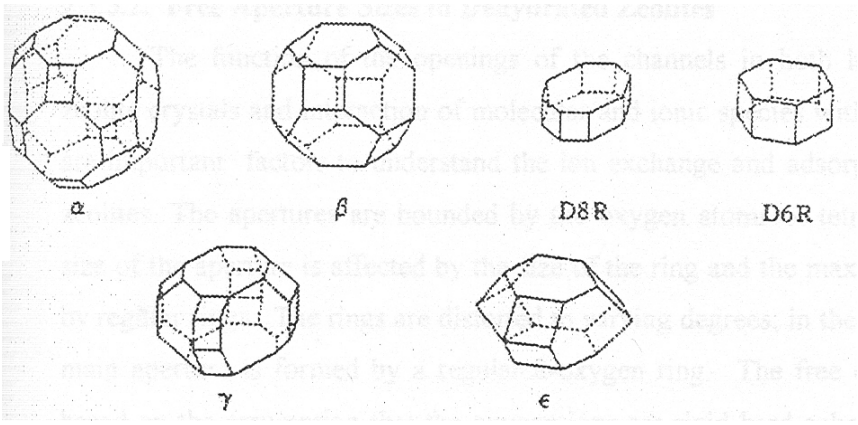

Figure 2.2. Some polyhedral units in zeolite frameworks (Barrer, 1968).

Even though there are over 100 known structure types only a few of these are feasible to be exploited and commercialized (Table 2.8).

Table 2.8. Zeolite discovery and use by decades (Schoonover and Cohn, 2000).

Decade	Known Structure Types	Commercialized Structure Types
1950-1969	27	3
1970-1979	11	1
1980-1989	26	2
1990-1999	61	5
Total	125	11

2.3.3. Properties of Zeolites

The variations in zeolite structure enable them to have variety of properties such as;

- high cation exchange capacity: 150-250 cmol/kg,
- low density: 2.1-2.2 g/cm^3,
- large void volume: up to 50%,
- catalytic properties,
- molecular sieve properties,
- structure stability when dehydrated,
- electrical conductivity,
- thermal insulation,

- adsorption of gases and vapors,
- selectivity for metals,
- low cost,
- capability to regenerate (Breck, 1974).

Among the properties stated above, ion exchange applications, adsorption of gases, liquids and vapors and catalytic activity of the zeolites are the most investigated and applied properties.

Zeolites are used as ion exchange agents in various fields from water treatment to health related activities. Different uses of zeolites as ion exchanges can be listed as removal of NH^{4+} from wastewater, detergent builder, metal removal and recovery and regeneration of artificial kidney (Flanigen, 1980).

Cation exchange capacity of zeolites depends on several factors surrounding the zeolite such as;

- structure of zeolite,
- temperature,
- charge and size of the cation,
- concentration of cation in surrounding,
- solvent.

Cation exchange capacities of several zeolites are given in Table 2.9.

Zeolites, having different pore sizes (Figure 2.3) are widely used as molecular sieves for adsorption applications. Zeolites as molecular sieves are commercially used mostly in purification by removal of small polar or polarizable molecules and bulk separation applications (Fajula et al., 1994; Barthomeuf, 1996). Some available commercial applications of purification can be listed as; drying of natural gas and refrigerant, CO_2 removal from natural gas and flue gas, sulfur compound removal, pollution abatement by removal of Hg, NO_x and SO_x and removal of organic and inorganic iodide compounds from commercial acetic acid feed streams. Some of the commercial bulk separation

Table 2.9. Cation exchange capacities of different zeolites (Singh and Kolay, 2002).

Zeolite	CEC (meq/100g)
Natrolite	530
Analcime	450
Levyite, Chabazite, Gmelinite	400
Edingtonite, Faujasite	390
Heulandite	330
Stilbite	320
Mordenite	230

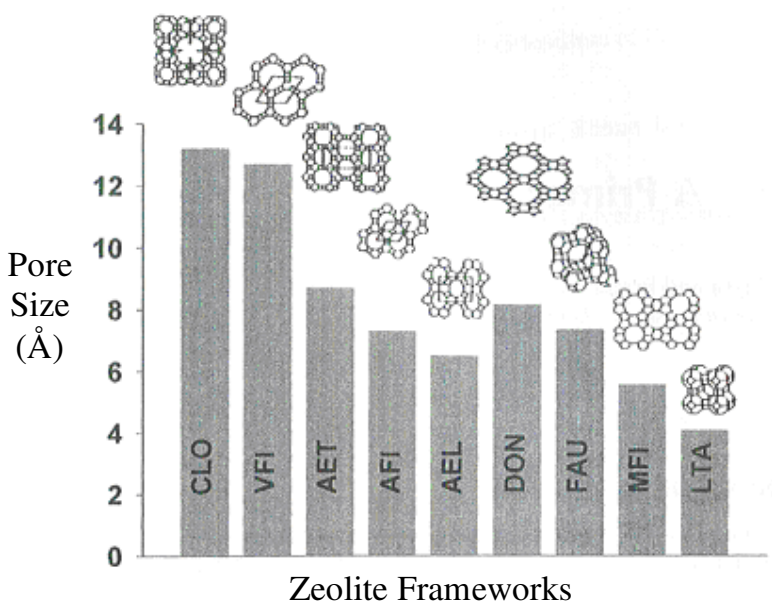

Figure 2.3. Comparison of pore size of different framework zeolites (Dutta et al., 2003).

applications are normal/iso-paraffin separation, xylene separation, olefin separation, separation of organic solvents, separation of O_2, CO_2, SO_2, NH_3 (Flanigen, 1980).

As zeolite properties are affected and can be modified by temperature or pressure, removal of undesired species within a mixture is also possible. Adsorption by zeolites is also a reversible process. Therefore, desorption/regeneration can be applied and zeolite can be reused decreasing the cost of the process. The desorption water should be treated before discharged.

Zeolites are also used in catalyst applications. Some of these applications may be listed as hydrocarbon transformation of zeolites, promotion of bimolecular reactions, conversion of polar oxygenated hydrocarbons to paraffins and aromatics, synthesis of organics. Iwamoto (1994) states that zeolites are potential catalysts due to their pore structures and ion exchange properties. Therefore, zeolites are evaluated as solid catalysts having significant roles for better environment. Advantages of using zeolites in these applications are ease of regeneration, availability to dope with metals, etc. (Dutta et al., 2003).

2.3.4. Clinoptilolite

Clinoptilolite, which is formed by the devitrification of volcanic glass in tuffs, is one of the widely used natural zeolite. Some of the fields that clinoptilolite is used are chemical sieving, gas adsorption, food additive, odor control agent, and water filtration (Anonymous, 2007a).

Clinoptilolite corresponds to Group 7 with its lamellar morphology. Other zeolites of this group are heulandite, stilbite, stellerite and brewsterite. The common property of Group 7 zeolites is their special configuration of tetrahedral. Each tetrahedron belongs to a $T_{10}O_{20}$ unit, as in Figure 2.1, which contain 4- and 5-rings (Breck, 1974).

The difference between clinoptilolite and other Group 7 elements is its stability towards dehydration. As well, clinoptilolite can readily adsorb H_2O, CO_2, O_2 and N_2. In addition, its thermal stability at 700°C in air is higher than other zeolites in Group 7 (Breck, 1974). Properties of clinoptilolite do not change by time. General properties of clinoptilolite are given in Table 2.10.

As in other zeolites, clinoptilolite is a good ion-exchanger. Characteristics such as SBU and void volume affect the capability and selectivity in ion exchange of zeolites. For clinoptilolite, the ion selectivity is as follows: $Cs^+ > K^+ > Sr^{2+} = Ba^{2+} > Ca^{2+} > Na^+ > Li^+ > Pb^{2+} > Ag^+ > Cd^{2+} \sim Zn^{2+} > Cu^{2+} > Na^+$ (Kesraoui-Ouki et al., 1994).

Table 2.10. Properties of clinoptilolite (Breck, 1974).

Structure Group	7
Chemical Composition	
Typical Oxide Formula	$(Na_2,K_2)O \cdot Al_2O_3 \cdot 10\ SiO_2 \cdot 8\ H_2O$
Typical Unit Cell Contents	$Na_6\ [(AlO_2)_6(SiO_2)_{30}] \cdot 24\ H_2O$
Variations	Ca, K, Mg also present; Na, K > Ca
	Si/Al = 4.25-5.25
Crystallographic Data	
Symmetry	Monoclinic
Space Group	I 2/m
Unit Cell Constant	a = 7.41 Å
(a, b, c, β1) Structural Locations	b = 17.89 Å
	c = 15.85 Å
	β1 = 91° 29’
Density	2.16 g/cm^3
Unit Cell Volume	2100 $Å^3$
Structural Properties	
Void Volume	0.34 cm^3/cm^3
Framework Density	1.71 g/cm^3
Effect of Dehydration	very stable – in air up to 700 °C
Largest Molecule Adsorbed	O_2
Kinetic Diameter	δ = 3.5 Å
Habit	Tabular, platy
Cleavage	[010]
Optical Properties	Biaxial (-), α = 1.476, β = 1.479, γ = 1.479

Clinoptilolite, which Turkey has large deposits, was obtained from Manisa–Gördeş, located at the Western Anatolia at the Aegean Region of Turkey. Zeolite ore that is excavated by special machinery is loaded to trucks by a crane and transported to the open storage area which is one kilometer away from the mining site (Tiryaki, 2005).

Zeolite reserves in Manisa-Gördeş region are estimated as 19,923,750 tons, of which approximately 90% is clinoptilolite. Zeolite consumption in Turkey is about 200,000 tons per year which creates a good market for zeolite (Tiryaki, 2005).

2.4. Fly Ash

Coal combustion products arising from energy generation are one of the most abundant waste streams worldwide. During 2007, only in the USA more than one billion tons of coal was burned generating over 130 million tons of coal combustion products (ACAA, 2008). Coal combustion products consist of fly ash being the most abundant, bottom ash, boiler slag and flue gas desulfurization residues. In 2001, over 60 million coal combustion products were generated in the EU member countries. Of the 60 million coal combustion products, 67.3% is fly ash (Berg and Feuerborn, 2001).

Every year, more than 500 million tons of fly ash is produced. Disposal or insufficient reuse of generated fly ash is a significant problem for the environment and the responsible authorities (Kikuchi, 1999). The amount of fly ash used at some activities in the USA is presented in Table 2.11. In 1930s, fly ash generated from thermal power plants started to increase. The change in fly ash production and use over the second half of the 20^{th} century in USA is presented in Figure 2.4 (Kelly and Kalyoncu, 2002). 1930s was also about the time when scientific research on fly ash had started, and it was found out that fly ash had similar physical and chemical properties as other pozzolanic materials.

Fly ash, which is fine powdered ferroaluminosilicate - containing silica (SiO_2), alumina (Al_2O_3) and iron oxides (Fe_2O_3), is made up of hollow glassy particles. The ferroaluminosilicate is enriched mainly by Ca, Mg, S, K and Na and trace elements such as As, B, Mo, Se and Sr (Page et al., 1979; El-Mogazi et al., 1988; USEPA, 1988; Mattigod et al., 1990). Its pozzolanic nature enables fly ash to form cementitious compounds by

reacting with calcium hydroxide in moist environment (Manz, 1999). As well, fly ash, which is an aluminosilicate, shows similar properties to zeolites when alkalized (Kikuchi, 1999).

According to researches conducted, one of the disposal methods of fly ash is landfilling which is considered unsafe in the long term (Suter et al., 1993; Danker et al., 2001). The main hazards associated with the disposal of fly ash and other coal combustion products are toxic trace metals and excessive concentration of soluble salts leaching from these metals (Adriano et al., 1980).

Table 2.11. Production and use of fly ash in the USA during the year 2007 (ACAA, 2008).

	Fly Ash (million tons)
Produced	71.700
Used in	
Concrete/concrete products/grout	13.705
Blended cement, raw feed for clinker	3.636
Flowable fill	0.112
Structural fills/embarkments	7.725
Road base/sub base	0.377
Soil modification/stabilization	0.857
Mineral filler in asphalt	0.017
Snow and ice control	0.000
Blasting grit/roofing granules	0.000
Mining applications	1.306
Gypsum panel products	0.000
Waste stabilization/solidification	2.680
Agriculture	0.050
Aggregate	0.135
Miscellaneous/other	1.026
TOTAL	31.626
% Use	44.1

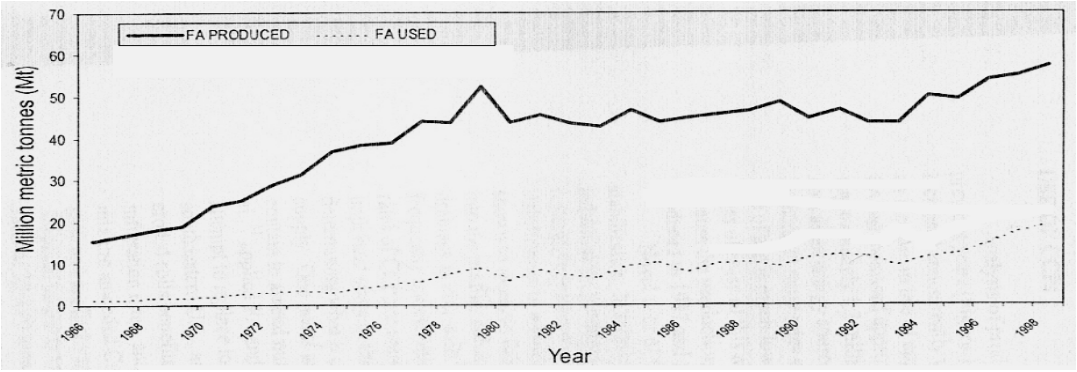

Figure 2.4. Production and use of fly ash between 1966 and 1998 in the USA (Kelly and Kalyoncu, 2002).

2.4.1. Production of Fly Ash

Fly ash is the residue of the combustion of finely grounded coal that is injected at high speeds in hot air in the thermoelectric power plants. About 80% of the coal ash, which is fly ash, is separated by mechanical filters and electrostatic precipitators from other coal combustion products; bottom ash, boiler slag, gypsum. Separated coal combustion products are either reused or landfilled (Mehta, 1983; Dhir, 1986; Styron and Perryman, 1992; Berg and Feuerborn, 2001).

2.4.2. Properties of Fly Ash

Fly ash may have different properties according to the quality and reactivity of coal, as well as the processing in the power plant. Properties of fly ash depend on factors such as;

- the source and uniformity of the coal,
- the physical and chemical properties of the coal,
- the degree of the pulverization of the coal and efficiency of the burning operation,
- the combustion environment (temperature level and oxygen supply),
- the uniformity of combustion,
- the settlement of fly ash, and

- the handling and storage methods (Atanur, 1971; Lane and Best, 1982; Little, 1995; Sear, 2001).

2.4.2.1. Physical Properties of Fly Ash. Fly ash particles differ in shape depending on combustion temperature, as well as cooling and solidification processes after combustion. Most of the fly ash particles are glassy and spherical. These particles are formed by burning the coal at 1400°C. At this temperature, minerals in the coal melt and form a spherical shape and rapid cooling causes the particles to remain in this amorphous, glassy spherical form. The particle sizes of spherical fly ash ranges between 0.5 and 200 μm. The spherical particles are usually sized below 50 μm. The irregular and angular particles are usually larger than 50 μm (Sear, 2001; Singh and Kolay, 2002; Tiryaki, 2005). Particle size of fly ash is an important parameter for water holding capacity of fly ash. As particle size of fly ash increases, water holding capacity of fly ash decreases and vice versa. (Sarkar and Rano, 2007).

Specific surface area of fly ash particles also vary according to the combustion temperature and cooling. These two parameters change the shape and size of fly ash, thus changing the specific surface area. The specific surface area of fly ash changes from 2500 to 5500 cm^2/g (Döven, 1998).

The average specific gravity of fly ash particles is between 1.9 and 2.9. Sometimes, fly ash contains high amount of unburned coal and hollow particles which decrease the specific gravity to less than 1.0, which causes the particles to float on water. As fly ash particles get finer, specific gravity of the particles increases (Della et al, 1984).

Color of fly ash depends on the type of the coal burnt, its carbon and ferrous particle content, loss on ignition and moisture. These factors cause the color of the fly ash to vary from light cream to black (Erdoğan, 1993; Döven, 1998; Yufen et al., 2005; Zaeni et al., 2010).

2.4.2.2. Chemical Properties of Fly Ash. According to American Society of Testing and Materials (ASTM C618) fly ash is classified as either class C or class F (Manz, 1999). Class F fly ash is produced by burning anthracite or bituminous coal, whereas, class C fly

ash is produced by burning of sub-bituminous and lignite coal. Among these two types, class F fly ash has pozzolanic nature, with total concentration of SiO_2, Al_2O_3, and Fe_2O_3 up to 70%. Class C fly ash contains higher concentrations of CaO, MgO and SO_3, therefore has self-cementing property in addition to its pozzolanic nature. Class C fly ash has total SiO_2, Al_2O_3, and Fe_2O_3 concentration maximum of 50% (Manz, 1999; Iyer and Scott, 2001). Table 2.12 shows compositions of fly ash of different types of coal.

Table 2.12. Composition of fly ash of various types of coal (Alonso and Wesche, 1991).

Parameter	Composition (%)			
	Anthracite	Bituminous	Sub-bituminous	Lignite
SiO_2	47 – 68	7 – 68	17 – 58	6 – 45
Al_2O_3	25 – 43	4 – 39	4 – 35	6 – 23
Fe_2O_3	2 – 10	2 – 44	3 – 19	1 – 18
CaO	0 – 4	1 – 36	2 – 45	15 – 44
MgO	0 – 1	0 – 4	0.5 – 8	3 – 12
Na_2O	---	0 – 3	---	0 – 11
K_2O	---	0 – 4	---	0 – 2
SO_3	0 – 1	0 – 32	3 – 16	6 – 30

2.4.3. Utilization of Fly Ash

Usage of fly ash in cement production is probably the most studied use option. Even though fly ash was recognized as pozzolanic material in 1914, the first significant study conducted dates back to 1937. The base for these studies is the resemblance of fly ash to volcanic ash that was used back in the Roman Period. The pozzolanic characteristic of volcanic ash improves the durability and strength of concrete, which is a crucial reason for the preservation of the structures (Halstead, 1986).

Class F fly ash is preferred as an ingredient for the Portland cement. Fly ash can replace cement up to 30%, increasing the chemical resistance and durability. In addition, researches conducted recently in India showed that 70% fly ash mixtures can be used in dam construction, increasing the workability with cement and reducing the water demand (TIFAC, 2008). Reuse of fly ash in cement production also reduces the emission of

greenhouse gases such as CO_2, because during the production of one ton of Portland cement, about one ton of CO_2 is emitted into the atmosphere, which is decreased by the addition of fly ash (The Loretti Group, 2008).

One of the uses of fly ash is for the sludge stabilization or solidification (Sajwan et al., 1995; Tiryaki, 2005). Mixing fly ash with soil increases both physical and chemical improvement of the soil by enhancing water-holding capacity (Punshon et al., 2002). Another field for fly ash is using it as fertilizer after converting fly ash to potassium silicate (Kikuchi, 1999).

Flowable fill, also known as controlled low strength material, is one other area that fly ash is used. Flowable fill is used as self-compacting backfill material instead of compacted earth (Baykal and Döven, 1996). The strength of flowable fill may vary from 1400 to 8300 kPa depending on the needs. Flowable fill includes Portland cement and filler material, such as sand. High fly ash concentration fills contain mostly class F fly ash and a small amount of Portland cement, whereas low fly ash concentration fills contain high percentages of filler material and a low percentage of class C fly ash (Hennis and Frishette, 1993).

The use of fly ash in asphalt concrete is substitutional for other mineral fillers, such as lime or Portland cement, which is used to fill the void and provide contact points between large aggregate particles. As well, the hydrophobic character of fly ash increases the durability of asphalt pavements against stripping. It is also reported that fly ash increases the stiffness of the asphalt concrete (Zimmer, 1970). According to a report of American Coal Ash Associtation (2003), fly ash mixtures having 7 days cuirng UCS values exceeding 2760 kPa can be considered for potential use as road bases. For fly ash mixtures to be used as pavement subsealings, 7 days cured mixtures should yield UCS values between 4100 and 5500 kPa and 28 days cured mixtures should yield UCS values above 8300 kPa.

Ash bricks – a type of brick – have been used in house construction since 1970s. However, these bricks fail due to humidity of the atmosphere, which causes the bricks to expand after chemical reactions. In May 2007, brick consisting of fly ash and water, which

is compressed at 4000 psi and cured at 66 °C steam bath for 24 hours, have been produced by Henry Liu. These bricks can stand more than 100 freeze-thaw cycles. Class C fly ash is used in these bricks due to its high CaO concentration, which gives the mixture self-cementing property (Anonymous, 2007b).

2.4.4. Fly Ash in Turkey

In Turkey, approximately 50 million tons of coal is consumed by thermoelectric power plants generating about 15 million tons of fly ash every year (Tiryaki, 2005). On the other hand, the amount of the fly ash utilized is at minimum due to insufficient handling and storage conditions, as well as the high cost of transportation (Döven, 1998). The amount of fly ash generated in Turkey is presented in Table 2.13.

2.5. Perlite

Perlite, which is an amorphous, silica rich volcanic rock, is formed by the hydration of obsidian, an igneous rock produced by lava that has not undergone crystal growth. When heated to temperatures around 900°C (glass transition temperature of perlite), perlite tends to soften by loosing its water content. This causes the expansion of perlite up to twenty times its original volume, thus forming “expanded perlite” (Perlite Institute Inc., 2008).

2.5.1. Properties of Perlite

The physical characteristics of expanded perlite are shown at Table 2.14. Even though chemical composition of perlite changes according to the source of extraction, a typical chemical analysis of perlite is shown in Table 2.15 (Perlite Institute Inc., 2008).

2.5.2. Utilization of Perlite

Perlite is used in many different applications due to its porosity, light weight, thermal and noise insulation, chemically inert and non-flammable structure. Most common areas of its usage are construction, horticulture and industrial applications (Karadaş, 2004).

Table 2.13. Amount of fly ash generated in thermoelectric power plants in Turkey (Tiryaki, 2005).

Thermoelectric Power Plant	Location	Amount of Coal Burned (10^3 ton/year)	Amount of Fly Ash Generated (10^3 ton/year)
Kemerköy	Muğla	1598	658
Çatalağzı (B)	Zonguldak	1659	747
Tunçbilet	Kütahya	1908	572
Yatağan	Muğla	5538	1661
Afşin - Elbistan	Kahramanmaraş	10970	2084
Yeniköy	Muğla	3413	1365
Çayırhan	Ankara	3696	1300
Soma (A)	Manisa	285	80
Soma (B)	Manisa	8664	3898
Seyitömer	Kütahya	5385	1993
Orhaneli	Bursa	1414	424
Kangal	Sivas	5195	1247
TOTAL		49725	16029

Table 2.14. Physical characteristics of perlite (Perlite Institute Inc., 2008).

Parameter	Value
Color	White
Refractive index	1.5
pH	6.5 – 8.0
Specific gravity	2.2-2.4
Raw perlite bulk density (kg/m^3)	1100
Expanded perlite bulk density (kg/m^3)	30-150
Glass transition temperature (°C)	871-1093
Melting point (°C)	~1400
Solubility in water	No

Its thermal insulating characteristic as well as light weight make perlite a suitable choice for construction applications. In addition to these basic properties, perlite provides noise insulation and enhances fire ratings. It is also resistant to rotting and termites. In construction applications, perlite is used as an aggregate in concrete, Portland cement and gypsum plasters, as well as under-floor insulation, ceiling tiles, roof insulation boards and chimney linings (Doğan, 2001).

Table 2.15. Chemical composition of perlite (Perlite Institute Inc., 2008).

Parameter	Composition (%)
SiO_2	70-75
Al_2O_3	12-15
Na_2O	3-4
K_2O	3-5
Fe_2O_3	0.5-2
MgO	0.2-0.7
CaO	0.5-1.5
Loss on ignition (including H_2O)	3-5

In horticultural applications, perlite is used for soilless growing mixes to provide aeration and moisture retention for plant growth. Neutral pH, sterility and weed-freeness are some of the advantages of using perlite in horticultural applications. It is also used in greenhouse growing and landscaping (Doğan, 2001).

Perlite is a common component in various industrial applications. It is used as filter media for pharmaceuticals, food products and wastewater, as well as swimming pools. The heat resistant property of perlite is taken into consideration in refractory brick manufacturing.

Table 2.16 shows different usages of expanded perlite in the USA (USDOI, 2008).

2.5.3. Perlite around the World

According to both national and international surveys, Turkey is the country with the highest amount of perlite reserves in the world (Doğan, 2001; Karadaş 2004; Bolen, 2007). A recent study conducted in the USA states that Turkey has more than 70% of world's perlite reserves. On the other hand, when the perlite production is compared, Greece and the USA lead the sector (Table 2.17).

Even though Turkey is not the largest perlite producer of the world, most of the perlite reserves are in Turkey, mainly Manisa, Biga, Soma, İzmir, Konya and Erzincan. Turkey is also an important perlite exporter as perlite production increases through years

(Table 2.18). In 2006, the main countries that Turkey exported perlite were Spain (19% of the export), Belgium (18%), Italy (14%) and India (11%) (Uyanık, 2007).

Table 2.16. Amount of expanded perlite used in different applications in the USA in 2007 (USDOI, 2008).

Use	Amount (metric tons)
Concrete aggregate	2,160
Fillers	74,700
Filter aid	41,000
Formed products	330,000
Horticultural aggregate	75,000
Laundries	875
Low-temperature insulation	1,660
Masonry- and cavity-fill insulation	3,380
Plaster aggregate	6,760
Other	39,100

Table 2.17. World perlite production and reserves in 2005 (Bolen, 2007).

Country	Amount of Production (10^3 tons)	Reserves (10^3 tons)
Greece	525	300,000
United States	508	200,000
Japan	240	--- *
Mexico	195	--- *
Hungary	145	--- *
Turkey	140	5,700,000
Other countries	200	1,500,000
TOTAL	1950	7,700,000

* Included in "Other countries"

Table 2.18. Perlite export and revenue of Turkey (Uyanık, 2007).

Year	Amount of Exported Perlite (10^3 tons)	Revenue (million $)
2004	216	7
2005	251	9
2006	259	9

3. MATERIALS AND METHODS

The research was conducted in three stages. In the first stage, sludge was mixed with the binders mentioned in the previous sections for S/S process to take place and solidified. In the second stage, the UCS values of the solidified samples were determined by UCS of cylindrical cement specimens test. And in the third stage, leaching characteristics of the selected solidified samples were determined by TCLP.

3.1. Experimental Setup

In the first stage of the research, sludge, mixed with the binders, was compacted by using Harvard Miniature Compaction Equipment (Figure 3.1). The system consists of mold, compaction tamper and specimen ejector. In this stage, compacted samples were cured in different media such as room temperature, humid room and aquarium for different periods such as 7, 14 and 28 days.

Figure 3.1. Harvard Miniature Compaction Apparatus, a) specimen ejector, b) compaction tamper, c) mold.

In the second stage of the research, the UCS values of the solidified products were determined by executing necessary calculations of the raw data. Unconfined compressive strength values of the cured samples were determined by using ELE International Digital Tritest 50 (Figure 3.2). The equipment consists of a dial ring and a flat plate attached to it. The prepared sample was placed below the ring, on an elevating plate and the elevation of the plate were recorded (deformation dial reading) as well as the load dial reading. In addition, the elevation rate (strain rate) can be determined prior to the test by manually entering the strain rate value.

Figure 3.2. ELE International Digital Tritest 50.

In the third stage of the research, Controls End-Over-End Shaker (Figure 3.3) was used for TCLP tests. For the preparation of the samples prior to the tests, 9.5 mm sieve is used as a requirement of the TCLP test. Tumbled samples were filtered through Whatman GF/F type glass fiber filter paper (0.7 μm). Filtrate collected was used as the leaching solutions for atomic absorption tests. Finally, the prepared samples were subjected to AAnalyst 300 Atomic Absorption Spectophotometer (Figure 3.4).

Figure 3.3. Controls End-Over-End Shaker.

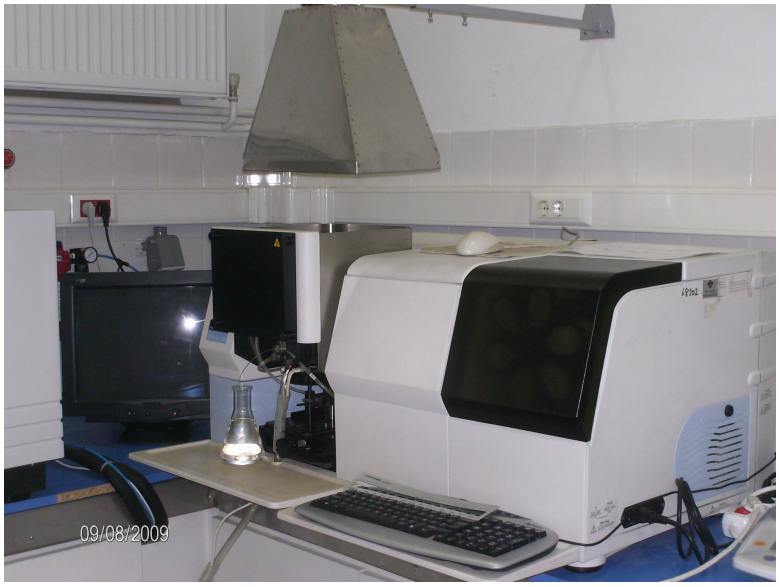

Figure 3.4. AAnalyst 300 Atomic Absorption Spectophotometer.

3.2. Materials Used

Materials used in this research are as follows:

- sewage sludge,
- clinoptilolite (53µm and 1mm),
- fly ash,
- perlite,

- lime,
- extraction fluid “I” and
- extraction fluid “II”.

Domestic wastewater treatment plant sludge used in the research was obtained from Paşaköy Wastewater Treatment Plant. Characteristics of the sludge used in the research are presented in Table 3.1.

Table 3.1. Characteristics of the sludge of Paşaköy Wastewater Treatment Plant.

Parameter	Value	Parameter	Value
Moisture Content (%)	98.48	Cu (mg/l)	1.726
Total Solids (%)	1.52	Fe (mg/l)	36.82
Volatile Solids (%)	0.8	Mg (mg/l)	60.08
BOD_5 (mg/l)	2300	Mn (mg/l)	2.002
COD (mg/l)	9300	Ni (mg/l)	0.538
Ca (mg/l)	409.2	Pb (mg/l)	0.260
Cr (mg/l)	1.176	Zn (mg/l)	6.968

The zeolite has been supplied by İncal Mineral Company, located in İzmir. Physical and chemical properties of clinoptilolite used in the research are presented in Tables 3.2 and 3.3 respectively.

Table 3.2. Physical characteristics of clinoptilolite (İncal Mineral Company, 2008).

Parameter	Value
Color	Ivory
Porosity (%)	40
Bulk Density (ton/m^3)	1.00
Water Retention (%)	40
Oil Retention (cm^3 oil/100 gr)	68
Melting Point (°C)	1300
pH	7.05 – 7.65
Purity (%)	92-96
Pore Size (Å)	4
Cation Exchange Capacity (meq/g)	1.6 – 2.2
Specific Surface Area (cm^2/gr)	3.9

Table 3.3. Chemical composition of clinoptilolite (İncal Mineral Company, 2008).

Mineral	Concentration (weight %)
SiO_2	65.72
Al_2O_3	10.88
TiO_2	0.07
Fe_2O_3	1.19
Na_2O	0.65
K_2O	2.98
CaO	2.55
MgO	0.98
P_2O_5	0.035
SO_3	0.06

Fly ash, is a waste generated from thermoelectric power plants that has to be disposed due to its hazardous waste content. One of the use options for fly ash is using it as binder in stabilization processes. Class C fly ash used in the research was supplied by Kemerköy Thermoelectric Power Plant, which is located in Muğla, Southwest of Turkey. The plant consists of three units, each with the capacity of 210 MW; 630 MW in total. Annual gross energy production was 3268 GWh in 2002 (Kantarcı, 2003). The type of coal used in the power plant is lignite. Even though, only one type of coal is used in the power plant, mined coal may not have the same characteristics over time. In addition, burning conditions in different units of the power plant cause changes in the chemical characteristics of fly ash. Four different types of fly ash have been used in the research, all from Kemerköy Thermoelectric Power Plant. Chemical composition of fly ash 1 (FA1) that was obtained from the Power Plants in 2003 is given in Table 3.4. Two other types of fly ash were obtained from two different units of the Power Plant in 2008. The compositions of Unit 1 fly ash (FA2), Unit 2 fly ash (FA3) and their weight equivalent mixture (FA4) are presented at Table 3.5. All of the fly ash used in the research are type C as explained in Section 2.4.2.2. The composition of the fly ash supplied by Kemerköy Thermoelectric Power Plant was determined by Akçansa Çimento San. Tic. A.Ş. (2008).

Perlite, which has large reserves in Turkey, ~70% of the perlite reserves of the world, was supplied by PERSAN Perlit Üretim Tic. San. Chemical composition of perlite used in the research is presented at Table 3.6. Three different sizes of expanded perlite used during

Table 3.4. Chemical composition of FA1 fly ash from Kemerköy Thermoelectric Power Plant (Kemerköy Thermoelectric Power Plant, 2003).

Mineral	Concentration (weight %)
SiO_2	16.75
Al_2O_3	9.1
Fe_2O_3	3.76
CaO	44.21
MgO	2.32
Na_2O	2.74
K_2O	1.37
SO_3	17.18
TiO_2	0.52
P_2O_5	0.21
Loss on Ingition	0.24

Table 3.5. Chemical composition of fly ash from Kemerköy Thermoelectric Power Plant (Akçansa Çimento San. Tic. A.Ş., 2008).

Mineral	Concentration (weight %)		
	FA2	FA3	FA4 FA2 + FA3 (1:1)
SiO_2	26.16	28.64	27.38
Al_2O_3	13.34	14.21	12.02
Fe_2O_3	6.61	7.59	6.91
CaO	39.85	35.94	39.64
MgO	3.00	3.52	3.24
Na_2O	0.34	0.40	0.35
K_2O	1.35	1.55	1.40
SO_3	8.15	6.84	7.65
Loss on Ingition	0.23	0.52	0.61

Table 3.6. Chemical composition of perlite (TÜBİTAK, 2008).

Parameter	Composition (%)
SiO_2	73.51
Al_2O_3	13.42
Na_2O	3.48
K_2O	6.03
Fe_2O_3	0.64
MgO	0.17
CaO	0.69

the research are namely, micronized perlite, P08 perlite, and P12 perlite. These names – commercial names– are given by the supplier in order to differentiate the sizes of the perlite granules. Granule sizes of the different types of perlite are as follows: micronized perlite < P08 perlite < P12 perlite.

Lime, which is a binder to activate pozzolanic reactions, is another material used in the research.

Extraction fluids "I" and "II" to be used in TLCP tests were prepared. Extraction fluid "I" was prepared by mixing 5.7 ml glacial acetic acid and 64.3 ml 1.0 N sodium hydroxide and diluting the mixture to one liter. For the preparation of extraction fluid "II", 5.7 ml glacial acetic acid is diluted to one liter.

3.3. Experimental Procedure

3.3.1. Characterization of the Sludge Used in the Research

Experiments to determine the characterization of the sludge obtained from Paşaköy Wastewater Treatment Plant were conducted. Moisture content, total solids and volatile solids, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were determined according to the methods given at the Standard Methods for the Examination of Water and Wastewater (APHA-AWWA-WPCF, 2005). In addition concentrations of Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn were determined according to 3111B. Direct Air-Acetylene Flame Method by atomic absorption spectroscopy (APHA-AWWA-WPCF, 2005). The charactestics of the sludge used in the research are presented at Table 3.1.

3.3.2. Sample Preparation

In a study conducted by Balkan (1999), clinoptilolite of different sizes were used in the solidification/stabilization of sludge. The reason 1 mm clinoptilolite was used in the experiment was the relative low cost of 1 mm clinoptilolite with respect to micronized clinoptilolite. According to the comparisons of the UCS values, solidified mixtures containing clinoptilolite with particle size 53μm yielded the best unconfined compressive

strength values. Therefore, in the research all the experiments were carried on by using clinoptilolite of 53μm particle size. Samples of sludge for S/S processing were prepared by mixing sludge with fly ash, lime and clinoptilolite. In order to homogenize the particulate matter first, fly ash, lime, clinoptilolite and perlite were mixed, and then sludge was added and mixed to obtain a relatively homogeneous mixture. Only in one experiment, clinoptilolite of 1 mm particle size was used to verify the results obtained by Balkan (1999). The amount of sludge used in the mixtures was the highest amount of sludge the mixtures can hold, so that the samples prepared in the molds would not disperse after removing from the molds. For mixtures containing FA1, it was observed that the mixture can not hold 30% or 27.5% sludge by weight in order to prepare mixtures to be solidified. So, sludge content of the mixtures was determined as 25%. Mixtures containing 25% sludge with different ratios of fly ash, zeolite and lime were prepared as preliminary studies. It was observed that FA2, FA3 and FA4 can not hold 20% or 25% sludge in the mixture. Therefore, for mixtures containing FA2, FA3 and FA4, different samples containing 15% and 17.5% sludge were prepared. By mixing sludge with different additives and applying solidification/stabilization process, waste volume increased by 2.5 to 4 times. On the other hand, the process aims to utilize the solidified mixtures as beneficial products instead of handling or treating them as wastes. Therefore, the increase in the volume of the waste is not significant with respect to the aim of the research.

Then, the mixtures were placed into the mold of Harvard Miniature Compaction Apparatus shown at Figure 3.1. The mixture was placed into the cylindrical mold in five layers by 15 tamping on each layer. After compaction, the samples were removed from the mold and wrapped with stretch film and aluminum foil in order to keep the sample moist. The samples were kept for curing at different media, such as at room temperature (~20°C), in aquarium (~15°C) and humid room (21°C, 70% humidity). They were cured for different durations, 7, 14 and 28 days. Each experiment was conducted by two parallel samples.

Cured mixtures of FA1 were subjected to unconfined compressive strength tests. According to the UCS data obtained for solidified samples in unconfined compressive strength tests, optimum mixture was determined by comparing the results of different mixtures. Mixture 10 / 20 / 45 / 25 (lime / zeolite / FA1 fly ash / sludge, % by weight) was

chosen as the optimum mixture for FA1 mixtures. Mixtures of 10 / 20 / 45 / 25 were prepared and cured at room temperature, humid room and aquarium for 7, 14 and 28 days. For samples containing FA2, FA3 and FA4, two different ratios were determined (10 / 20 / 55 / 15 and 10 / 20 / 52.5 / 17.5) and mixtures were prepared for solidification.

In further studies, perlite was added to the mixtures of sludge, fly ash, zeolite and lime. Perlite was added to mixtures containing FA1 having mixture ratios of 10 / 15 / 5 / 45 / 25 (lime / clinoptilolite / perlite / fly ash / sludge, %) for solidification. Mixtures containing FA2, FA3 and FA4 were prepared with the ratio of 10 / 15 / 5 / 52.5 / 17.5. All mixtures prepared were cured in room temperature for 7, 14 and 28 days.

Later on, in order to simplify the process different non-standard techniques were applied. In one set of experiments prepared samples were cured in room temperature and humid room without wrapping for 7, 14 and 28 days. In another set of experiments, samples cured for 7, 14 and 28 days were unwrapped and left at room temperature for moisture loss and weight stabilization. Moisture loss and weight stabilization of the samples lasted around three weeks for each sample.

3.3.3. Unconfined Compressive Strength Test

Mixtures cured at different media for different periods were subjected to unconfined compressive strength tests. Before running the test, top and bottom surfaces of the solidified samples were straightened manually. Then, the sample weight, height and diameter of the cured samples were measured. These values were used in the calculation of the UCS values of the solidified samples as explained below.

The strain rate for the test was set as 0.5 mm/min. During the UCS test, dial ring with a load ring constant of 0.0254 kN/division was used. During the tests, the values of deformation and load dial readings were recorded at each 0.1 mm strain. The significant dial reading is the value obtained when the sample was broken.

An example of the calculation of the UCS values of a selected sample is given in Table 3.7. Calculation for the UCS value of a sample is performed as follows:

- Columns 1 and 2 are the recorded deformation and load dial reading values in the UCS test.
- In order to determine the sample deformation indicated at column 3, the reading at column 1 is divided by 100.
- Unit strain, which is indicated in column 4, is determined by dividing the value of sample deformation (column 3) by the height of the sample.
- In column 5, area correction factor is calculated by subtracting the value in column 4 from one.
- Corrected area in column 6 is calculated by dividing the initial bottom area of the solidified sample by area correction factor.
- Total load on sample in column 7 is determined by multiplying the load dial reading (column 2) with the load ring constant.
- Sample stress, unconfined compressive strength, which is indicated in column 8 is calculated by dividing the total load on sample (column 7) by the corrected area (column 6), which are converted to m^2. At Table 3.7, UCS values are given in kPa (kN/m^2) (Balkan, 1999; Bowles 1992; Tiryaki, 2005).

Table 3.7. Determination of UCS values of 28 days cured samples in room temperature.

1	2	3	4	5	6	7	8
Deformation Dial Reading	Load Dial Reading	Sample Deformation (mm)	Unit Strain (mm/mm)	Area Correction Factor	Corrected Area (cm^2)	Total Load on Sample (kN)	Sample Stress (kPa)
0	0	0.0	0.0000	1.0000	8.7616	0.0000	0
20	37	0.2	0.0026	0.9974	8.7840	0.9398	1070
40	93	0.4	0.0051	0.9949	8.8066	2.3622	2682
60	151	0.6	0.0077	0.9923	8.8292	3.8354	4344
80	213	0.8	0.0102	0.9898	8.8520	5.4102	6112
100	275	1.0	0.0128	0.9872	8.8749	6.9850	7870
120	332	1.2	0.0153	0.9847	8.8980	8.4328	9477
140	380	1.4	0.0179	0.9821	8.9211	9.6520	10819

Weight of sample: 111.85 gr

Diameter of sample: 3.34 cm

Initial bottom area: 8.7571 cm^2

Height of sample: 7.83 cm

Load ring constant: 0.0254 kN/division

3.3.4. Leaching Test by Toxicity Characteristic Leaching Procedure (TCLP)

TCLP of US EPA was applied only to solidified samples having high UCS values. TCLP tests are used to determine the mobility of organic and inorganic contaminants present in the liquid and solid wastes (USEPA, 1989).

Before the leaching test, solidified samples were pulverized and passed through a 9.5 mm sieve according to the TCLP standards. Before performing the leaching procedure, the type of the extraction fluid that was going to be used was determined. 5 gr S/S processed and pulverized sample was mixed with 96.5 ml of distilled water in a beaker covered by a watch-glass. The mixture was mixed by magnetic stirrer for 5 minutes. Then the pH of the mixture was recorded. According to the procedure, if the pH is lower than 5.0, extraction fluid "I" should be used. If the pH is higher than 5.0, 3.5 ml of 1 N hydrochloric acid is to be added and heated at 50 °C for 10 minutes. After cooling, if pH is lower than 5.0, extraction fluid "I", otherwise extraction fluid "II" should be used. In this research both extraction fluid "I" and extraction fluid "II" were used for different samples.

After determining the extraction fluid to be used, 5 gr of pulverized sample and 100 ml of extraction fluid were placed in a glass bottle. The mixtures were tumbled for 18 hrs. After tumbling, mixtures were filtered through Whatman GF/F glass fiber filter paper (0.7 µm). Filtered liquids were tested for their metal concentrations (Cr, Cu, Fe, Mn, Ni and Zn) by atomic absorption spectrophotometer.

4. RESULTS

4.1. Unconfined Compressive Strength Tests

In previous studies conducted by different researchers, it was observed that fly ash-zeolite-lime mixture yielded better results than fly ash-lime or zeolite-lime mixtures for sludge solidification (Tiryaki, 2005). Therefore, in this study, mixtures of fly ash-zeolite-lime mixtures have been used. In addition, perlite was added to the mixture in some experiments. All the samples were prepared according to the procedure mentioned in Section 3.3.2. The samples were cured in different media for 7, 14 and 28 days. Ratio of sludge in the mixture was determined according to the highest amount of sludge that the mixture can hold in order to prepare samples that would not fall apart prior to wrapping. This ratio was 25% for experiments conducted with FA1, and 17.5% for the experiments conducted with FA2, FA3 and FA4.

Table 4.1 shows the UCS values of the solidified samples prepared with different ratios of FA1, zeolite, lime and sludge mixtures at the preliminary tests. According to the UCS values, the optimum ratio to be used in the rest of the study was determined.

When the preliminary studies of mixtures prepared with FA1 (Table 4.1) is evaluated, it was observed that the highest UCS value (10819 kPa) was obtained at the mixture 11.6 / 21.1 / 42.3 / 25 (lime / clinoptilolite / fly ash / sludge, % by weight) cured at room temperature for 28 days. The sample of the same mixture cured for 14 days also showed high UCS value, 7335 kPa, when compared to other mixtures prepared in different ratios and cured for 14 days. 7 days cured mixtures of 10 / 30 / 35 / 25 showed low UCS values with respect to other mixtures presented at Table 4.1. When the UCS values of the other four mixtures presented at Table 4.1 were compared, it was observed that all solidified samples cured for 28 days yielded UCS values between 6000 and 9500 kPa. Among these mixtures, mixture with the ratio of 10 / 20 / 45 / 25 yielded the best results. Having high UCS values, which were also close to the mixture of 11.6 / 21.1 / 42.3 / 25, mixture with the ratio of 10 / 20 / 45 / 25 (lime / clinoptilolite / fly ash / sludge, % by weight) was

Table 4.1. UCS values of mixtures prepared with FA1 in the preliminary test.

Composition (Lime / Zeolite / Fly Ash / Sludge, % by weight)	Media	Curing Period (Days)	UCS (kPa)
11.6 / 21.1 / 42.3 / 25	Room Temperature	7	2432
	Room Temperature	14	7335
	Room Temperature	28	10819
	Aquarium	28	9524
	Humid Room	28	8695
10 / 30 / 35 / 25	Room Temperature	7	2137
	Aquarium	7	1791
	Humid Room	7	1797
11.6 / 10 / 53.4 / 25	Room Temperature	7	2732
	Room Temperature	14	5103
	Room Temperature	28	7900
	Aquarium	28	8161
10.2 / 15.2 / 49.8 / 24.8	Room Temperature	7	4262
	Room Temperature	28	6317
	Aquarium	28	7641
10 / 20 / 45 / 25	Room Temperature	7	5283
	Room Temperature	14	8356
	Room Temperature	28	9507
	Aquarium	28	7907
	Humid Room	28	6998
10 / 12.5 / 52.5 / 25	Room Temperature	7	3510
	Room Temperature	14	5229
	Room Temperature	28	7839
	Aquarium	28	6032
	Humid Room	28	6031

selected to be used in the rest of the research. Table 4.2 shows the UCS values obtained at the solidified sample of the mixture 10 / 20 / 45 / 25 and the changes in the weights of the samples before and after curing. The samples were cured in three different media: room temperature, humid room and aquarium. In addition to curing the wrapped samples, parallel samples were prepared and unwrapped after curing. The unwrapped samples were left in room temperature till their weights have stabilized and came to constant weight and no more moisture loss occurred. Weight stabilization was achieved in about three weeks.

Table 4.3 shows the UCS values of two different ratios of the solidified mixtures (10 / 20 / 55 / 15 and 10 / 20 / 52.5 / 17.5) with fly ash from two different units of the thermoelectric power plant, FA2 and FA3 and the changes in the weights of the samples

Table 4.2. UCS values of the solidified mixture (10 / 20 / 45 / 25) prepared with FA1 and cured in different media and curing periods.

Composition (L / Z / F / S, % by weight)	Media	Curing Period (Days)	UCS (kPa)	Weight Loss (%)
10 / 20 / 45 / 25	Room Temperature	7	6262	0.15
		14	10975	0.08
		28	13380	0.28
	Room Temperature + Weight Stabilization in Air	7	9950	15.51
		14	17210	14.02
		28	15896	14.96
10 / 20 / 45 / 25	Humid Room	7	8881	0.03
		14	11953	0.03
		28	15472	0.18
	Humid Room + Weight Stabilization in Air	7	17607	15.03
		14	18717	14.20
		28	14552	13.14
10 / 20 / 45 / 25	Aquarium	7	5775	0.37
		14	11865	0.93
		28	14464	0.10
	Aquarium + Weight Stabilization in Air	7	14256	14.59
		14	16585	12.81
		28	19592	14.57

before and after curing. In addition, fly ash from these different units has been mixed with ratio of 1:1, FA4, and mixtures with different ratios were prepared (Table 4.3). The chemical compositions of the fly ash are presented at Table 3.5.

Even though initial studies (Balkan, 1999) indicated that usage of clinoptilolite of 1 mm particle size in the mixture yielded lower UCS values, solidification of sludge with fly ash, lime and clinoptilolite of 1 mm particle size was applied in several experiments. This experiment was important, due to the low price of non-micronized clinoptilolite. The UCS results of the mixtures of FA2, FA3 and FA4 with non-micronized clinoptilolite, lime and sludge and the changes in the weights of the samples before and after curing are presented in Table 4.4. Since, clinoptilolite of 1 mm particle size can hold less sludge than the micronized clinoptilolite, less amount of sludge (15% sludge) was used in these experiments.

Beside the application of different additives and ratios in the production of the solidified samples in conventional methods, some other non-conventional applications were also tested for the solidification of sludge. In this stage of the research, the prepared mixtures were cured without wrapping. The UCS values of these solidified samples and the changes in the weights of the samples before and after curing are given in Table 4.5.

When the effect of perlite is investigated, it is seen that perlite lightens the material and enhances the thermal insulation property of the material. Therefore, several tests were run in order to see the effect of perlite on unconfined compressive strength of the mixtures. For this, perlite of three different sizes was used. Perlite was added to the mixtures in the ratios of 10 / 15 / 5 / 45 / 25 (lime / zeolite / perlite / fly ash / sludge, % by weight)

Table 4.3. UCS values of solidified mixtures containing FA2, FA3 and FA4 fly ash.

Composition (L / Z / F / S, % by weight)	Media	Curing Period (Days)	UCS (kPa)	Weight Loss (%)
10 / 20 / 55 / 15 FA2	Room Temperature	7	3579	0.09
		14	3997	0.03
		28	4733	0.12
	Humid Room	7	2837	0.03
		14	3331	0.07
		28	6097	0.10
10 / 20 / 55 / 15 FA3	Room Temperature	7	6565	0.08
		14	6852	0.07
		28	7129	0.11
	Humid Room	7	3872	0.06
		14	7470	0.57
		28	8320	0.07
10 / 20 / 52.5 / 17.5 FA2	Room Temperature	7	5892	0.10
		14	6794	0.02
		28	9399	0.03
	Humid Room	7	3183	0.13
		14	6051	0.05
		28	7373	0.07
10 / 20 / 52.5 / 17.5 FA3	Room Temperature	7	6204	0.03
		14	9807	0.08
		28	11571	0.07
	Humid Room	7	4670	0.12
		14	9120	0.06
		28	10734	0.02
10 / 20 / 52.5 / 17.5 FA4	Room Temperature	7	6102	0.13
		14	10037	0.04
		28	10607	0.06
	Humid Room	7	4419	0.10
		14	9343	0.19
		28	10824	0.03

Table 4.4. UCS values of solidified mixtures containing 1 mm clinoptilolite.

Composition (L / Z / F / S, % by weight)	Media	Curing Period (Days)	UCS (kPa)	Weight Loss (%)
10 / 20 / 55 / 15 FA2	Room Temperature	7	2049	0.20
		14	2816	0.13
		28	2002	0.28
	Humid Room	7	1583	0.23
		14	2455	0.25
		28	1827	0.38
10 / 20 / 55 / 15 FA3	Room Temperature	7	3227	0.15
		14	4003	0.24
		28	4806	0.22
	Humid Room	7	2608	0.07
		14	3733	0.19
		28	4257	0.19
10 / 20 / 55 / 15 FA4	Room Temperature	7	3337	0.12
		14	3610	0.05
		28	4554	0.09
	Humid Room	7	2089	0.03
		14	2992	0.07
		28	3843	0.02

Table 4.5. UCS values of mixtures solidified without wrapping.

Composition (L / Z / F / S, % by weight)	Media	Curing Period (Days)	UCS (kPa)	Weight Loss (%)
10 / 20 / 45 / 25 FA1	Room Temperature	7	2479	19.22
		14	1179	19.67
		28	2652	17.57
10 / 20 / 45 / 25 FA1	Humid Room	7	3858	11.34
		14	4000	10.77
		28	5202	10.75
10 / 20 / 52.5 / 17.5 FA2	Room Temperature	7	2646	10.78
		14	2753	10.50
		28	1852	10.01
10 / 20 / 52.5 / 17.5 FA3	Room Temperature	7	2622	11.42
		14	1605	11.41
		28	1856	10.42
10 / 20 / 52.5 / 17.5 FA4	Room Temperature	7	1825	15.35
		14	2156	11.05
		28	766	13.34

prepared with FA1 and 10 / 15 / 5 / 52.5 / 17.5 prepared with FA2, FA3 and FA4. The reason for preparing these mixtures was to compare the UCS values of the solidified mixtures containing perlite with the UCS values of the solidified mixtures without perlite. The UCS values of solidified mixtures containing perlite are given in Table 4.6.

Table 4.6. Comparison of the UCS values of the solidified mixtures with and without perlite.

Composition (L / Z / P / F / S, % by weight)	Media	Curing Period (Days)	UCS (with perlite) (kPa)	*UCS (without perlite) (kPa)*	Decrease in Weight (%)
10 / 15 / 5 / 45 / 25 FA1 Micronized Perlite	Room Temperature	7	4578	*6262*	10.4
		14	5429	*10975*	11.1
		28	7034	*13380*	11.7
	Room Temperature + Weight Stabilization in Air	7	10075	*9950*	
		14	9852	*17210*	
		28	10278	*15896*	
10 / 10 / 10 / 45 / 25 FA1 Micronized Perlite	Room Temperature	7	2654	*6262*	16.6
		14	3184	*10975*	18.2
		28	4773	*13380*	16.1
	Room Temperature + Weight Stabilization in Air	7	5849	*9950*	
		14	7067	*17210*	
		28	6292	*15896*	
10 / 15 / 5 / 45 / 25 FA1 P08 Perlite	Room Temperature	7	4903	*6262*	9.4
		14	7019	*10975*	9.8
		28	8631	*13380*	9.4
	Room Temperature + Weight Stabilization in Air	7	7618	*9950*	
		14	10369	*17210*	
		28	8669	*15896*	
10 / 15 / 5 / 45 / 25 FA1 P12 Perlite	Room Temperature	7	4074	*6262*	9.6
		14	6527	*10975*	10.0
		28	8995	*13380*	10.3
	Room Temperature + Weight Stabilization in Air	7	8366	*9950*	
		14	7151	*17210*	
		28	9240	*15896*	
10 / 15 / 5 / 52.5 / 17.5 FA2 P08 Perlite	Room Temperature	7	937	*5892*	17.0
		14	1838	*6794*	15.8
		28	2439	*9399*	16.5
10 / 15 / 5 / 52.5 / 17.5 FA2 P12 Perlite	Room Temperature	7	781	*5892*	16.9
		14	1245	*6794*	14.5
		28	1693	*9399*	16.6
10 / 15 / 5 / 52.5 / 17.5 FA3 P08 Perlite	Room Temperature	7	1910	*6204*	18.9
		14	2948	*9807*	16.9
		28	3768	*11571*	17.7
10 / 15 / 5 / 52.5 / 17.5 FA4 P08 Perlite	Room Temperature	7	1563	*6102*	14.1
		14	2813	*10037*	12.5
		28	2441	*10607*	12.8
10 / 15 / 5 / 52.5 / 17.5 FA4 P12 Perlite	Room Temperature	7	1082	*6102*	20.3
		14	1680	*10037*	19.1
		28	2606	*10607*	20.1

4.2. Toxicity Characteristic Leaching Procedure Tests

UCS values of solidified samples of different ratios of lime, zeolite, fly ash and sludge, cured at different media and periods, have been evaluated. The samples having high UCS values among their sets had been subjected to Toxicity Characteristic Leaching Procedure (TCLP) Test.

Table 4.7 shows the leaching results of the selected samples from the solidified mixtures of FA1. Metal leaching results for the solidified mixtures of FA2, FA3 and FA4 are given at Table 4.8. Table 4.9 presents the metal leaching results of the solidified samples cured without wrapping. Leaching results of the solidified samples containing perlite are presented at Table 4.10. Leaching limits of related metals according to the Hazardous Waste Control Regulation of Turkey (ÇOB, 2005a) are given at the top of each table.

Table 4.7. Leached metal concentrations of solidified mixtures containing FA1.

Composition	Media	Curing Period (Days)	UCS (kPa)	Cr (mg/l)	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Ni (mg/l)	Zn (mg/l)
Inert Waste				< 0.050	< 0.200			< 0.040	< 0.400
Non-hazardous Waste				0.050 – 1	0.200 – 5			0.040 – 1	0.400 – 5
Hazardous Waste				1 – 7	5 – 10			1 – 4	5 – 20
10 / 20 / 45 / 25	Humid Room	7	8881	0.054	0.036	0.330	0.017	0.005	0.317
	Humid Room	14	11553	0.054	0.016	0.390	0.019	0.005	0.254
	HR + Weight Stabilization	7	17607	0.053	0.008	0.066	0.009	0.020	0.194
	HR + Weight Stabilization	14	18717	0.147	0.015	1.945	0.146	0.036	0.443
10 / 20 / 45 / 25	Aquarium	7	5775	0.053	0.017	0.116	0.035	0.018	0.219
	Aquarium	14	11865	0.046	0.011	0.172	0.028	0.020	0.198
10 / 20 / 45 / 25	Room Temperature	7	6262	0.041	0.031	0.093	0.005	0.023	0.189
	Room Temperature	14	10975	0.088	0.024	0.079	0.022	0.019	0.223
	RT + Weight Stabilization	7	9950	0.066	0.025	0.081	0.012	0.023	0.204
	RT + Weight Stabilization	14	17210	0.098	0.017	0.051	0.051	0.033	0.182

Table 4.8. Leached metal concentrations of solidified mixtures containing FA2, FA3 and FA4.

Composition	Media	Curing Period	UCS (kPa)	Cr (mg/l)	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Ni (mg/l)	Zn (mg/l)
Inert Waste				< 0.050	< 0.200			< 0.040	< 0.400
Non-hazardous Waste				0.050 – 1	0.200 – 5			0.040 – 1	0.400 – 5
Hazardous Waste				1 – 7	5 – 10			1 – 4	5 – 20
FA2 10 / 20 / 52.5 / 17.5	Room Temperature	7	5892	0.036	0.022	0.038	0.007	0.033	0.170
	Room Temperature	14	6794	0.027	0.010	0.042	0.000	0.017	0.306
	Room Temperature	28	9399	0.065	0.017	0.080	0.005	0.000	0.286
	Humid Room	14	6051	0.052	0.010	0.046	0.000	0.000	0.180
FA3 10 / 20 / 52.5 / 17.5	Room Temperature	7	7529	0.073	0.022	0.100	0.003	0.021	0.202
	Room Temperature	14	9807	0.137	0.018	0.020	0.000	0.024	0.304
	Room Temperature	28	11571	0.124	0.013	0.051	0.000	0.027	0.298
	Humid Room	14	9120	0.114	0.020	0.127	0.007	0.025	0.321
FA4 10 / 20 / 52.5 / 17.5	Room Temperature	7	6891	0.057	0.036	0.044	0.000	0.017	0.301
	Room Temperature	14	10037	0.069	0.015	0.053	0.000	0.007	0.315
	Humid Room	14	9343	0.068	0.009	0.171	0.006	0.025	0.313

Table 4.9. Leached metal concentrations of mixtures cured without wrapping.

Composition	Media	Curing Period (Days)	UCS (kPa)	Cr (mg/l)	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Ni (mg/l)	Zn (mg/l)
Inert Waste				< 0.050	< 0.200			< 0.040	< 0.400
Non-hazardous Waste				0.050 – 1	0.200 – 5			0.040 – 1	0.400 – 5
Hazardous Waste				1 – 7	5 – 10			1 – 4	5 – 20
FA1 10 / 20 / 45 / 25	RT + Unwrapped	7	2479	0.130	0.022	0.012	0.007	0.015	0.617
FA1 10 / 20 / 45 / 25	HR + Unwrapped	7	3858	0.091	0.010	0.070	0.005	0.010	0.125
FA2 10 / 20 / 52.5 / 17.5	RT + Unwrapped	7	2646	0.071	0.005	0.077	0.007	0.010	0.203
FA3 10 / 20 / 52.5 / 17.5	RT + Unwrapped	7	2622	0.133	0.013	0.075	0.003	0.024	0.194
FA4 10 / 20 / 52.5 / 17.5	RT + Unwrapped	7	1825	0.102	0.006	0.038	0.000	0.014	0.195

Table 4.10. Leached metal concentrations of solidified mixtures containing different types of perlites.

Composition	Media	Curing Period (Days)	UCS (kPa)	Cr (mg/l)	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Ni (mg/l)	Zn (mg/l)
Inert Waste				< 0.050	< 0.200			< 0.040	< 0.400
Non-hazardous Waste				0.050 – 1	0.200 – 5			0.040 – 1	0.400 – 5
Hazardous Waste				1 – 7	5 – 10			1 – 4	5 – 20
10 / 15 / 5 / 45 / 25 P08 Perlite	RT + Weight Stabilization	7	7618	0.065	0.021	0.273	0.015	0.013	0.207
	Room Temperature	14	7019	0.067	0.023	0.672	0.024	0.016	0.208
	Room Temperature	28	8631	0.055	0.021	1.376	0.044	0.029	0.250
10 / 15 / 5 / 45 / 25 P12 Perlite	RT + Weight Stabilization	7	8366	0.082	0.010	0.078	0.010	0.014	0.256
	Room Temperature	14	6524	0.065	0.016	0.054	0.005	0.017	0.176
	Room Temperature	28	8995	0.057	0.014	0.023	0.007	0.009	0.224

5. EVALUATION

5.1. Evaluation of Sludge Characteristics

The composition of the domestic wastewater sludge collected from the secondary settling tank of Paşaköy Wastewater Treatment Plant is given at Table 3.1. Total solid content of the sludge is 1.52%. BOD_5 and COD values of the sludge, which are measured by titrimetric method, are 2300 and 9300 mg/l respectively. When the metal concentrations are evaluated, it is observed that Mg, Fe, Zn, Mn and Cu are the dominant metals with the concentrations of 60.08, 36.82, 6.968, 2.002 and 1.726 mg/l respectively. Among the metals that were characterized, the Hazardous Waste Control Regulation of Turkey has set limit for Cr, Cu, Ni and Zn in order to categorize the waste as "inert", "non-hazardous" or "hazardous" waste (ÇOB, 2005a). The concentrations of these metals within the sludge used in the project are 1.176, 1.726, 0.538 and 6.968 mg/l respectively. Among these metals, the concentrations of Cr and Zn cause the sludge to be classified as hazardous waste.

5.2. Evaluation of the UCS Values of the Solidified Mixtures Prepared with FA1

Preliminary tests were conducted with samples prepared by different ratios of lime, zeolite, fly ash (FA1) and sludge. The UCS results are given at Table 4.1. Prepared mixtures were cured in different media and for periods of 7, 14 and 28 days. The highest UCS value (10819 kPa) was observed at the mixture 11.6 / 21.1 / 42.3 / 25 (lime / zeolite / fly ash / sludge), 28 days curing period at room temperature. The next high UCS values (9524 and 8695 kPa) also belong to the same mixture cured for 28 days period in aquarium and humid room respectively.

Some other good high results were achieved with the mixtures of 11.6 / 10 / 53.4 / 25 and 10 / 20 / 45 / 25. 28 days cured samples of the mixture 11.6 / 10 / 53.4 / 25 also showed high UCS values of 7900 kPa at room temperature and 8161 kPa at humid room. On the other hand, UCS values of the mixtures of 10 / 20 / 45 / 25 cured for 28 days were 9507, 7907 and 6998 kPa respectively at room temperature, aquarium and humid room.

When the UCS values of mixtures cured for 14 days at room temperature are evaluated, it was observed that the best results (7335 and 8356 kPa) were obtained at the mixtures of 11.6 / 21.1 / 42.3 / 25 and 10 / 20 / 45 / 25 respectively. After evaluating the results of the preliminary tests, the mixture of the ratio of 10 / 20 / 45 / 25 with FA1 was decided to be used for the rest of the studies, as explained in Section 4.1.

When the UCS values of the mixture 10 / 20 / 45 / 25 at Table 4.2 are evaluated, it is observed that the samples cured at humid room had yielded better results than the ones cured at room temperature or at aquarium. The mixtures that were cured for 14 and 28 days all have UCS values higher than 10000 kPa. The results are presented at Figure A.1 in the appendix.

When the UCS values of the cured mixtures are compared with the UCS values of cured and weight stabilized mixtures, it is seen that the UCS values of the weight stabilized samples are higher than the samples which are cured but not weight stabilized (Figures A.2-A.5). This shows that curing continues after unwrapping the samples, which also decreases the weight of the samples due to moisture loss. It can be concluded that weight stabilization and curing in air after initial curing cause the samples to loose moisture, thus being lighter. In addition, unconfined compressive strength test results show that weight stabilized samples are stronger. The UCS values of weight stabilized samples range from 13000 to 19000 kPa. The highest UCS value of 19592 kPa was obtained at the solidified mixture of 10 / 20 / 45 / 25 in aquarium for 28 days and then weight stabilized in air (Table 4.2). Weight stabilization of cured mixtures takes about 3 weeks period at 18-25 °C and weight loss is in the range of 13-15%. On the other hand, weight loss of the mixtures only cured in room temperature, humid room or aquarium without weight stabilization is in the range of 0-1.0%.

When the UCS values obtained from the solidified mixtures prepared with FA1 are compared with the Turkish Standard 5893 on “Concrete – Classification with respect to Compressive Strength” (TS, 1999), it was observed that the UCS values of samples cured in different media for 28 days are in the range of C12/15 concrete with the UCS range of 12000-15000 kPa. C12/15 concrete is used in the construction of the separatory walls of the buildings. Also, the UCS values of samples cured in different media for 14 and 28 days

and weight stabilized in room temperature are in the range of C16/20 concrete with the UCS range of 16000-20000 kPa. C16/20 concrete is used in the construction of the low-rise buildings (BUĞTAŞ, 2009).

5.3. Evaluation of the UCS Values of the Solidified Mixtures Prepared with FA2, FA3 and FA4

It should be noted that different types of fly ash is generated in different processes in a thermoelectric power plant. FA2 and FA3 were the two different types of fly ash obtained from Kemerköy Thermoelectric Power Plant and FA4 is the mixture of these fly ashes in the ratio of 1:1. It was also observed that the particle size of fly ash affects the amount of sludge that could be held within the mixture. It is observed that mixtures containing FA2, FA3 and FA4 can not hold 20% or 25% sludge within the mixture. In the preparation of the mixtures to be solidified, it was observed that the highest amount of sludge that these mixtures can hold was 17.5%. This is the reason why sludge content of the mixtures prepared with FA2, FA3 and FA4 was 15% and 17.5%.

When the Table 4.3 is evaluated, it is observed that in both mixtures of FA3 (10 / 20 / 55 / 15 and 10 / 20 / 52.5 / 17.5) yielded higher UCS values than the mixtures of FA2 (Figures A.6-A.7). Also, the mixture containing 17.5% sludge yielded higher results than the mixture containing 15% sludge. When the UCS values of the mixtures of FA3 and FA4 containing 17.5% sludge are compared, it is seen that the UCS values of all them are close to each other (Table 4.3 and Figure A.7).

When the media for the stabilization of samples are compared, it is observed that for mixtures containing 15% sludge cured at humid room yielded better results than the ones cured at room temperature (Figure A.6). For the mixtures of FA2, the highest UCS value of 6097 kPa is achieved at 28 days curing in humid room. The highest UCS value for FA3 is 8320 kPa achieved by 28 days curing in humid room.

On the other hand, room temperature medium yielded higher results for the mixtures containing 17.5% sludge, even though the UCS values obtained in each medium are close to each other (Figure A.7). For mixtures containing 17.5% sludge, the highest UCS values

were obtained at the mixtures prepared with FA3. This mixture, cured for 28 days at room temperature, yielded the UCS value of 11571 kPa and the same mixture cured for 28 days in humid room yielded the UCS value of 10734 kPa. For the mixtures of FA4, the highest UCS values of 10607 kPa and 10824 kPa were obtained by 28 days curing at room temperature and in humid room respectively. Samples cured for 14 days in room temperature also yielded UCS values higher than 10MPa, 10037 kPa. The weight loss of cured samples is in the range of 0-0.60%.

As shown in Tables 3.4 and 3.5, FA1 contains ~44% CaO, whereas CaO concentration of FA2, FA3 and FA4 varies between 35-40%. As mentioned before, CaO is one of the minerals that affect the self cementing property of fly ash. Therefore, 4-9% difference in CaO content is regarded as one of the reasons why mixtures of FA1 containing 25% sludge yielded higher UCS values than mixtures of FA2, FA3 and FA4 containing 17.5% sludge.

UCS values obtained in preliminary and final experiments indicate that FA1 mixture of 10 / 20 / 45 / 25 % by weight yielded the highest unconfined compressive strength results. Taking these into consideration, FA1 mixture of 10 / 20 / 45 / 25 % by weight is considered as the best mixture within the research. When the UCS values of this mixture are compared to the UCS values obtained at other researches conducted with different types of cements, it is observed that the UCS values of this mixture are much higher that the UCS values obtained at the other researches. The maximum UCS value obtained by mixing sewage sludge with magnesium oxychloride cement is 8000 kPa (Jianli et al., 2010). In another research conducted by Cheilas et al. (2007), sewage sludge was mixed with cement and jarosite/alunite mixtures. The highest UCS value obtained was 6500 kPa. On the other hand, while UCS values as high as 15000 kPa is obtained at some solidified mixtures, almost all samples cured for 14 and 28 days yielded UCS values about 10000 kPa in this study conducted with zeolite and fly ash rather than cement. Thus, cost of this process was decreased.

Although, according to the researches conducted by other researchers, using 1 mm clinoptilolite in the mixtures had given lower UCS values with respect to 53 μm clinoptilolite, its cheaper price makes it used for further studies (Balkan, 1999). In this

stage of the research, sludge content of the mixtures were determined as 15% due to lower water holding capacity of 1 mm clinoptilolite with respect to 53 µm clinoptilolite. When the results of the tests conducted with the mixtures containing 1 mm clinoptilolite (Table 4.4) are evaluated, it is observed that the UCS values obtained from all the mixtures are below 5000 kPa. Mixtures cured at room temperature yielded higher results than the mixtures cured in humid room. UCS values obtained from mixtures containing FA3 are higher than mixtures containing FA2 and FA4 (Figure A.8). The highest values of 4806 and 4554 kPa were obtained at mixtures of FA3 and FA4 cured at room temperature for 28 days, respectively. Weight loss of the solidified samples is in the range of 0-0.40%.

5.4. Evaluation of the UCS Values of the Unwrapped Mixtures

Even though it is not a standard process, prepared mixtures were cured in room temperature and humid room without wrapping. The UCS values are given at Table 4.5. When the UCS results of the mixtures cured at room temperature are evaluated, it is seen that mixtures prepared with FA2, FA3 and FA4 show decrease in the UCS values after curing for 14 or 28 days. The UCS values of the cured mixtures containing FA2 showed a decrease from 2753 kPa to 1852 kPa at 28 days curing. Cured mixtures containing FA3 showed a decrease in UCS values from 2622 kPa to 1605 kPa at 14 days curing. Similar observations are made for the cured mixtures containing FA4. Mixtures cured for 14 days yielded the UCS value of 2156 kPa, whereas the same mixture cured for 7 days yielded the UCS value of 766 kPa. On the other hand, UCS values of samples prepared with FA1 are in the same range regardless of curing period (Figure A.9). The highest UCS values obtained from the mixtures cured without wrapping are 2753 and 2652 kPa, which belong to the mixture prepared with FA2 and cured for 14 days and the mixture prepared with FA1 and cured for 28 days, respectively.

The UCS values obtained at the mixtures prepared with FA1 yielded higher values than mixtures prepared with FA2, FA3 or FA4. This is most probably due to the higher CaO concentration of FA1. Therefore mixture of the same ratio containing FA1 was prepared to be cured in humid room. Results, shown at the Table 4.5, indicate that humid room is a better medium than the room temperature for the solidification of the unwrapped mixtures in yielding higher UCS values. In contrary to the samples cured in room

temperature, the UCS values obtained at the samples cured in humid room has shown increase, exceeding 5000 kPa, as curing period gets longer (Figure A.10).

It is observed that curing unwrapped samples in humid room yields similar results to the curing of wrapped samples, due to the fact that humid room enables unwrapped samples to hold the moisture in the samples which is needed for the curing of the mixtures.

When the weight loss of cured samples is evaluated, it is seen that weight loss of the cured samples are higher than the samples that were wrapped and cured in different media (Tables 4.2 and 4.3). For mixture prepared with FA1 cured in room temperature, the weight loss is in the range of 17.5-20.0%. Weight loss of the mixtures of FA1 cured in humid room is in the range of 10.5-11.5%. Finally, weight loss mixtures prepared with FA2, FA3 and FA4 are in the range of 10.0-15.5%. On the other hand, the UCS values obtained from the curing of unwrapped mixtures are lower than the UCS values of the mixtures cured after wrapping.

5.5. Evaluation of the UCS Values of the Mixtures Containing Perlite

In this section of the study, effect addition of perlite to the UCS values of solidified mixtures is examined. The reason for adding perlite to the mixtures is to decrease the weight of the solidified mixtures because of perlite's low density and increasing the thermal insulation property. The effect of perlite on thermal insulation of solidified mixtures could not be studied due to constraints in sample preparation for thermal conductivity tests.

When the UCS values of the solidified mixtures prepared with FA1 and 5% perlite, cured at room temperature are evaluated, it is observed that mixtures containing P08 and P12 perlite have yielded higher UCS values than of micronized perlite (Figure A.11). The highest UCS values of 8631 and 8995 kPa were achieved for mixtures containing P08 and P12 perlite cured for 28 days, respectively.

Comparison of mixtures prepared with FA1 containing perlite to mixtures without perlite shows that perlite addition causes decrease in the UCS values in the range of 50-

80% according to the type of the perlite and the curing period (Figure A.12). It should be noted that the compared solidified mixtures containing perlite and without perlite have the same sludge and fly ash ratios by weight.

The UCS values of solidified mixtures prepared with FA1 left for weight stabilization after curing did not give similar results to the samples that were cured at room temperature without weight stabilization (Figures A.11 and A.13). The highest UCS value of 10369 kPa was obtained at the solidified mixture containing P08 perlite and cured for 14 days. The solidified mixture containing micronized perlite cured for 7 and 28 days also yielded high UCS values, 10075 and 10278 kPa respectively. As mentioned in Section 5.2, the weight stabilization of cured samples in room temperature took about three weeks.

The effect of increasing perlite in the mixtures was also investigated. 5 and 10% micronized perlite were added to the mixtures prepared with 45% FA1 and 25% sludge by weight. It is observed that even though increase of perlite decreases the weight of the cured samples, it also decreases the UCS values (Figure A.13).

When the sample weights of the solidified mixtures of FA1 (25% sludge) prepared with and without perlite are compared (Table 4.6), it is observed that the decrease in weight is about 10% for mixtures containing 5% perlite and up to 18% for mixtures containing 10% perlite (Figure A.14).

When the UCS values of samples prepared by using FA2, FA3 and FA4 are evaluated, it is observed that samples containing P08 perlite yielded higher UCS values than the mixtures containing P12 perlite in all mixtures (Figures A.15-A.16). Among the mixtures prepared with P08 perlite, mixtures containing FA3 yielded the highest UCS values of 1910 kPa for 7 days curing, 2948 kPa for 14 days curing and 3768 kPa for 28 days curing.

As in the previous tests conducted with the mixtures without perlite, mixtures prepared with FA1 yielded higher UCS values than mixtures prepared with FA2, FA3 or FA4. It is believed that this is due to higher CaO concentration of FA1 (Figure A.17).

Weight comparison of solidified mixtures containing perlite with respect to mixtures without perlite having the same fly ash and sludge ratio for the mixtures of FA2, FA3 and FA4 indicated 12.5 to 20% decrease in sample weight. The highest weight decrease was achieved with the mixtures of P12 and FA4, which was around 20% for all solidified mixtures (Figure A.18).

5.6. Evaluation of Leaching Tests

The results of the leaching experiments conducted according to the Toxicity Characteristic Leaching Procedure (TCLP) are presented at Tables 4.7, 4.8, 4.9 and 4.10. Solidified mixtures having higher UCS values among its sets had been chosen to be subjected to leaching tests. The leaching results, composed of different leached metals, were compared with the limit values of the Hazardous Waste Control Regulation of Turkey (ÇOB, 2005a). Among the six metals tested, the concentration limits of Cr, Cu, Ni and Zn are defined in the Hazardous Waste Control Regulation of Turkey. Each metal is categorized as inert, non-hazardous or hazardous waste according to its concentration. The value of each category for each metal is given at the top of each table.

Leaching test results of mixtures prepared using FA1 are presented in Table 4.7. When the results are evaluated it is seen that some of the solidified mixture fall into the category of inert waste, whereas all of them qualify the limits of non-hazardous wastes. Except chromium, concentrations of all the leached metals are in the range of inert waste limits according to the Hazardous Waste Control Regulation of Turkey (Figures B.1-B.3). The highest leached metal concentration within the research is Fe concentration, 1.945 mg/l, of the solidified mixture prepared with FA1 and cured at humid room for 14 days and weight stabilized. The value obtained was considered as an experimental error. Afterwards, when the leached metal concentration of other metals of the same sample is evaluated, it is observed that all metals have given higher leached metal concentrations with respect to the other mixtures of the same set. It is believed that the situation is due to an impurity (Table 4.7). Regardless of this sample, highest metal concentrations are achieved by Fe and Zn.

Table 4.8 shows the leaching test results of cured samples prepared with FA2, FA3 and FA4. When the metal concentrations are evaluated it is observed that all samples fall

into the category of non-hazardous wastes. In addition, two samples (mixtures prepared with FA2 and cured at room temperature for 7 and 14 days) fall into the category of inert wastes (Table 4.8 and Figures B.4-B.6). The metal concentration which exceeds the limits of inert wastes is Cr. Metals having highest concentrations are Cr, Fe and Zn.

Leaching test results of cured samples without wrapping are given at Table 4.9. All samples fall into the category of non-hazardous wastes according to the Hazardous Wastes Control Regulation of Turkey. Again, Cr concentration exceeds the limit for inert wastes in addition to Zn concentration in one of the samples (Table 4.9 and Figures B.7-B.8). Cr and Zn are the metals having the highest leached metal concentrations at the TCLP tests.

Table 4.10 shows the leaching test results of mixtures prepared with FA1 and P08 or P12 perlite. When the leaching results are evaluated, it is observed that all samples fall into the category of non-hazardous wastes according to the Hazardous Wastes Control Regulation of Turkey. As in previous samples, Cr concentration exceeds the limit for inert wastes. Metals with highest concentrations are Fe and Zn (Table 4.10 and Figures B.9-B.10).

5.7. Economic Analysis

The system used in the research should be economically feasible in order to be able to apply in real life. Therefore, the final disposal cost of sludge and fly ash by incineration or landfilling in addition to present construction materials is compared with the cost of solidification of sludge with fly ash, clinoptilolite and lime in order to obtain solidified products that can be used in construction applications. The economic analysis is conducted by calculating estimated transportation costs of raw materials clinoptilolite and fly ash from İzmir and Muğla to İstanbul, sludge and lime from Asian Side of İstanbul to European Side of İstanbul. Transportation of sludge and fly ash for final disposal are considered as to be from the origin of the waste Paşaköy and Muğla respectively to İzaydaş. All the calculations are done with respect to the mixture of ratio of 10 / 20 / 45 / 25, which yielded the highest UCS values in the research. Also, the transportation cost of cement is estimated as transportation from European Side of İstanbul to Asian Side of İstanbul. The economic analysis is given at Table 5.1.

Table 5.1. Economic analysis of the research.

	Raw materials	Price (TL/ton)	Ratio in the Mixture (%)	Final Price (TL)
Product cost (10 / 20 / 45 / 25)	Cost and transporation of clinoptilolite	230	20	46
	Transportation of fly ash	53	45	24
	Transportation of sludge	34	25	8.50
	Cost and transporation of lime	767	10	77
	TOTAL	***	100	155.50
Treatment of wastes	Transportation of sludge	34	25	8.50
	Landfilling of sludge (1)	200	25	50
	Incineration of sludge (2)	900	25	225
	Transportation of fly ash	34	45	15.30
	Landfilling of fly ash	240	45	108
	TOTAL 1	***	***	181.80
	TOTAL 2	***	***	356.80
Cement use in construction	Transportation of cement	16	100	16
	Cost of cement	91	100	91
	TOTAL	***	100	107
Waste treatment + Cement use in construction	TOTAL 1	***	***	288.80
	TOTAL 2	***	***	463.80

When Table 5.1 is evaluated, it is observed that solidification of 250 kg sludge in order to achieve 1 ton of construction material costs 155.50 TL. The total cost of treating the wastes used the mixture is 181.80 TL for landfilling of sludge and fly ash, 356.80 TL for incineration of sludge and landfilling of fly ash. On the other hand, using cement in construction costs 107 TL/ton. In an environmentalist perspective, when the cost of waste treatment is added to the cost of cement, total cost increases to the range of 288.80 - 436.80 TL. In addition, the cost of the land of the landfill area and lifetime are not included to the economic analysis. The cost analysis indicates that the applicability of the solidification method used in the research is significant for national economy.

6. CONCLUSION

Large amount of sludge generated by domestic wastewater treatment is still a significant environmental problem. This research was aimed to investigate a novel method for domestic wastewater sludge handling which can enable the use of sludge by stabilization/solidification method by using cheap natural products. At the research conducted, sludge was mixed with different types of fly ash (FA1, FA2, FA3 and FA4) with lime, zeolite and perlite. Fly ash is a by-product of thermoelectric power plant which can be obtained free of cost. Zeolite and perlite are cheap, natural products, both abundant in Turkey. The solidified mixtures were examined for their unconfined compressive strength and metal leaching values. It is seen that domestic wastewater sludge can be solidified/stabilized by a mixture of fly ash and other additives that can yield products of high compressive strength and low leaching and the obtained products can be used in construction applications.

Solidification was achieved by different standard and non-standard methods in order to examine the effect of different media. High UCS values have been achieved by different solidified mixtures, which indicate the probability of the mixtures to be used in the field of construction.

The highest UCS values of mixtures prepared with FA1 were achieved by 28 days curing at room temperature, 13380 kPa; 28 days curing in humid room, 15472 kPa and 28 days curing in aquarium, 14464 kPa. When the UCS values of samples that were also left for weight stabilization in room temperature are evaluated, it is observed that UCS value of 17210 kPa was obtained at curing for 14 days at room temperature, 18717 kPa at curing for 14 days in humid room and finally 19592 kPa at curing for 28 days in aquarium (Table 4.2). The UCS values of samples cured in different media for 28 days are in the range of C12/15 concrete. In addition, the samples cured at different media for 14 and 28 days and weight stabilized yielded UCS values in the range of C16/20 concrete with respect to TS 5893. C12/15 and C16/20 concretes are used in the construction of the separatory walls and the low-rise buildings, respectively.

Changes in physical and chemical composition of fly ash affect different attributes such as water holding capacity of fly ash. This consequently affects the water holding capacity of the mixtures prepared for solidification. Therefore it is not possible to give a general formula for the percentages of sludge, fly ash, zeolite and lime that would be used in the process. When the properties of the mixtures prepared with FA2 are examined (Table 4.3), it is observed that the highest UCS values were 9399 and 7373 kPa, achieved at the mixtures containing 17.5% sludge and cured at room temperature and in humid room for 28 days, respectively. The highest results for mixtures prepared with FA3 and 17.5% sludge were, 11571 and 10734 kPa for the mixtures cured at room temperature and at humid room for 28 days, respectively. The highest UCS values of 10607 and 10824 kPa were achieved at mixtures prepared with FA4 and cured at room temperature and at humid room for 28 days, respectively.

Another set of samples were cured at room temperature without wrapping. It was thought that this application would be the most probable and feasible method to obtain products to be used in different construction applications (Table 4.5). The highest UCS values of 2479 and 2652 kPa were achieved at the mixtures prepared with FA1 and cured for 7 and 14 days respectively. The mixtures prepared with FA2 and cured for 7 and 14 days had the highest UCS values of 2646 and 2753 kPa respectively. Finally the highest UCS value of 2622 kPa was obtained at the mixture prepared with FA3 and cured for 7 days. On the other hand it is observed that as curing period extends, the UCS values decreases for the mixtures prepared with FA2, FA3 and FA4 due to excess moisture loss during solidification. When the UCS values of FA1 mixtures cured at room temperature and humid room are evaluated, it is observed that the highest value of 5202 kPa was achieved at the mixtures cured in humid room for 28 days. All the samples cured in humid room had higher UCS values than samples cured at room temperature.

Perlite, being a light and good insulator, was also used in the preparation of some mixtures. In the mixtures containing FA1, UCS values as high as 10000 kPa were achieved when the cured samples were left for weight stabilization in air (Table 4.6). The highest UCS values of 8631 and 8995 kPa were achieved at mixtures prepared with FA1 and P08 perlite cured for 28 days at room temperature without weight stabilization afterwards and mixtures prepared with FA1 and P12 perlite cured for 28 days at room temperature without

weight stabilization afterwards, respectively. Addition of 5% perlite to mixtures prepared with FA1 caused a decrease of almost 10% in solidified sample weight. Addition of perlite to mixtures prepared with FA2, FA3 and FA4 caused drastic decrease in the UCS results, all values being below 4000 kPa. Due to constraints in sample preparation and lack of feasible standard methods, the samples were not tested for insulation property.

In all the experiments conducted, it was observed that mixtures prepared with FA1 yielded better UCS results than mixtures prepared with FA2, FA3 or FA4. It is believed that one of the reasons for the outcome is the higher CaO concentration of FA1.

The samples having high UCS values among their sets were exposed to leaching tests by TCLP method. Leached metal concentrations of Ni and Cu are within the limits of inert wastes with respect to the Hazardous Waste Control Regulation of Turkey. Whereas, the leached metal concentrations of Cr and Zn are higher than the limit values for inert wastes indicated at the Regulation. Concentrations of Cr and Zn were within the limits of non-hazardous wastes. Therefore the solidified samples are categorized as non-hazardous wastes, rather than inert wastes.

The economical analysis conducted indicates that the use of the product obtained at the research in the construction sector instead of cement is significantly economical for the nation.

It can be concluded that solidified domestic wastewater sludge can be efficiently used in different construction applications without any environmental threat due to their high UCS values and low metal leaching, as well as abundance of the natural and cheap solidification additives in Turkey.

7. RECOMMENDATIONS

The study conducted can be advanced by the applying different tests in order to detect the efficiency of the solidification/stabilization process as well as the applicability of the products in the construction field. Recommendations for further studies can be summarized as:

- Physical tests such as permeability testing and durability testing (freeze-thaw and wetting-drying) can be applied in order to control the efficiency of different solidification/stabilization processes,

- Thermal insulation tests can be applied both to mixtures that do not contain perlite and that contain perlite in order to compare the effect of perlite as well as comparing the results of different materials used in the construction applications,

- Different fiber and metal additives can be added to the mixtures in order to increase the UCS values of the products.

REFERENCES

ACAA, American Coal Ash Association 2003. Fly Ash Facts for Highway Engineers, FHWA-IF- 03-019, Colorado.

ACAA, American Coal Ash Association, 2008. 2007 Coal Combustion Product (CCP) Production & Use Survey Results (Revised). Colorado.

Adriano, D.C. Page, A.L., Elseewi, A.A., Chang, A.C., Straughan, I., 1980. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: A review. Journal of Environmental Quality, 9, 333-334.

Akçansa Çimento San. Tic. A.Ş., 2008. Kimyasal Analiz Raporu. İstanbul.

Alonso, J.L., Wesche, K., 1991. Characterization of Fly Ash. Report of Technical Committee, 67-FAB, RILEM, London.

Anonymous, 2007a. Amethyst Galleries http://www.galleries.com/minerals/silicate/ clinopti/ clinopti.htm

Anonymous, 2007b. Popular Science http://www.popsci.com/scitech/article/2007-05/ invention-awards-green-brick

APHA-AWWA-WPCF, 2005. Standard Methods for the Examination of Water and Wastewater, 21st edition, American Public Health Association, New York.

ASKI, 2007. Ankara'da Çamur Yönetimi, Türkiye'de Çamur Yönetimi Toplantısı, Çevre ve Orman Bakanlığı, Ankara.

Atanur, A., 1971. Uçucu Küllerin Kimyasal ve Fiziksel Vasıfları ve Yapı Malzemesi Olarak Kullanılması, TC Bayındırlık Bakanlığı Karayolları Genel Müdürlüğü, Yayın No. 193, Ankara.

Balkan, M., 1999. Development of Appropriate Low Cost Industrial Sludge Solidification Systems, M. S. Thesis, Boğaziçi University.

Barrer, R.M., 1968. Chemical Industry, 1203.

Barrer, R.M., 1978. Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, New York.

Barthomeuf, D., 1996. Basic zeolites: characterization and uses in adsorption and catalysis, Catalysis Reviews Science and Engineering, 38, 521-612.

Baveye, P., McBridge, M.B., Bouldin, D., Hinesly, T.D., Dahdoh, M.S.A., Abdel-Sabour, M.F., 1999. Mass balance and distribution of sludge-borne trace elements in a silt loam following long-term application of sewage sludge. Science of The Total Environment, 227(1), 13-28.

Baykal, G., Döven, A.G., 1996. Utilization of Fly Ash as Flowable Fill, Sixth Turkish Congress on Soil Mechanics and Foundation Engineering, İzmir, 24-25 October 1996, 453-464.

Berg, J., Feueerborn, H.J., 2001. Production and utilization of CCPs in Europe: Fly ash and cement and concrete. European Coal Combustion Products Association, Essen, Germany.

Biernacki, J.J., Vazrala, A.K., Wayne Leimer, H., 2008. Sintering of a class F fly ash, Fuel, 87(6), 782-792.

Bolen, W.P., 2007. U.S. Geological Survey, Mineral Commodity Summaries. Washington DC.

Bowles, J. E., 1992. Engineering Properties of Soils and Their Measurements, McGraw-Hill Inc., New York.

Breck, D.W., 1974. Zeolite Molecular Sieves, John Wiley & Sons, New York.

BUĞTAŞ BETON, http://www.bug-tasbeton.com.tr/urun.asp, (accessed July 2009).

Carbonell, G., Pro, J., Gomez, N., Babin, M.M., Fernandez, C., Alonso, E., Tarazona, J.V., 2009. Sewage sludge applied to agricultural soil: Exotoxicological effects on representative soil organisms. Exotoxicology and Environmental Safety, 72(4), 1309-1319.

Cheilas, A., Katsioti, M., Georgiades, A., Malliou, O., Teas, C., Haniotakis, E., 2007. Impact of hardening conditions on to stabilized/solidified products of cement-sewage sludge-jarosite/alunite. Cement Concrete and Composites, 29, 263-269.

Conner, J.R., Hoeffner, S.L., 1998. A critical review of stabilization/solidification technology. Critical Reviews in Environmental Science and Technology, 28(4), 397-462.

Council of the European Communities, 1986. Council Directive of 12 June 1986 on the Protection of the Environment, and in Particular of Soil, When Sewage Sludge is Used in Agriculture (86/278/EEC). Official Journal of the European Communities. L181(6)29.

Çınar, S., 2001. Effect of Various Type of Sludge Codisposal on the Solid Waste Stabilization in Landfills, M.S. Thesis, Boğaziçi University.

ÇOB, 2005a. Tehlikeli Atıkların Kontrolu Yönetmeliği. Çevre ve Orman Bakanlığı, Ankara.

ÇOB, 2005b. Toprak Kirliliği Kontrolu Yönetmeliği, Çevre ve Orman Bakanlığı, Ankara.

Danker, R., Adriano, D.C., Barton, C., Punshon, T., 2001. Revegetation of Coal Fly Ash – Reject Landfill, Proceedings of 6th International Conference on the Biogeochemistry of Trace Elements, Guelph, Canada, July 29- August 2, 2001.

Dean, R.B., Suess, M.J., 1985. The risk to health of chemicals in sewage sludge applied to land. Waste Management and Research, 3, 251-278.

Della, R., Della, M., Luke, W., Karen, D.S., 1984. Characterization of Fly Ash and Its Reactions in Concrete, Materials Research Society, Pittsburgh.

Demir, I., Başpınar, M.S., 2008. Effect of silica fume and expanded perlite addition on the technical properties of the fly ash-lime-gypsum mixture. Construction and Building Materials, 22(6), 1299-1304.

Demirboğa, R., Gül, R., 2003. The effects of expanded perlite aggregate, silica fume and fly ash on the thermal conductivity of lightweight concrete. Cement and Concrete Research, 33, 723-727.

Department of Environment-UK, 1989. Code of Practice for Agricultural Use of Sewage Sludge, UK.

Dhir, R.K., 1986. Pulverized Fuel Ash: In Concrete Technology and Design, Cement Replacement Materials, Vol. 3, Blacky and Sons Ltd., 447-481.

Doğan, M., 2001. Sulu Ortamda Perlitin Yüzey Yükünün ve Adsorpsiyon Özelliklerinin İncelenmesi, PhD Thesis, Balıkesir University.

Döven, A.G., 1998. Lightweight Fly Ash Aggregate Production Using Cold Bonding Agglomeration Process, Ph.D. Dissertation, Boğaziçi University.

Dutta, P.K., Auerbach, S.M., Carrado, K.A., 2003. Handbook of Zeolite Science and Technology, Marcel Dekker, Inc., Florida.

El-Mogazi, D.D., Lisk, D.J. Weinstein, L.H., 1988. A review of physical, chemical and biological properties of fly ash and effects on environmental ecosystems. Science of the Total Environment, 74, 1-37.

Epstein, E., 2003. Land Applications of Sewage Sludge and Biosolids, Lewis Publishers, Florida.

Erdoğan, Y., 1993. Atık Malzemelerin İnşaat Endüstrisinde Kullanımı – Uçucu Kül ve Yüksek Fırın Cürufu, Endüstriyel Atıkların İnşaat Sektöründe Kullanılması Sempozyum Kitabı, TMMOB, Ankara, 18-19 Kasım 1993, 1-8.

Erol, M., Küçükbayrak, S., Ersoy-Meriçboyu, A., 2008. Characterization of sintered coal fly ash. Fuel, 87(7), 1334-1340.

Fajula, F., Plee, D., 1994. Advanced zeolite science and applications. Studies in Surface Science and Catalysis, 85, 633-651.

FAO, 1992. Wastewater Treatment and Usage in Agriculture. Food and Agricultural Organization of the United Nations, Rome.

Filibeli, A., Ayol, A., 2008. Türkiye'de Arıtma Çamuru Potansiyeli: Yasal Mevzuat, Arıtma Çamurlarının Özellikleri ve Yararlı Kullanım Alternatiflerinin Değerlendirilmesi", Türk-Alman Katı Atık Günleri 2008 Sempozyum Kitabı, İzmir, 27-29 Kasım 2008, 133-146.

Flanigen, E.M., 1980. Molecular sieve zeolite technology – the first twenty-five years. Pure and Applied Chemistry, 52, 2191-2211.

Güleç. Ş.B., 1999. Determination of the Remaining Stabilization Potential of Landfilled Solid Waste by Sludge Addition, M.S. Thesis, Boğaziçi University.

Halstead, W.J., 1986. Use of Fly Ash in Concrete. NCHRP 127 - Transportation Research Board, National Research Council, Washington DC.

Hennis, K.W., Frishette, C.W., 1993. A New Era in Control Density Fill, Proceedings of the 10th International Ash Utilization Symposium, Kentucy.

Hermann, I., Svensson, M., Ecke, H., Kumpiene, J., Maurice, C., Andreas, L., Lagerkvist, A., 2009. Hydraulic conductivity of fly ash-sewage sludge mixes for use in landfill cover liners. Water Research, 43(14), 3541-3547.

Incal Mineral Company, 2008. The Physical and Chemical Composition of Clinoptilolite. İncal Mineral Company Report, İzmir.

Iwamoto, M., 1994. Zeolites in Environmental Catalysis, Proceedings of the 10th International Zeolite Conference, Germany, 17-22 July 1994, Vol. 84/B, 1395-1409.

Iyer R.S., Scott, J., 2001. Power station fly ash – a review of value-added utilization outside of the construction industry. Resources Conservation & Recycling, 31, 217-228.

IZSU, 2007. İzmir'de Çamur Yönetimi, Türkiye'de Çamur Yönetimi Toplantısı, Çevre ve Orman Bakanlığı, Ankara.

Jamali, M.K., Kazi, T.G., Arian, M.B., Afridi, H.I., Memon, A.R., Jalbani, N., Shah, A., 2008. Use of sewage sludge after liming as fertilizer for maize growth. Pedosphere, 18(2), 203-213.

Jianli, M., Youcai, Z., Jinmei, W., Li, W., 2010. Effect of magnesium oxychloride cement on stabilization/solidification of sewage sludge, Construction and Building Materials, 24, 79-83.

Kantarcı, M.D., 2003. The effects of three thermo electric power plants on Yerkesik-Denizova Forests in Muğla Province (Turkey). Water, Air, and Soil Pollution: Focus, 3, 205-213.

Karadaş, M., 2004. Perlitin Bazı Yüzey Aktif Madde Çözeltilerindeki Elektrokinetik ve Adsorpsiyon Özellikleri, M.S. Thesis, Balıkesir University.

KASKI, 2005. Kayseri Atıksu Arıtma Tesisi Çamurlarının Bertaraf Edilmesi, I. Ulusal Arıtma Çamurları Sempozyumu, İzmir, 23-25 March 2005, 289-298.

Kelly, T.D., Kalyoncu, R., 2002. Coal Combustion Products Statistics. US Geological Survey Minerals Yearbook.

Kemerköy Thermoelectric Power Plant, 2003. Kemerköy Thermoelectric Power Plant Report: The Chemical Composition of the Fly Ash. Muğla.

Kesraoui-Ouki, S., Cheeseman, C.R., Perry, R., 1994. Natural zeolite utilisation in pollution control: A review of applications to metal's effluents. Journal of Chemical Technology and Biotechnology, 59, 121-126.

Kikuchi, R., 1999. Application of coal ash to environmental improvement. Transformation into zeolite, potassium fertilizer, and FGD absorbent. Resoureces Conservation & Recycling, 27, 333-346.

Lane, R.O., Best, J.F., 1982. Properties and use of fly ash in Portland cement concrete. Design and Construction, 4, 81-92.

Little, D.N., 1995. Stabilization of pavement subgrades and base courses with lime, National Lime Association, Kendall/Hunt Publishing Company, USA.

Liu, H.F., Liptak, B.G. Bois, P.A., 1997. Environmental Engineers' Handbook, Lewis Publishers, Florida.

Logan, T.J., Lindsay, B.J., Goins, L.E., Ryan, J.A., 1997. Field assessment of sludge metal bioavailability to crops: Sludge rate response. Journal of Environmental Quality, 26(2), 534-550.

Magic Mineral, http://www.magicmineral.com/natural_zeolites.htm (accessed May 2008).

Manz, O.E., 1999. Coal fly ash: a retrospective and future look. Fuel, 78, 133-136.

MASKI, 2007. Malatya Atıksu Arıtma Çamurlarının Tarımsal Amaçlı Kullanımı, Türkiye'de Çamur Yönetimi Toplantısı, Çevre ve Orman Bakanlığı, Ankara.

Mattigod, S.V., Rai, D., Eary, L.E., Ainsworth, C.C., 1990. Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements. Journal of Environmental Quality, 19, 188-201.

Mehta, P.K., 1983. Pozzolanic and cementious by products as mineral admixtures for concrete, fly ash, silica fume, slag and other mineral by-products in concrete. American Concrete Institute, 79(1), 1-46.

Meier, W.M., 1968. Molecular Sieves. Society of Chemical Industry, London.

Morisson, R.D., 1981. Potential health impacts of subsurface sewage sludge disposal upon groundwater resources. Studies in Environmental Sciences, 17, 305-307.

Mumpton, F. A., 1977. Mineralogy and Geology of Natural Zeolites. Reviews in Mineralogy, Vol. 4, Mineralogical Society of America. Washington, DC.

Page, A.L., Elseewi, A.A., Straughan, I., 1979. Physical and chemical properties of fly ash from coal-fired power plants with references to environmental impacts. Residue Reviews, 71, 83-120.

PCA, Portland Cement Accociation, 2008. http://www.cement.org/waste/wt_ss.asp

Perlite Institute Inc., 2008. http://www.perlite.org/product_guides/1%20Basic%20Facts%20 about%20Perlite.pdf

Punshon, T., Adriano, D.C., Weber, J.T., 2002. Restoration of drastically eroded land using coal fly ash and poultary biosolid. Science of the Total Environment, 296, 209-225.

Raven, L.P., Loeppert, R.H., 1997. Trace element composition of fertilizers and soil amendments. Journal of Environmental Quality, 26, 551-557.

RCRA, Resource Conservation and Recovery Act, 1976. U.S. Code Title 42 – Public health and welfare, Chapter 82, Solid waste disposal, http://www.access.gpo.gov/uscode/title42/ chapter82_.html

Rodger, G.K., Davies, I.M., Topping, G., 1992. Retention of trace metal contaminants in the sediment at an accumulating sewage sludge disposal site. Water Research, 26(1), 111-120.

Rubin, A.R., Safley, L.M., Zublena, J.P., 1991. Land application of municipal sludge – advantages and concerns. Soil Facts, North Carolina Cooperative Extension Service, North Carolina State University College of Agriculture & Life Scineces.

Sajwan, K.S., Ornes, W.H., Youngblood, T., 1995. The effect of fly ash/sewage sludge mixtures and application rates on biomass production. Journal of Environmental Science and Health Part A, 30(6), 1327-1337.

Sangwan, P., Kaushik, C.P., Garg, V.K., 2008. Vermiconversion of industrial sludge for recycling the nutrients. Bioresource Technology, 99(18), 8699-8704.

Sarkar, A., Rano, R., 2007. Water holding capacities of fly ashes: effect of size fractionation. Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 29(5), 471-482.

Schoonover, M.W., Cohn, M.J., 2000. New materials discovery for industrial applications. Topics in Catalysis, 13, 367-372.

Sear, L.K.A., 2001. Properties and Use of Coal Fly Ash: A Valuable Industrial By-Product, Thomas Telford Publishing, Great Britain.

Singh, D.N., Kolay, P.K., 2002. Simulation of ash-water interaction and its influence on ash characteristics. Progress in Energy and Combustion Science, 28, 267-299.

Sopper E., 1993. Municipal Sludge Use in Land Reclamation, CRC Press.

Spence, R., Shi, C., 2005. Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes, CRC Press, Florida.

Styron, R.W., Perryman, L.W., 1992. Lightweight Aggregate Derived from the Combustion of Coal, 10th International Ash Use Symposium, Florida, 3, 90-110.

Suter, G.W., Luxmoore, R.J., Smith, E.D., 1993. Compacted soil barriers at abandoned landfill sites are likely to fail in long term. Journal of Environmental Quality, 22, 217-226.

Şahin, V., 1996. Heavy Metal Removal from Industrial Wastewaters by Ion Exchange on Clinoptilolite, M. S. Thesis, Boğaziçi University.

Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2003. Wastewater Engineering: Treatment and Reuse, Fourth Edition, McGraw-Hill.

The Loretti Group, 2008. Greenhouse Gas Emission Reductions from Blended Cement Production, Arlington, Massachusetts.

TIFAC, Technology, Information, Forecasting and Assessment Council, Department of Science and Technology, Government of India, http://www.tifac.org.in/index.php?option=com_researchviewdetail&researchID=44&Itemid=211 (accessed June 2008).

Tiryaki, E., 2005. Optimization of the Solidification and Stabilization of Industrial Wastewater Sludge with Natural Additives, M.S. Thesis, Boğaziçi University.

TS, 1999. Beton-Basınç Dayanımına Göre Sınıflandırma. TS 5893 ISO 3893. Türk Standartları Enstitüsü, Ankara.

TÜBİTAK, 2008. Analiz Raporu. Malzeme ve Kimya Teknolojileri Araştırma Ensitüsü, İstanbul.

TÜİK, 2007. Belediye Atıksu Temel Göstergeleri 1994-2006, Ankara.

TÜİK, 2008. Haber Bülteni - Belediye Atıksu İstatistikleri 2006, Ankara.

USDOI, US Department of the Interior, 2008. 2007 Minerals Yearbook, US Geological Survey.

USEPA, 1980. Guide to the Disposal of Chemically Stabilized and Solidified Waste. Washington DC. EPA/SW- 872.

USEPA, 1988. Wastes from the Combustion of Coal by Electricity Power Plants. Washington DC.

USEPA, 1989. Stabilization/Solidification of CERCLA and RCRA Wastes. Washington DC. EPA/625/6-89/022.

USEPA, 1993. Technology Resource Document – Solidification/Stabilization and Its Application to Waste Materials. Washington DC. EPA/530/R-93/012.

USEPA, 1999. Biosolids Generation, Use and Disposal in the United States. Office of Solid Waste and Emergency Response, US Environmental Protection Agency, Washington DC. EPA/530/R-99/009.

USEPA. Summary of the Resource Conservation and Recovery Act http://www.epa.gov/lawsregs/laws/rcra.html (accessed December 2007).

Uyanık, T., 2007. Maden ve Mineraller, TC Başbakanlık Dış Ticaret Müsteşarlığı İhracatı Geliştirme Etüt Merkezi.

Yufen, Y., Gousheng, G., Qingru, C., 2005. Preparation and characteristics of composite micro-bead particles. Powder Handling Process, 17(1), 28-31.

Zaeni, A., Bandyopadhyay, S., Yu, A., Rider, J., Sorrell, C.S., Dain, S., Blackburn, D., White, C., 2010. Colour control in fly ash as a combined function of particle size and chemical composition. Fuel, 89(2), 399-404.

ZEO-TECH Corp.. http://www.zeotechcorp.com/Zeolite.asp (accessed June 2008).

Zimmer, F.V., 1970. Fly Ash as a Bituminous Filler, Proceedings of the Second Ash Utilization Symposium, USA.

APPENDIX A. The UCS Values of the Solidified Samples

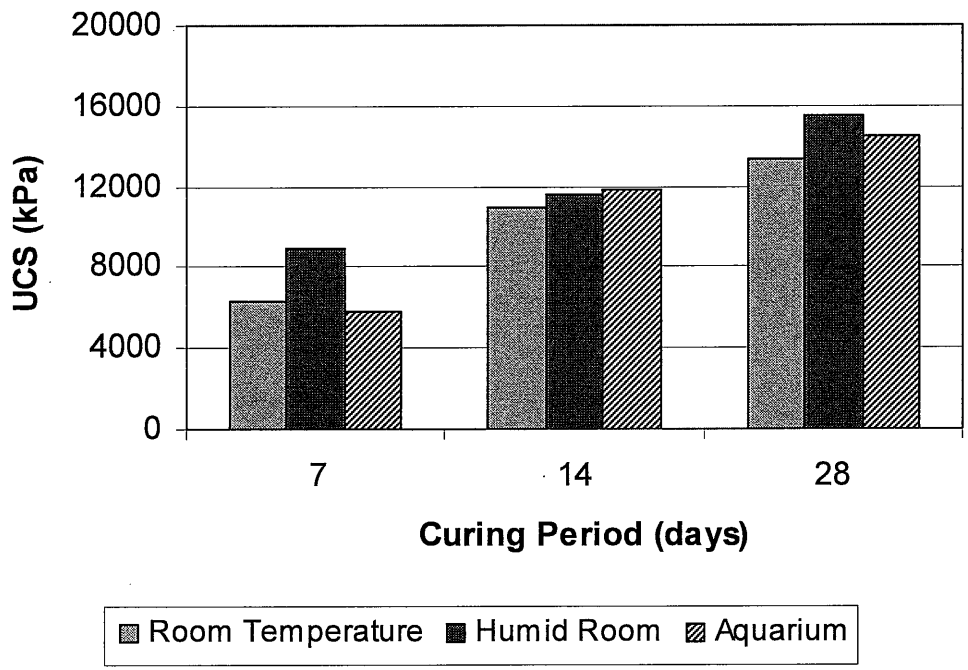

Figure A.1. The UCS values of mixtures prepared with FA1 and cured in different media

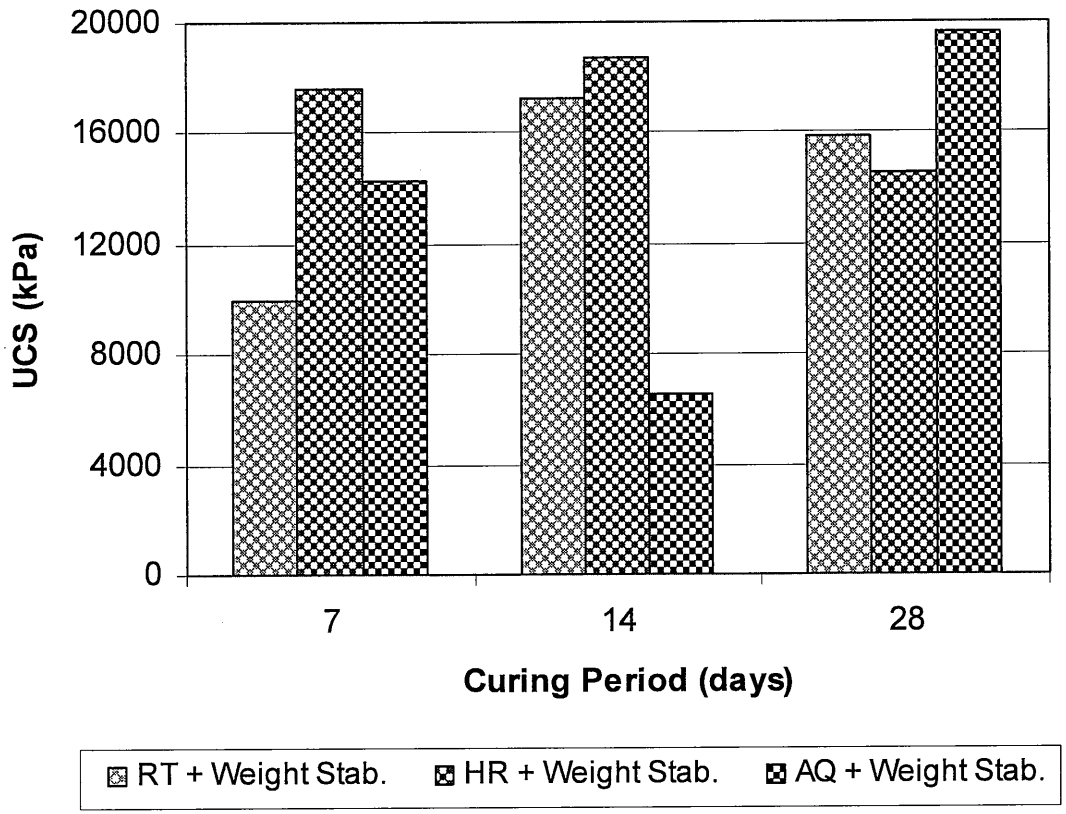

Figure A.2. The UCS values of mixtures prepared with FA1 and cured in different media with weight stabilization after curing

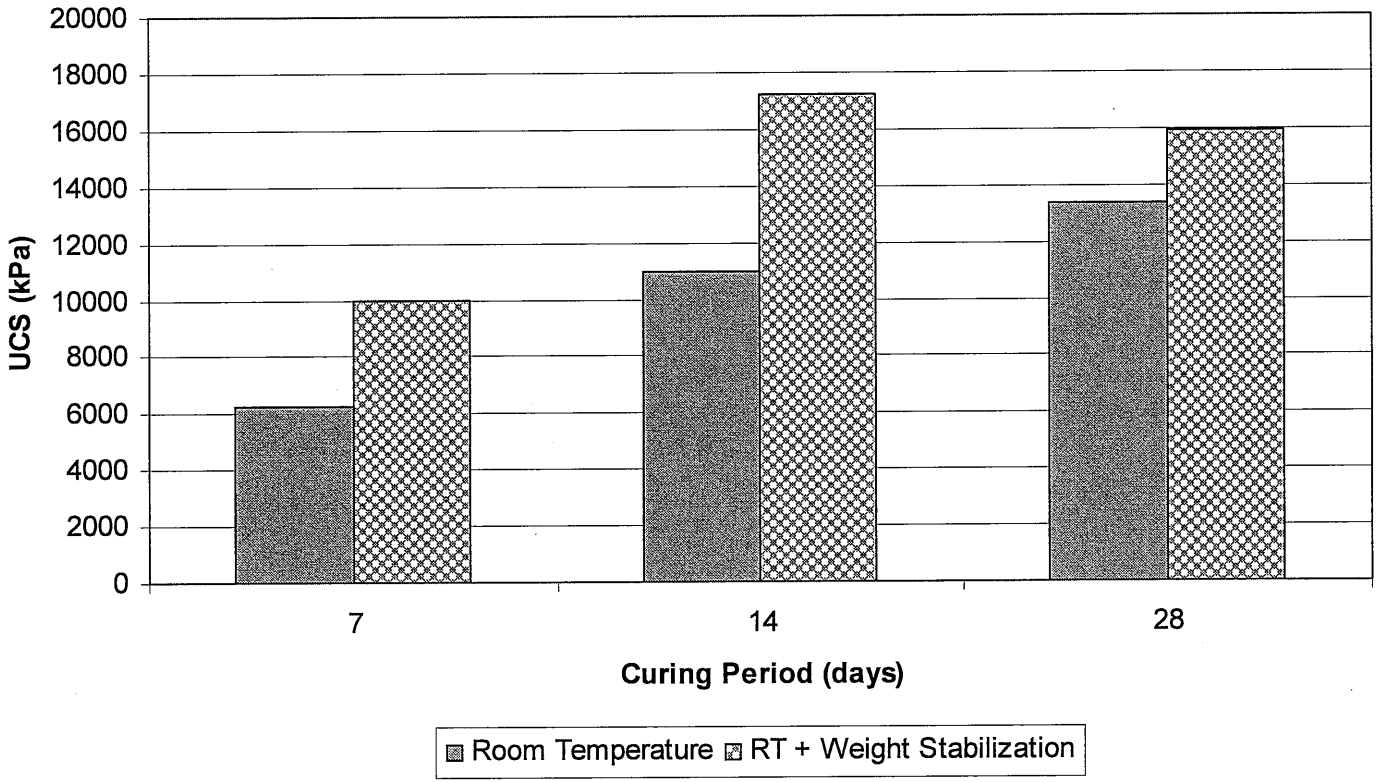

Figure A.3. Comparison of the UCS values of mixtures prepared with FA1 and cured at room temperature and left for weight stabilization

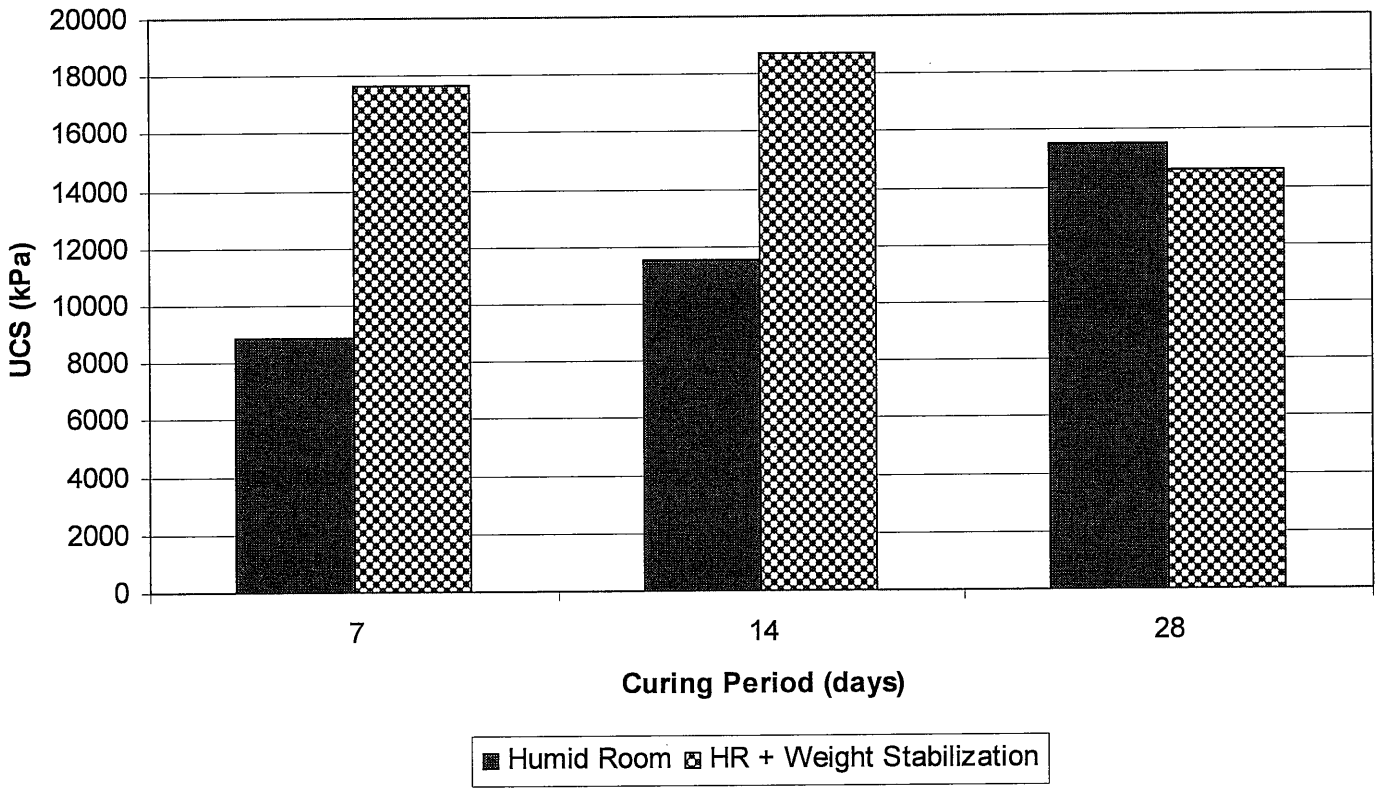

Figure A.4. Comparison of the UCS values of mixtures prepared with FA1 and cured in humid room and left for weight stabilization

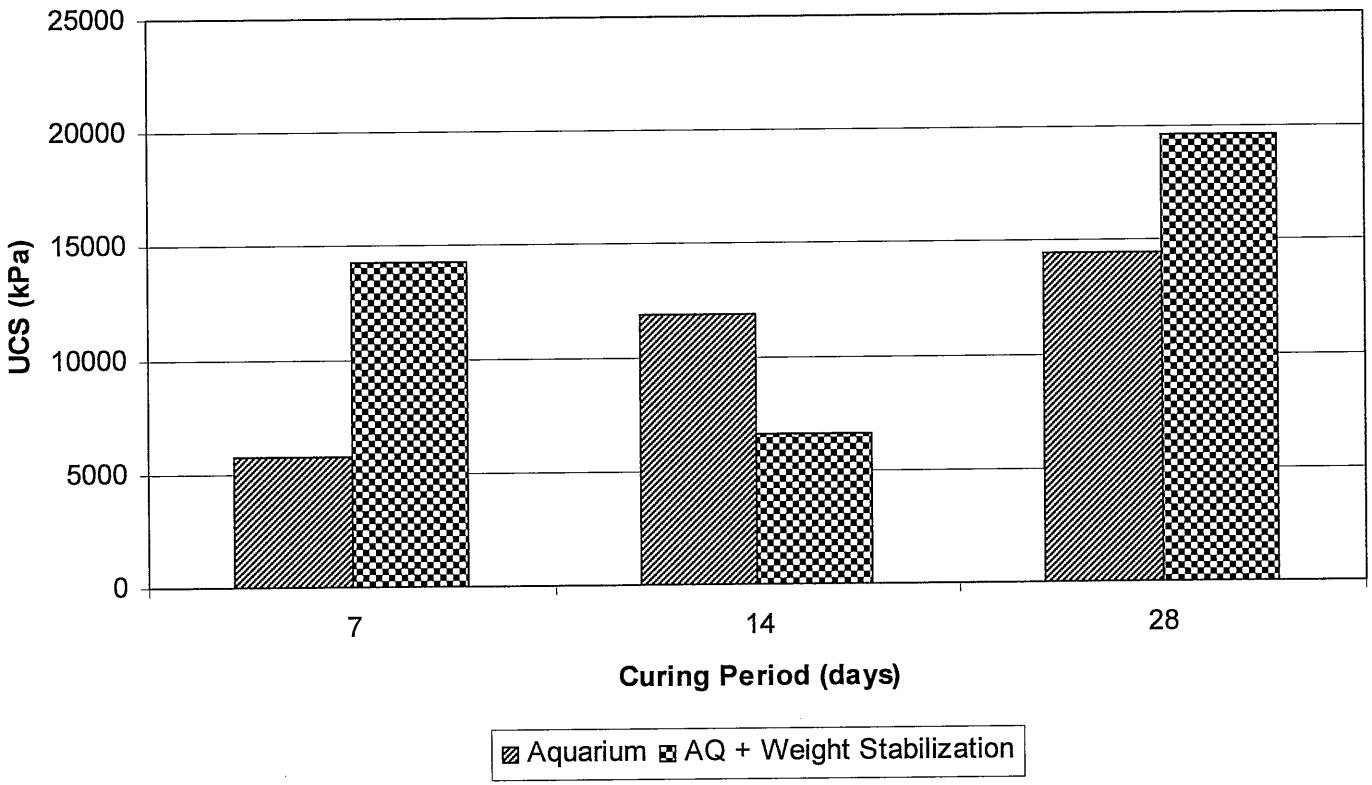

Figure A.5. Comparison of the UCS values of mixtures prepared with FA1 and cured in aquarium and left for weight stabilization

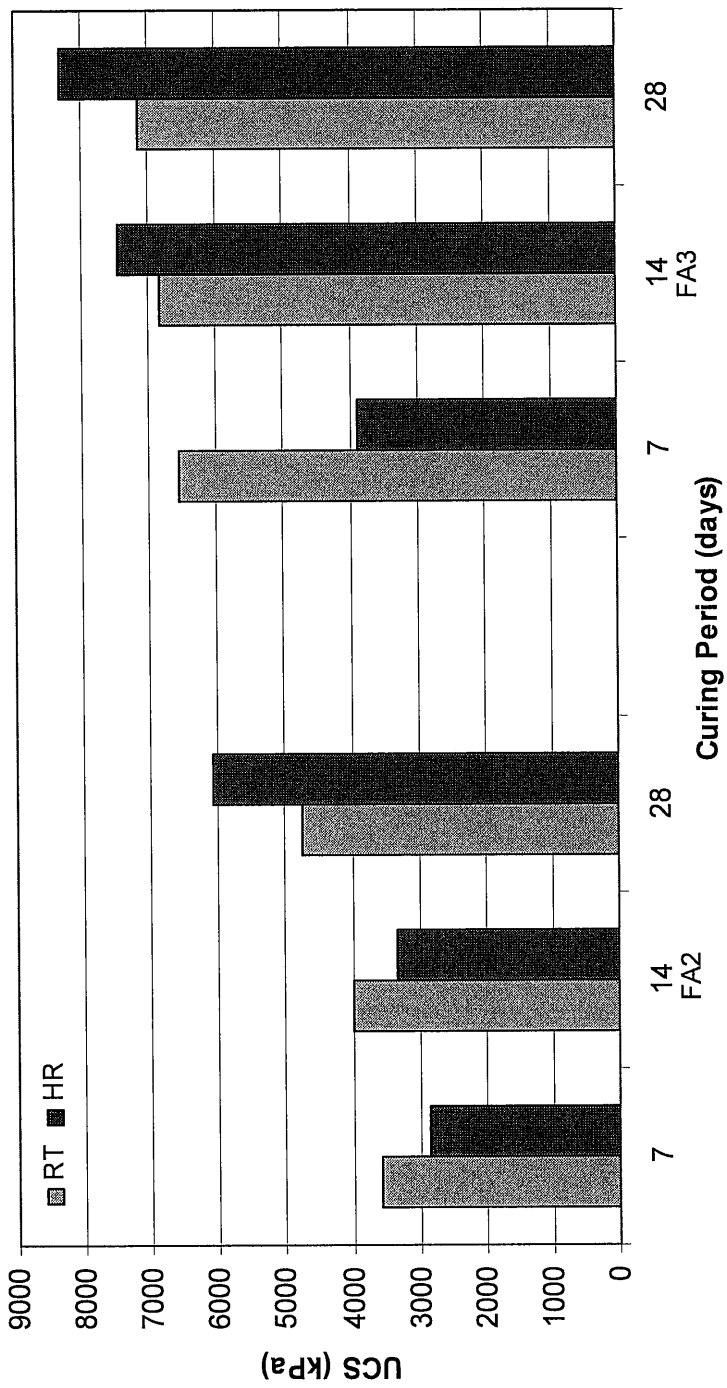

Figure A.6. Comparison of the UCS values of mixtures prepared with FA2 and FA3 containing 15% sludge and cured at different media and periods

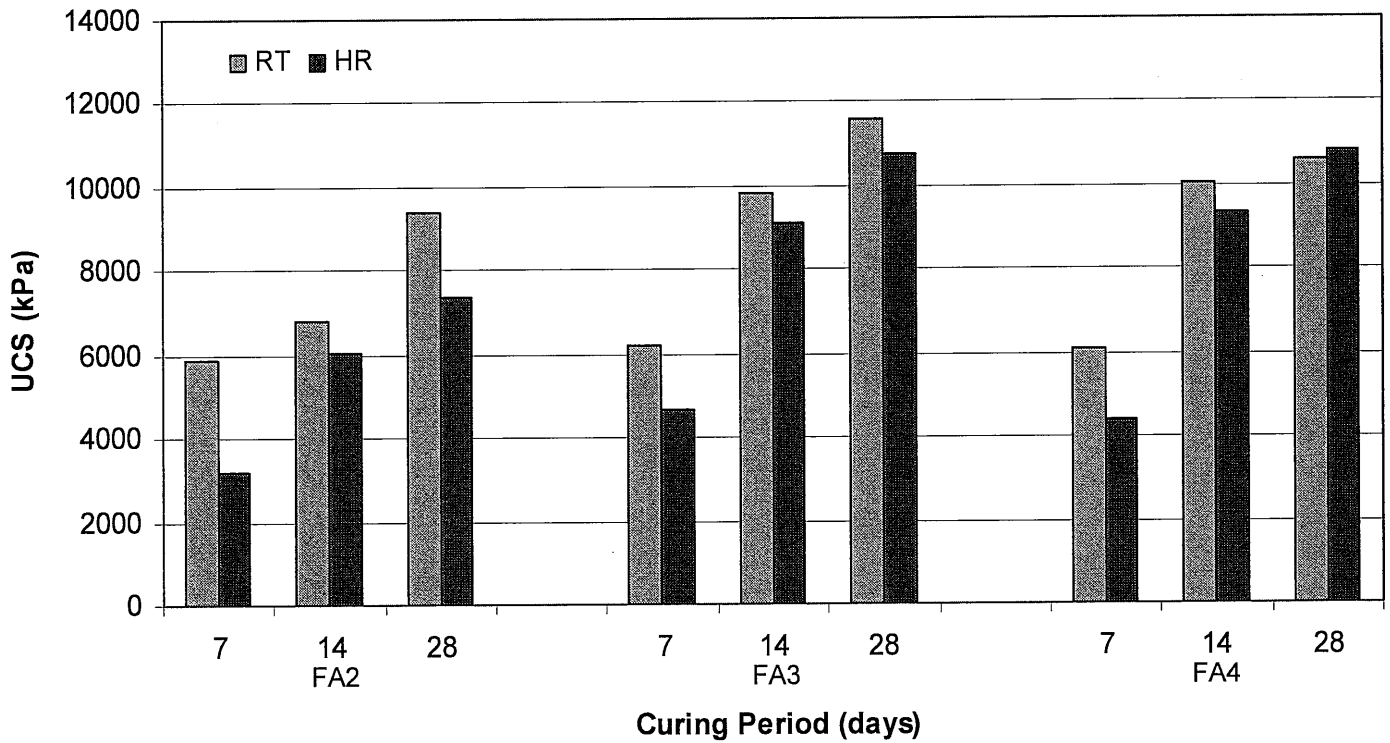

Figure A.7. Comparison of the UCS values of mixtures prepared with FA2, FA3 and FA4 containing 17.5% sludge and cured at different media and periods

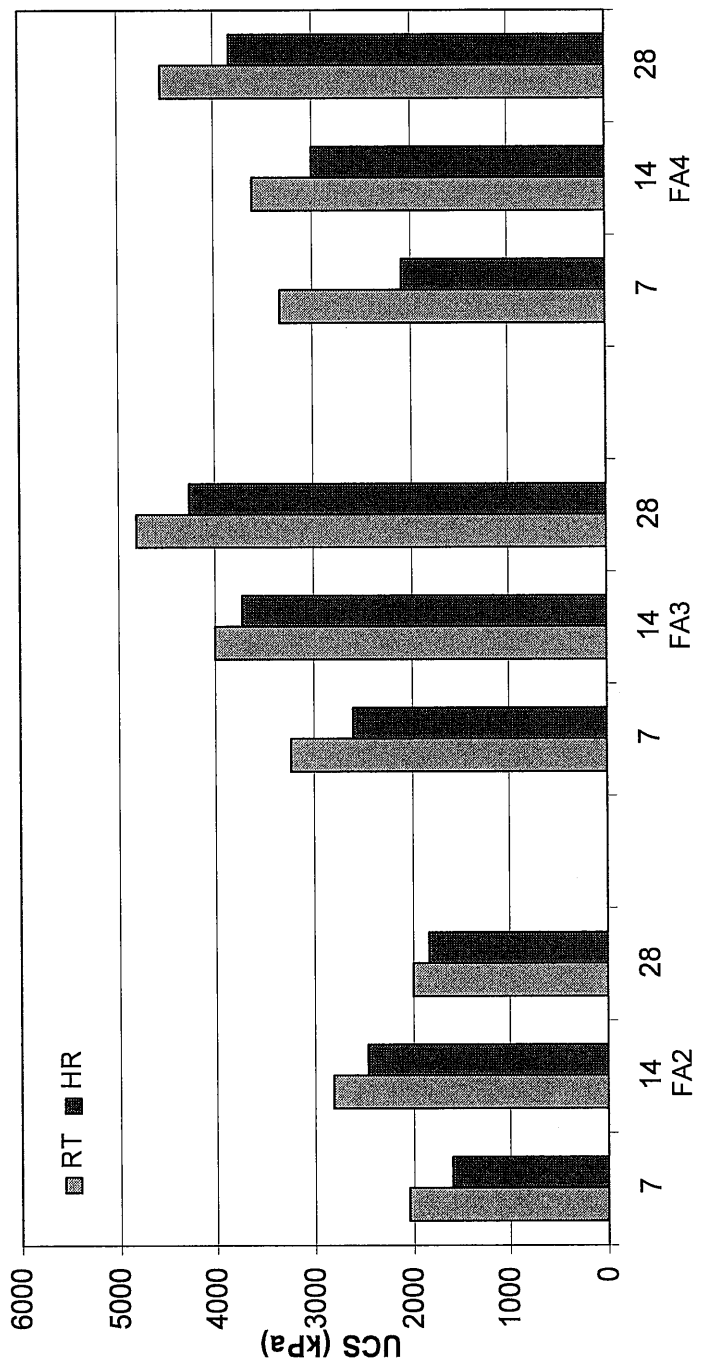

Figure A.8. Comparison of the UCS values of mixtures prepared with 1 mm clinoptilolite and cured at different media and periods

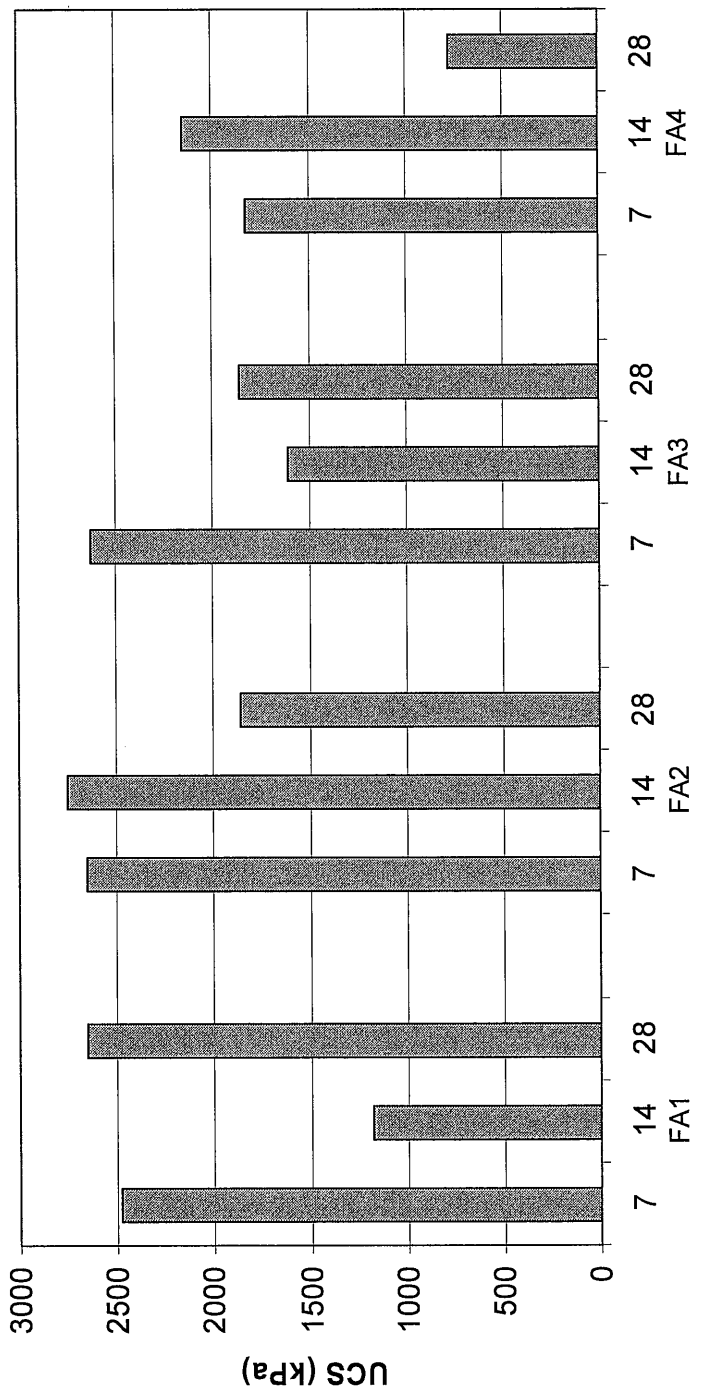

Figure A.9. Comparison of the UCS values of mixtures cured at room temperature without wrapping

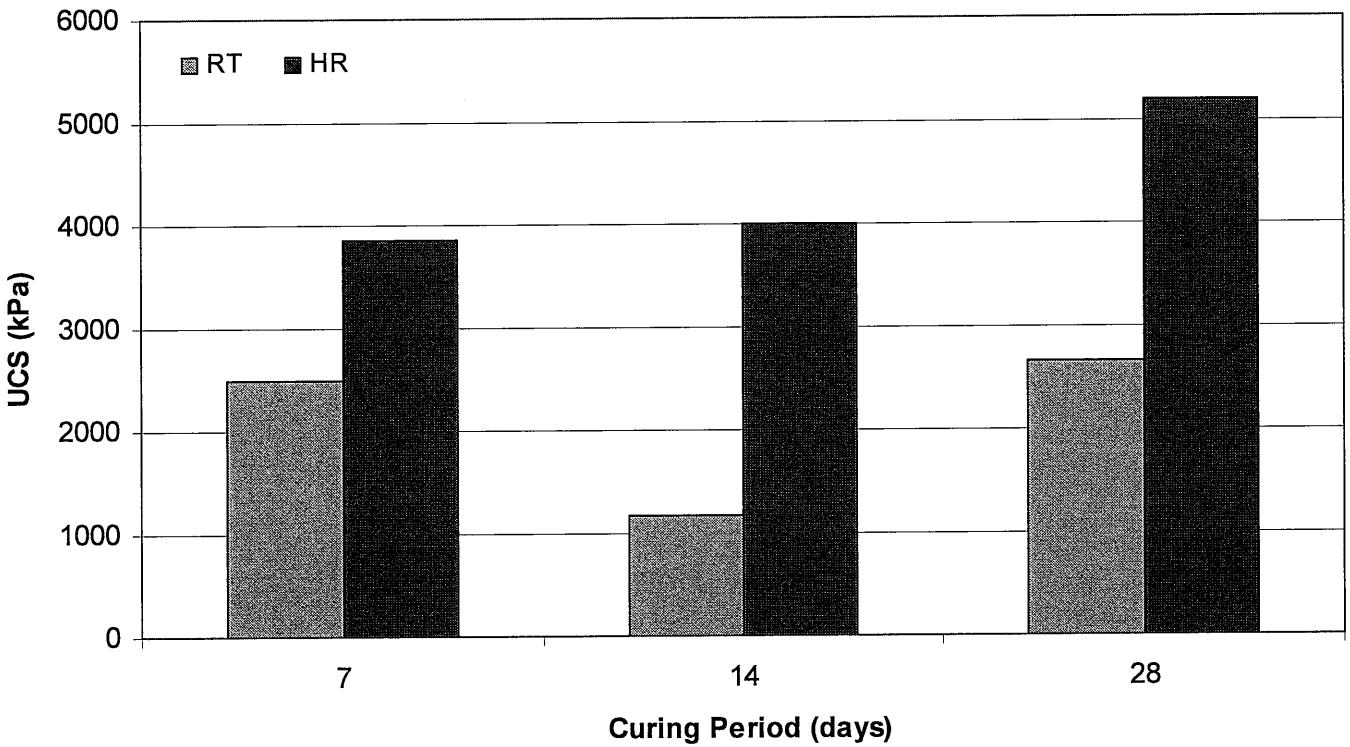

Figure A.10. Comparison of the UCS values of mixtures prepared with FA1 and cured without wrapping in different media and periods

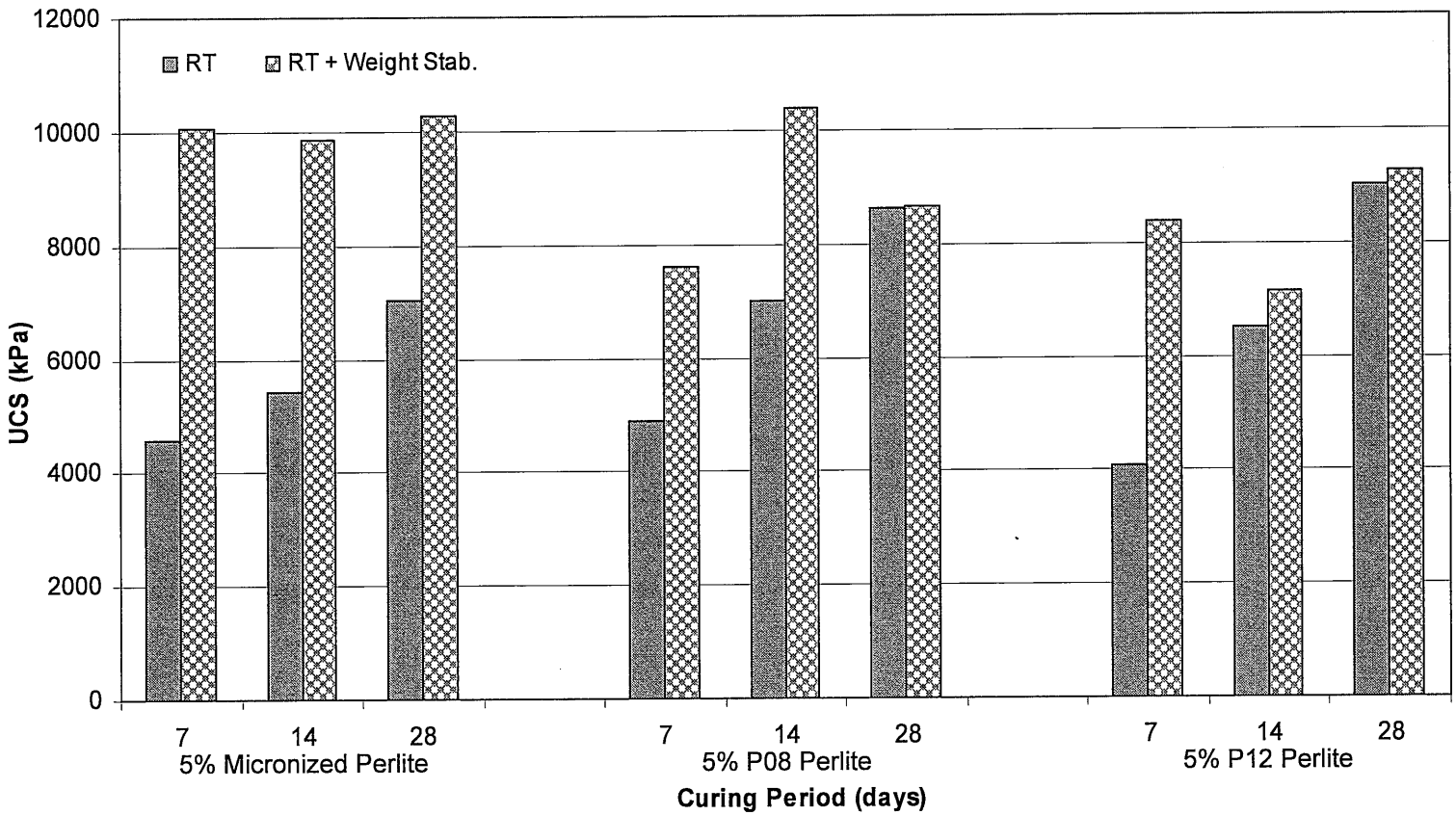

Figure A.11. Comparison of the UCS values of mixtures prepared with FA1 and containing different types of perlite cured at room temperature and left for weight stabilization for different periods

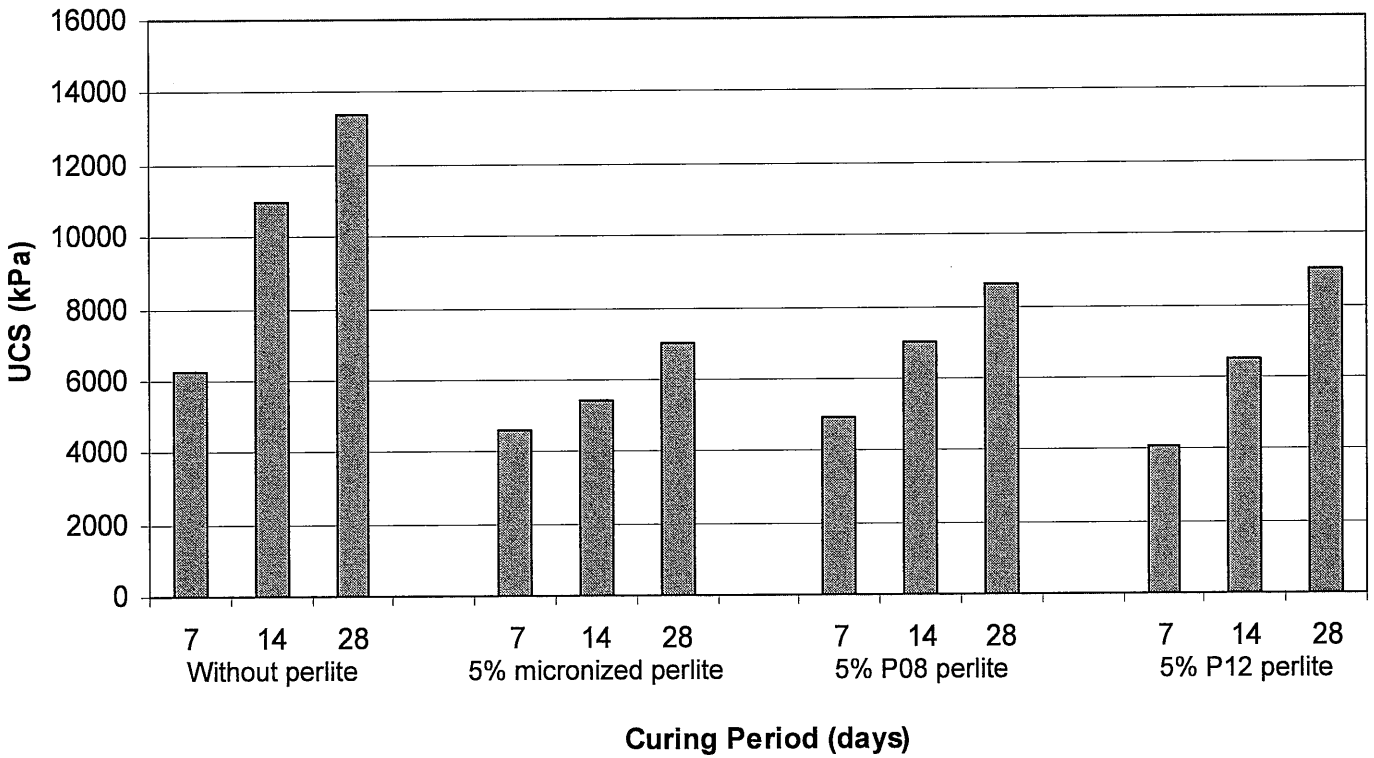

Figure A.12. Comparison of the UCS values of FA1 mixtures prepared with and without perlite cured at room temperature for different periods

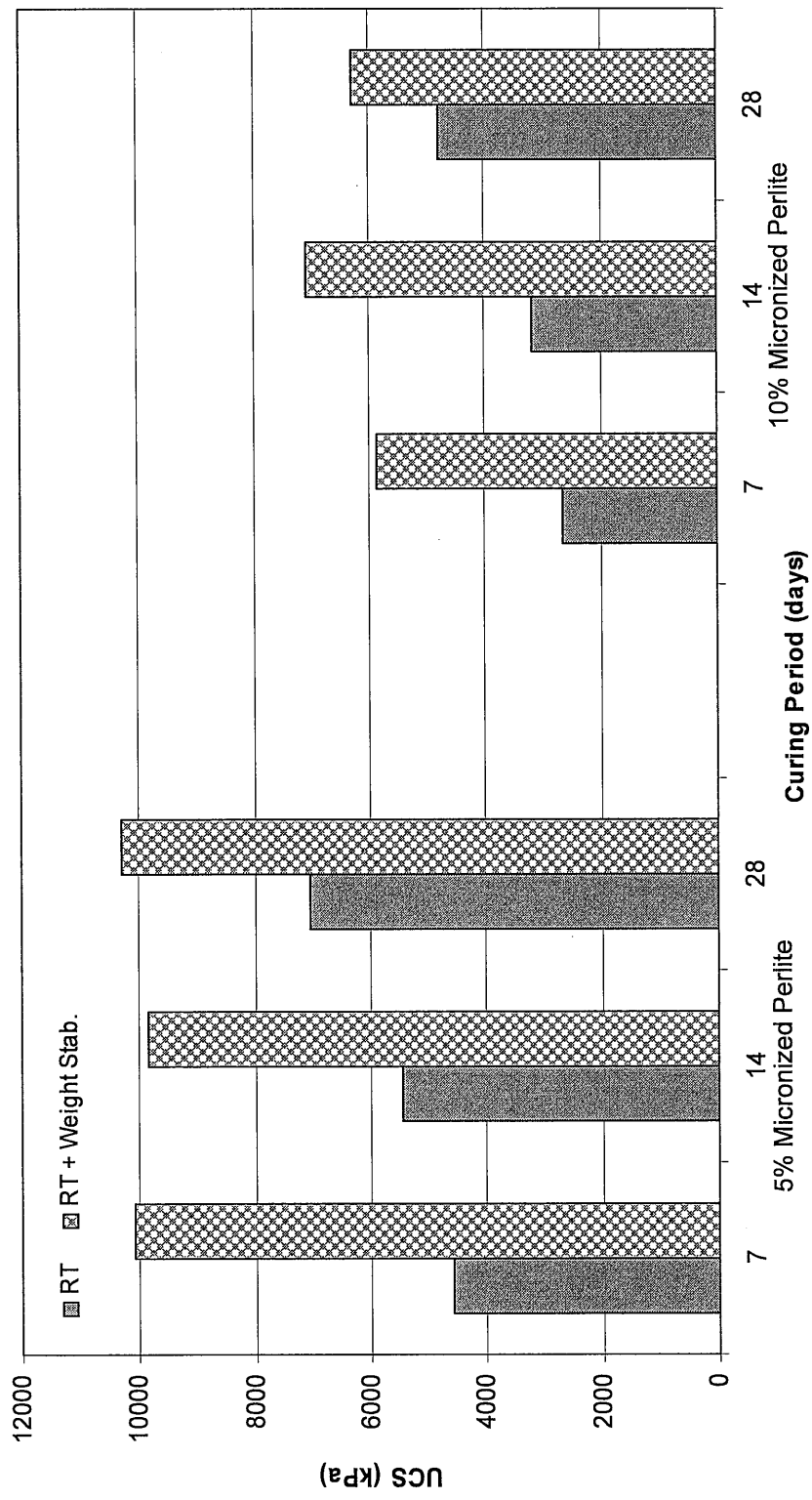

Figure A.13. Comparison of the UCS values of mixtures prepared with FA1 containing different amounts of micronized perlite for different periods

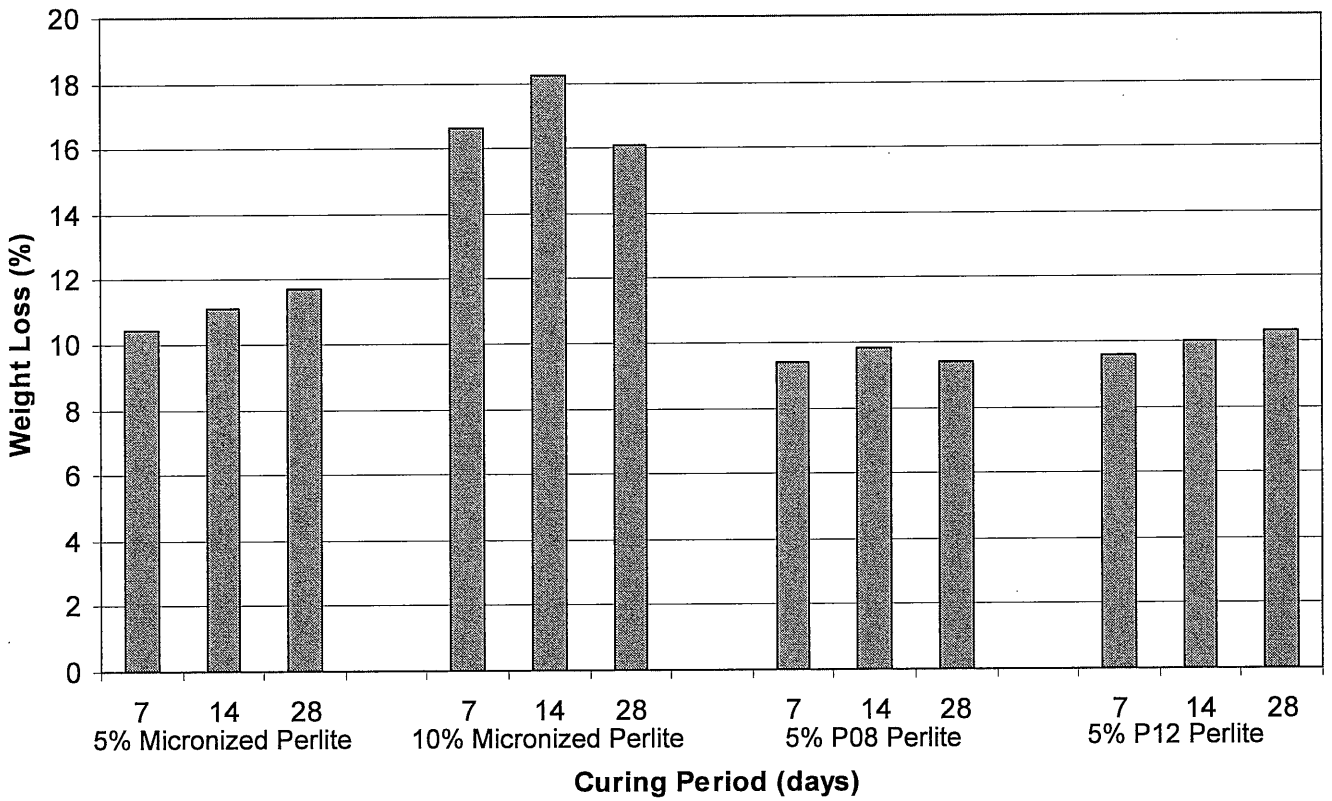

Figure A.14. Weight loss ratio of solidified mixtures prepared with FA1 containing perlite with respect to solidified mixtures without perlite

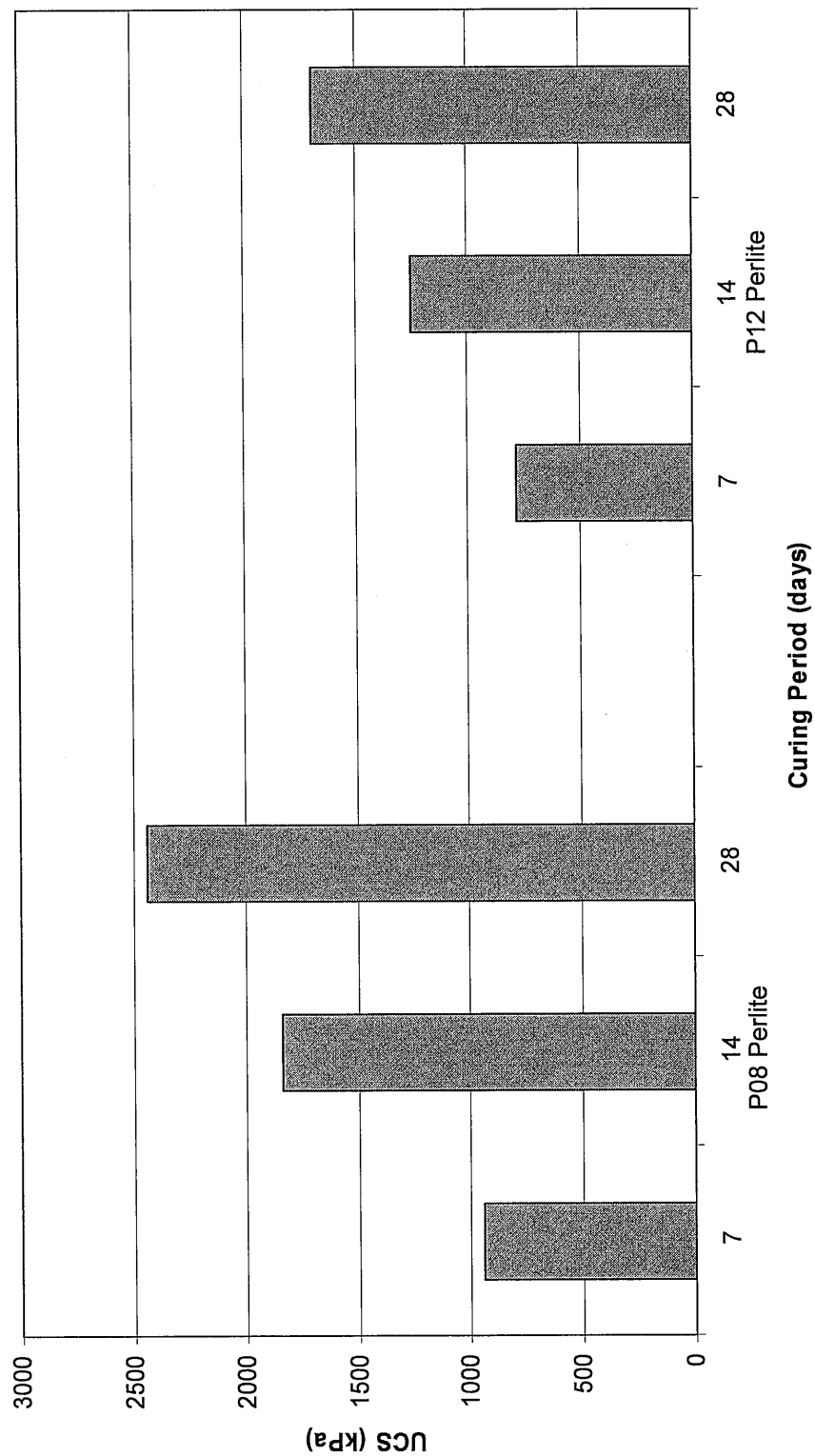

Figure A.15. The UCS values of mixtures prepared with FA2, containing different types of perlite and cured at room temperature for different periods

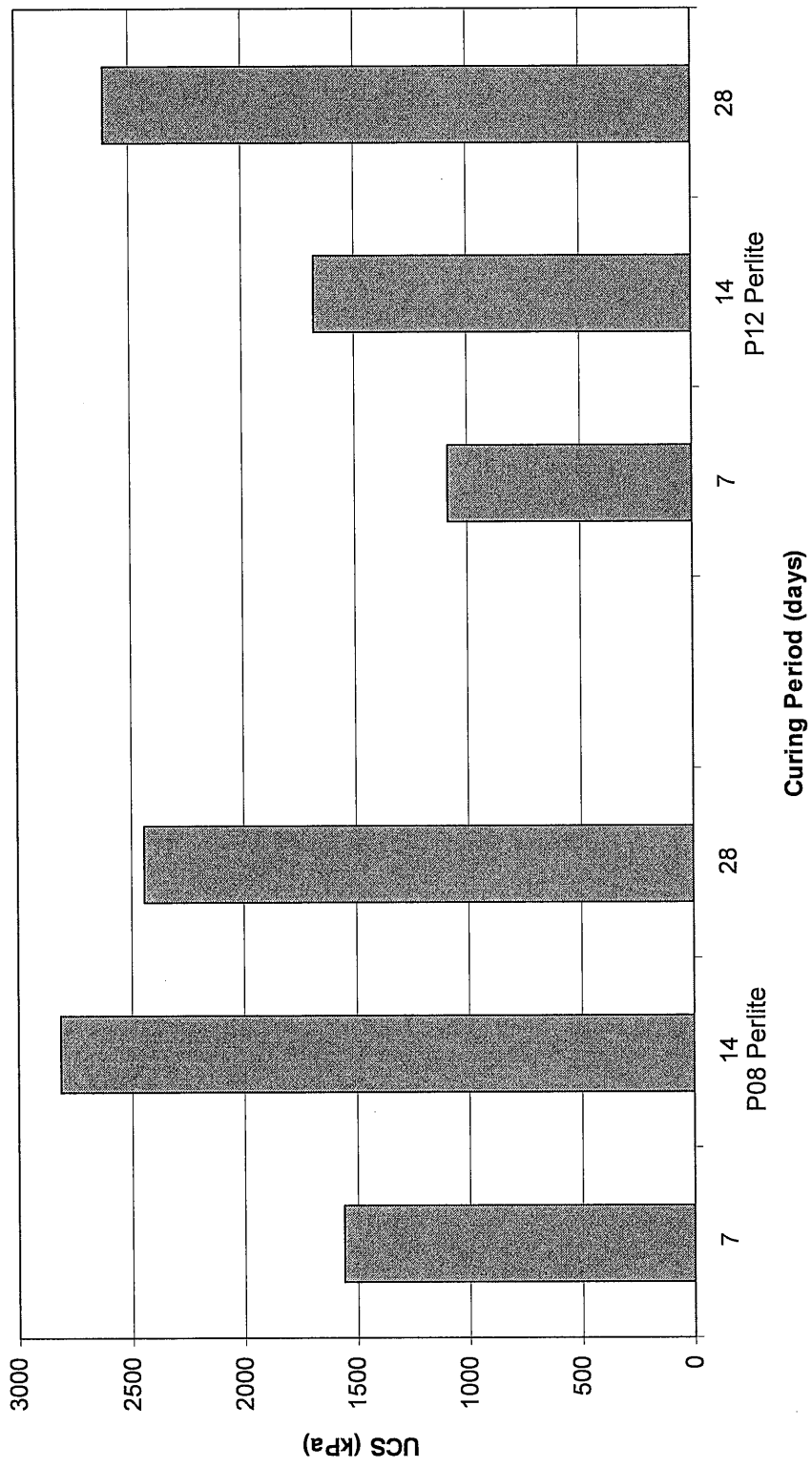

Figure A.16. The UCS values of mixtures prepared with FA4, containing different types of perlite and cured at room temperature for different periods

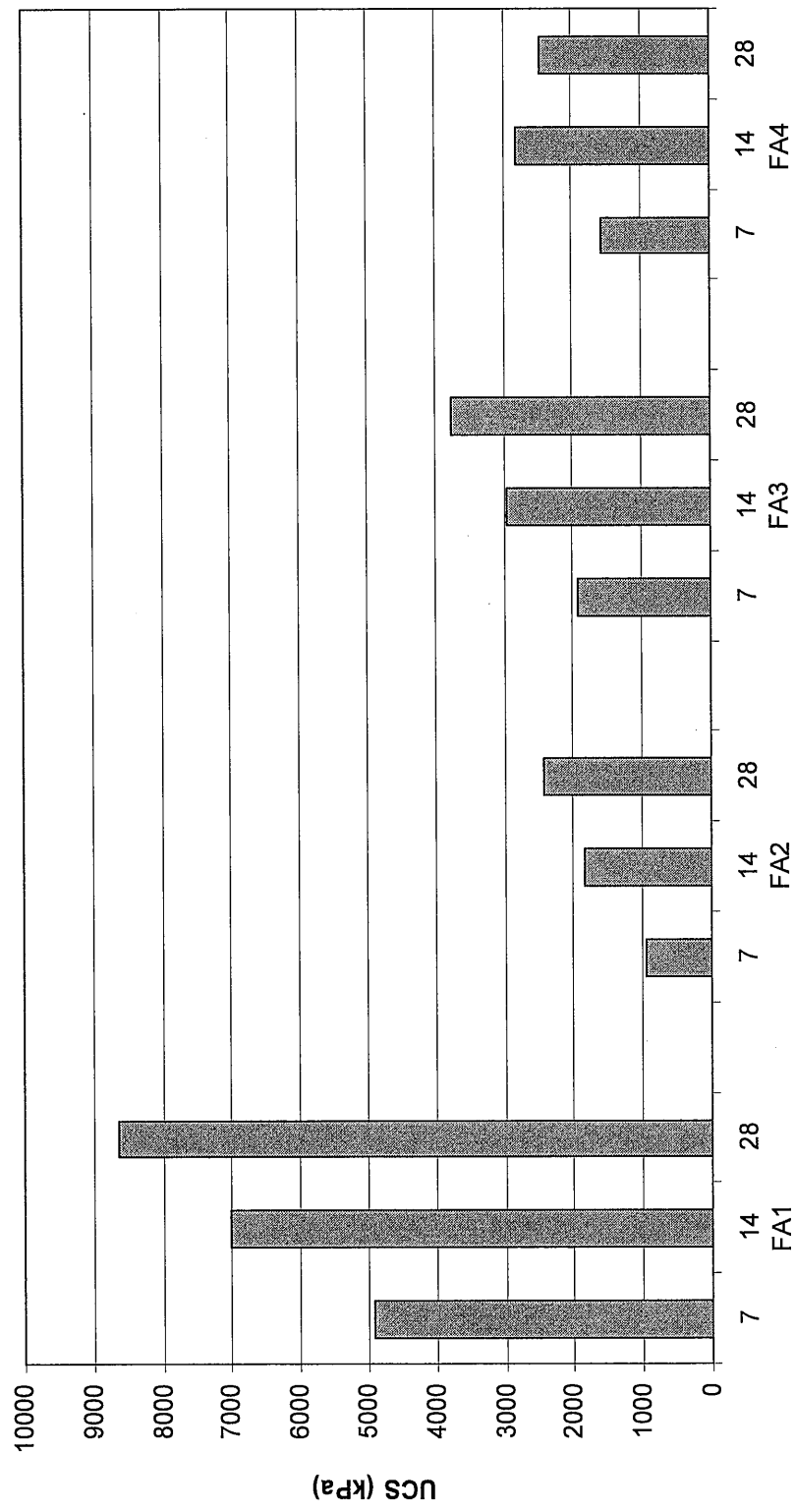

Figure A.17. Comparison of the UCS values of mixtures prepared with P08 perlite and cured at room temperature for different periods

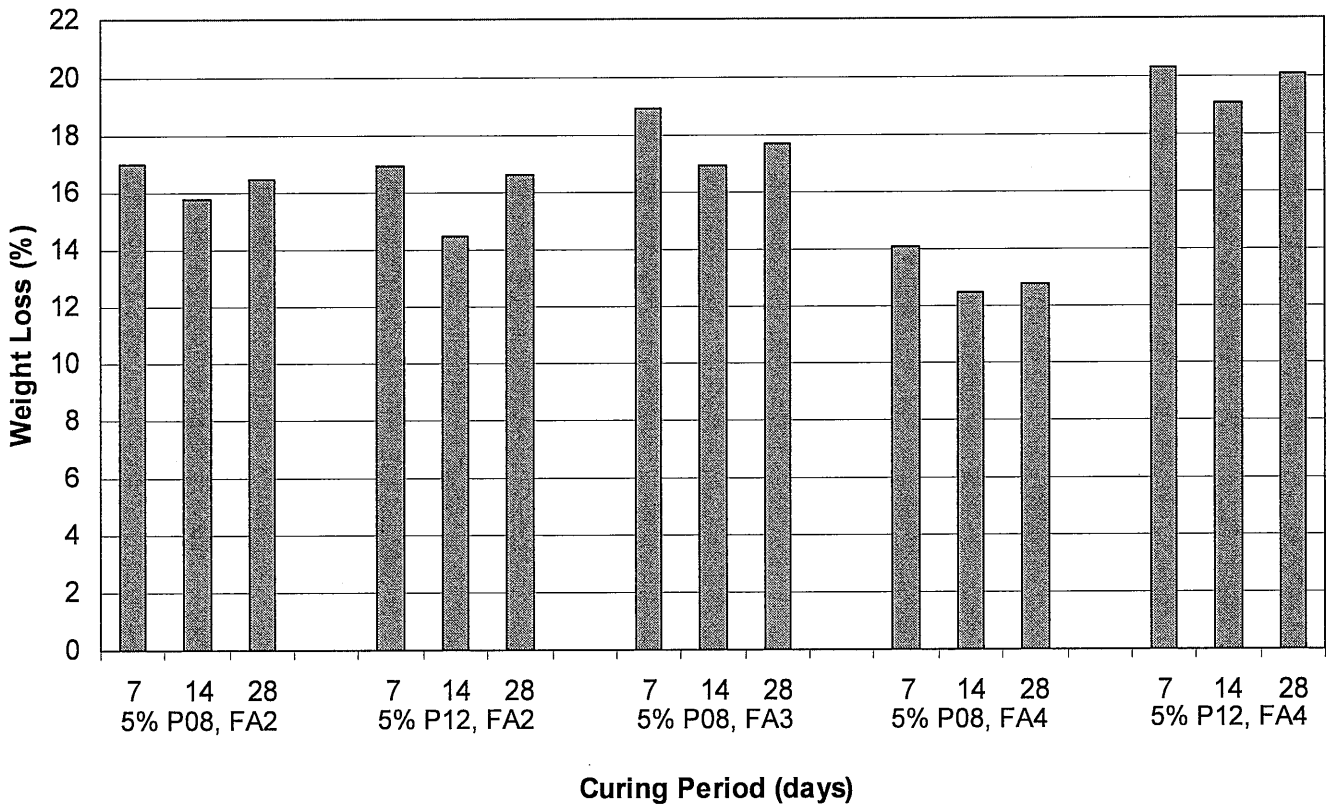

Figure A.18. Weight loss ratio of solidified mixtures prepared with FA2, FA3 and FA4 containing perlite with respect to solidified mixtures without perlite

APPENDIX B. The Leached Metal Concentrations of the Solidified Samples

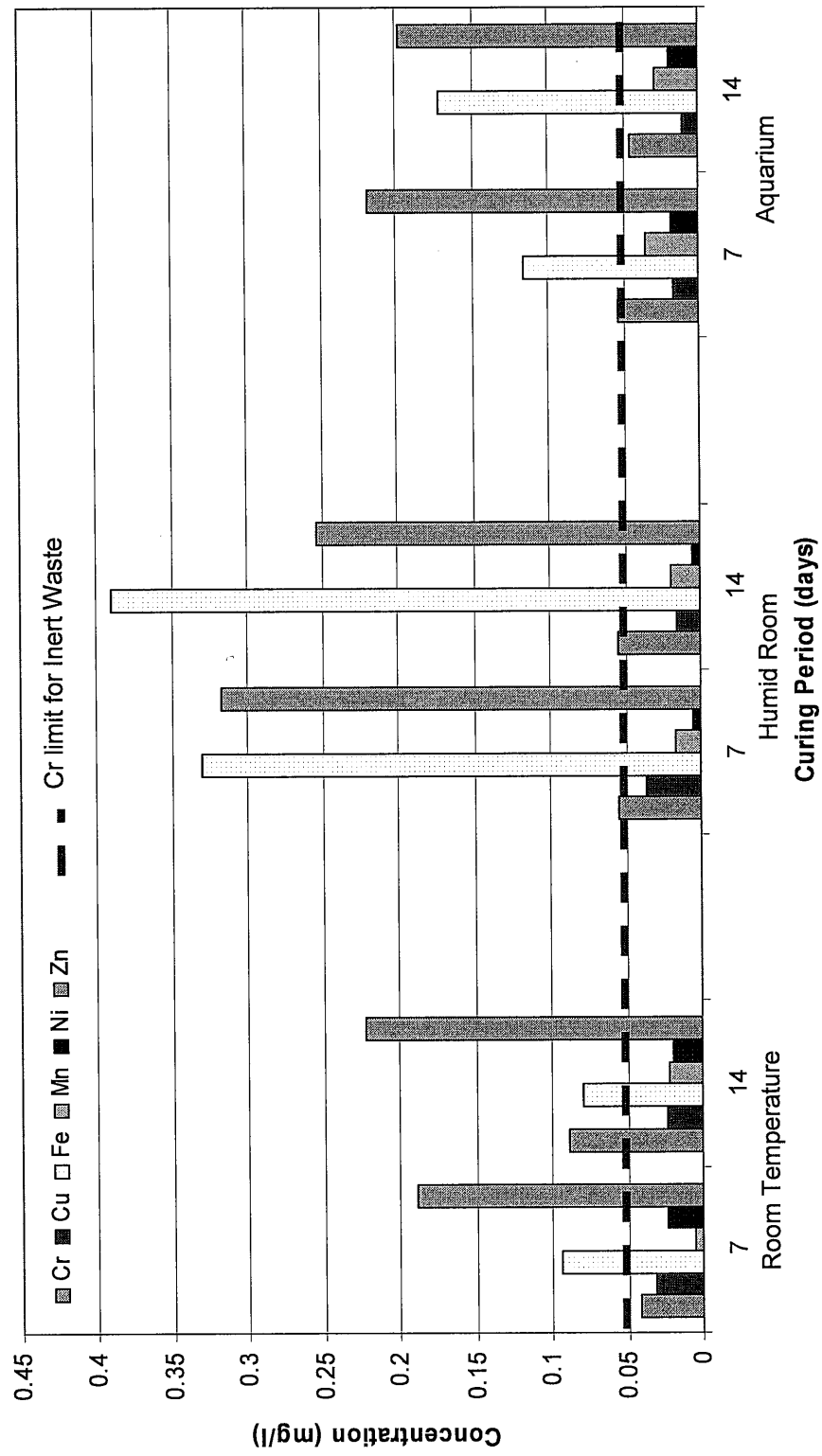

Figure B.1. Leaching results of mixtures prepared with FA1 and cured at different media and periods

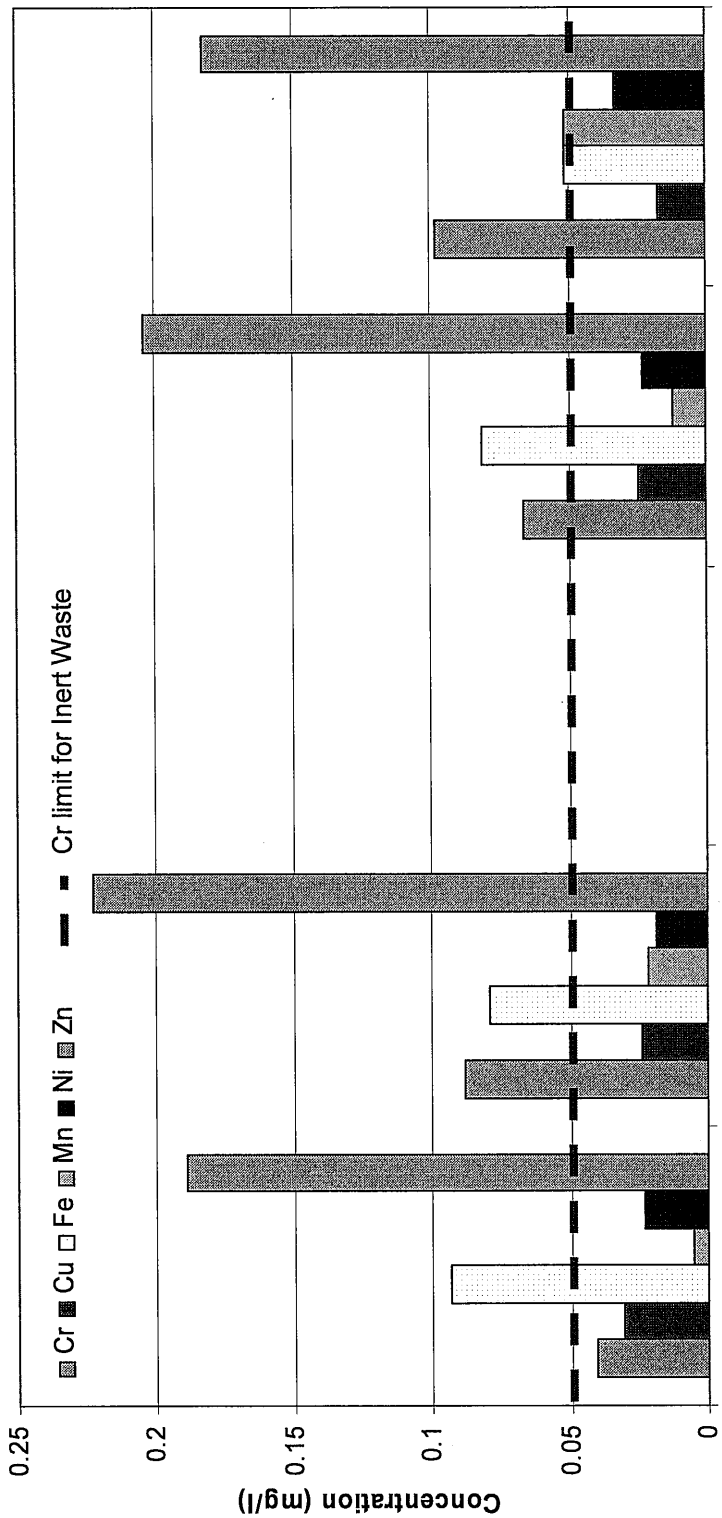

Figure B.2. Leaching results of mixtures prepared with FA1 and cured at room temperature for different periods

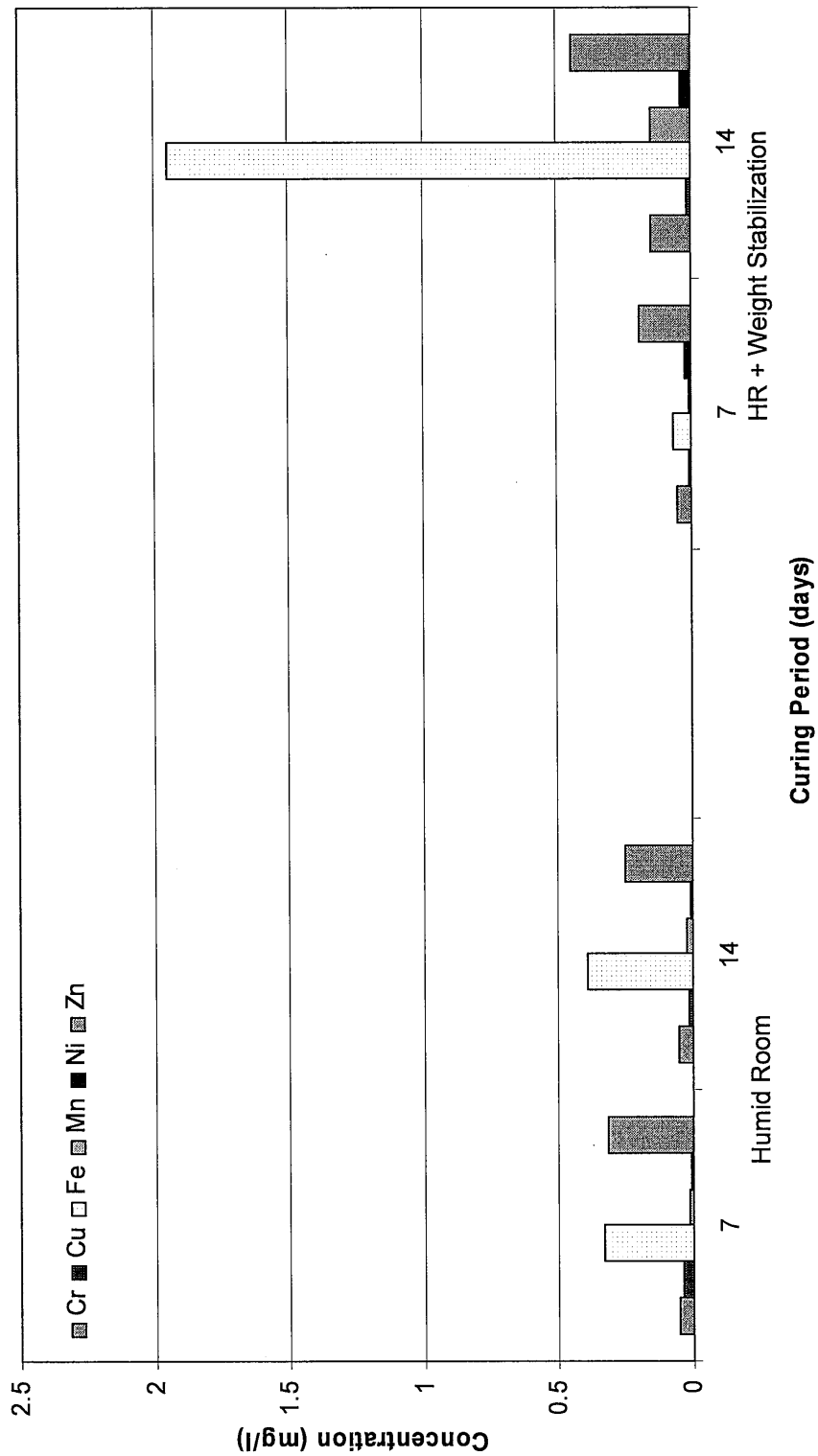

Figure B.3. Leaching results of mixtures prepared with FA1 and cured in humid room for different periods

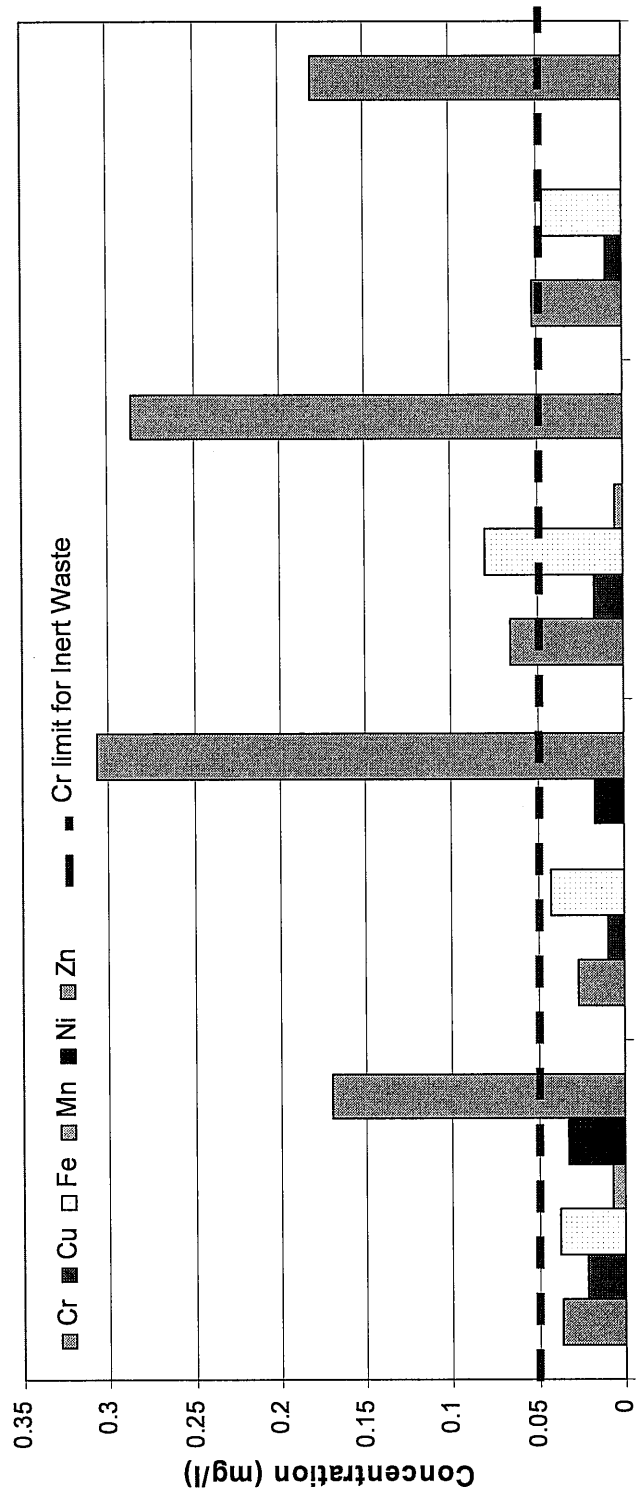

Figure B.4. Leaching results of mixtures prepared with FA2 and cured at different media and periods

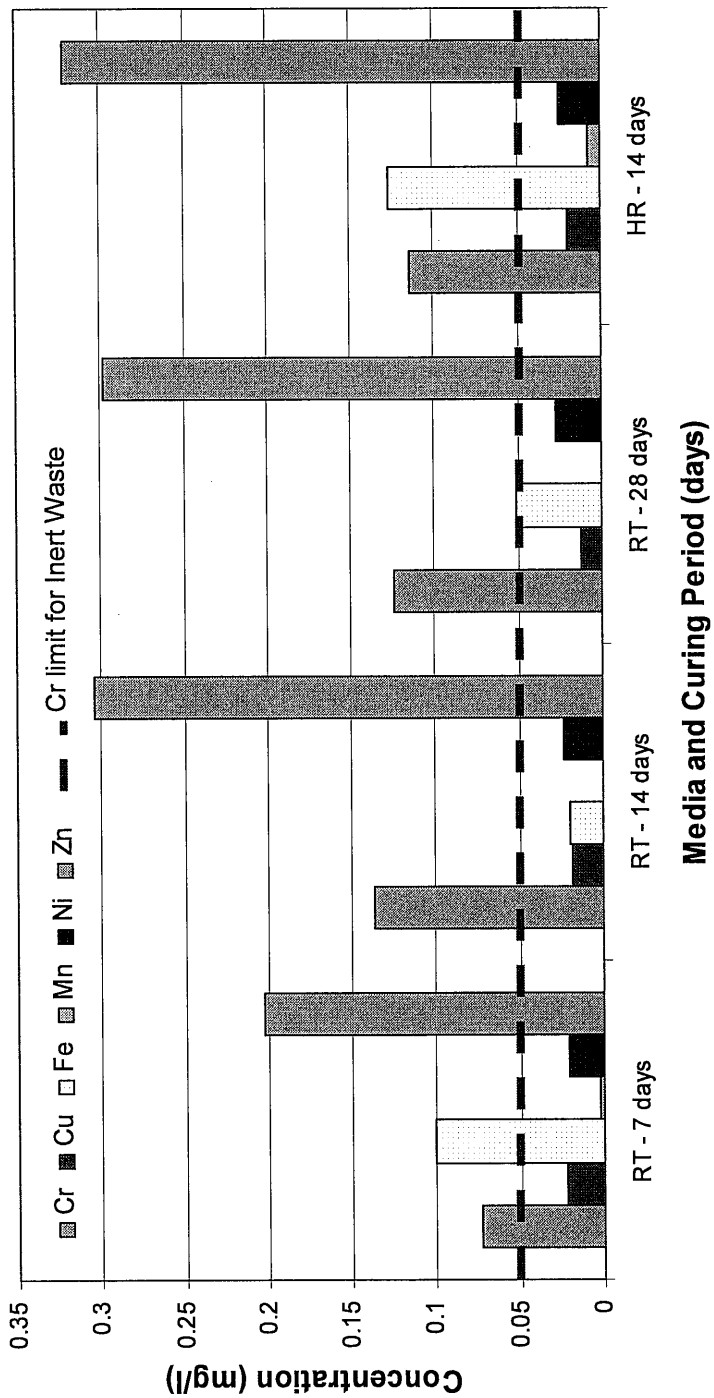

Figure B.5. Leaching results of mixtures prepared with FA3 and cured at different media and periods

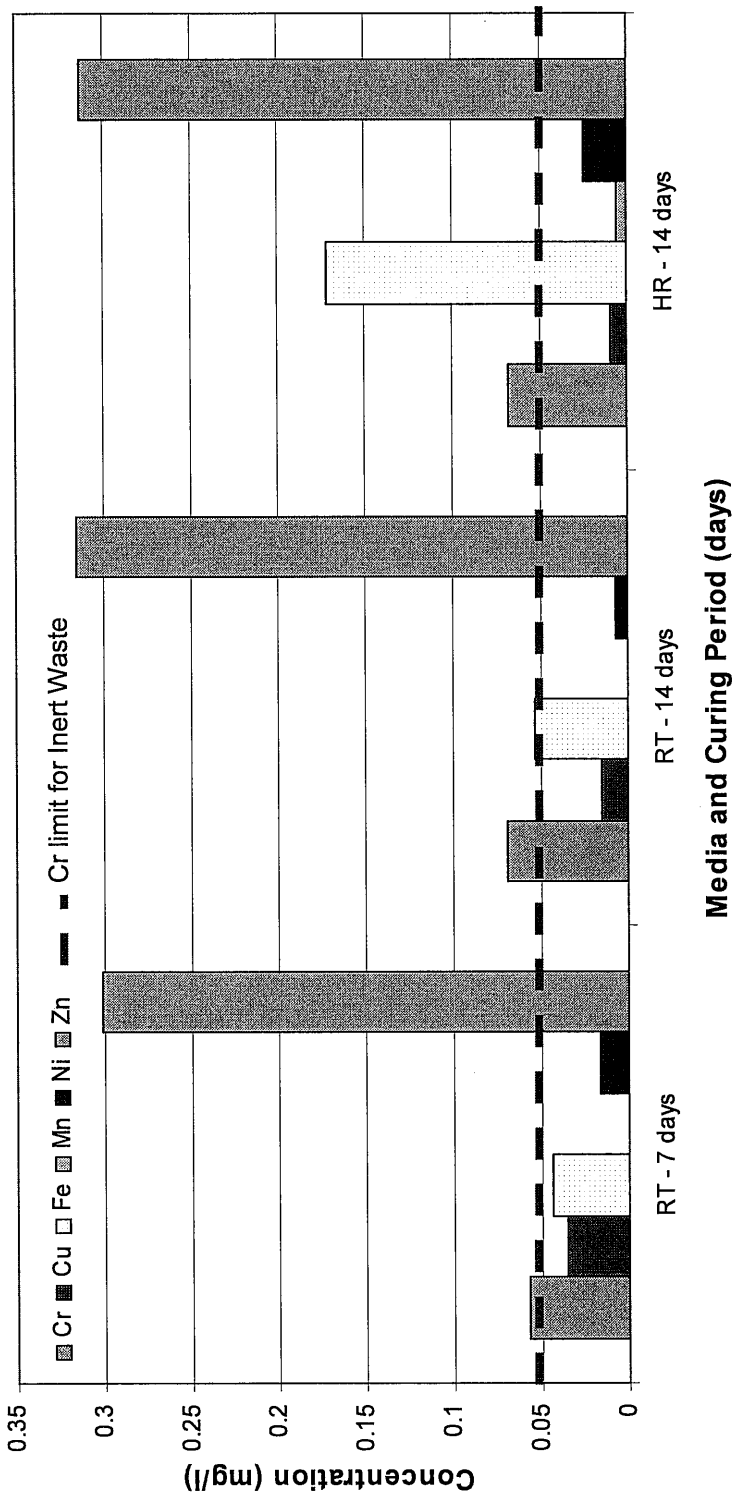

Figure B.6. Leaching results of mixtures prepared with FA4 and cured at different media and periods

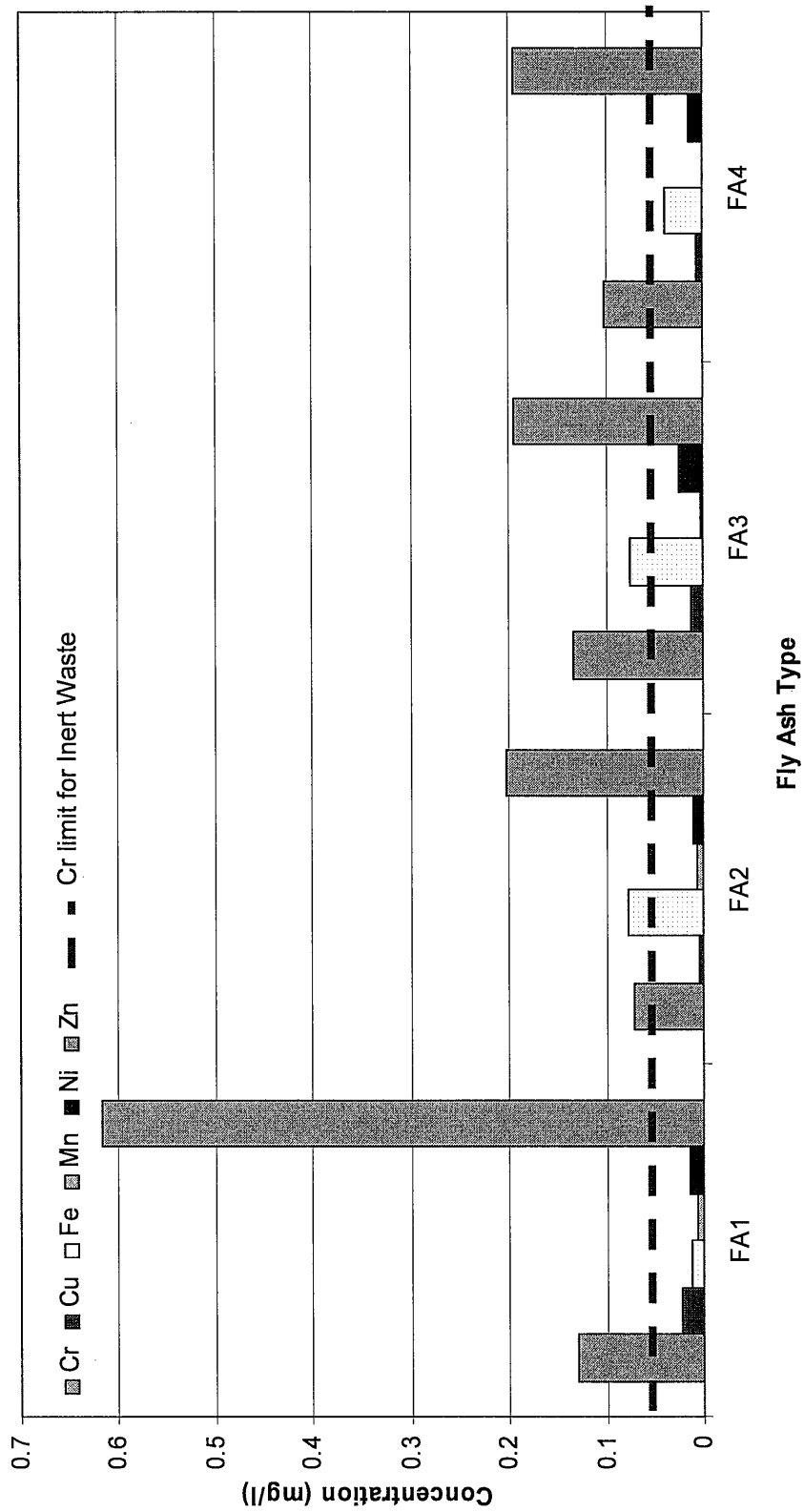

Figure B.7. Leaching results of mixtures cured unwrapped at room temperature and periods

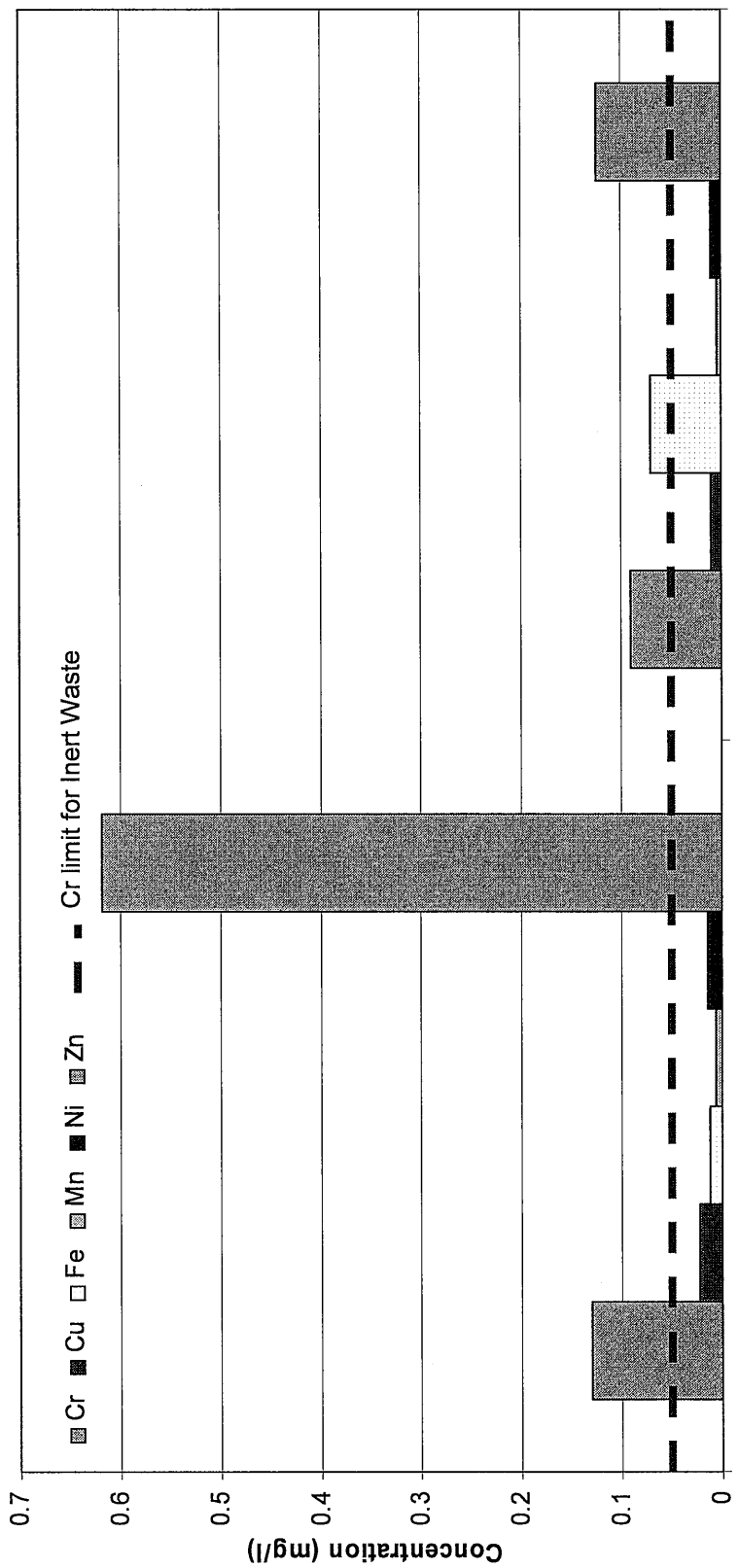

Figure B.8. Comparison of leaching results of mixtures prepared with FA1 and cured unwrapped at different media and periods

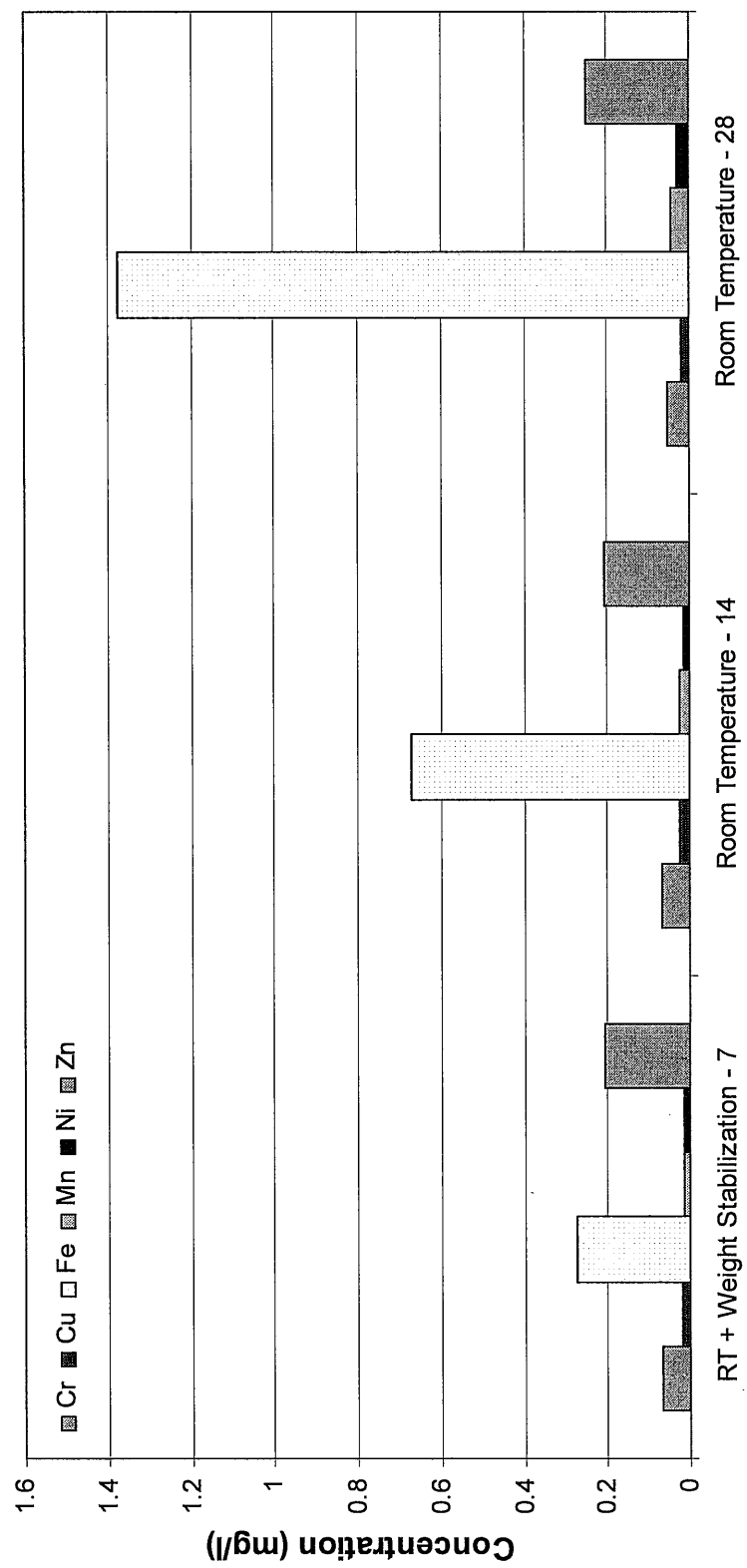

Figure B.9. Leaching results of mixtures prepared with FA1 and P08 perlite

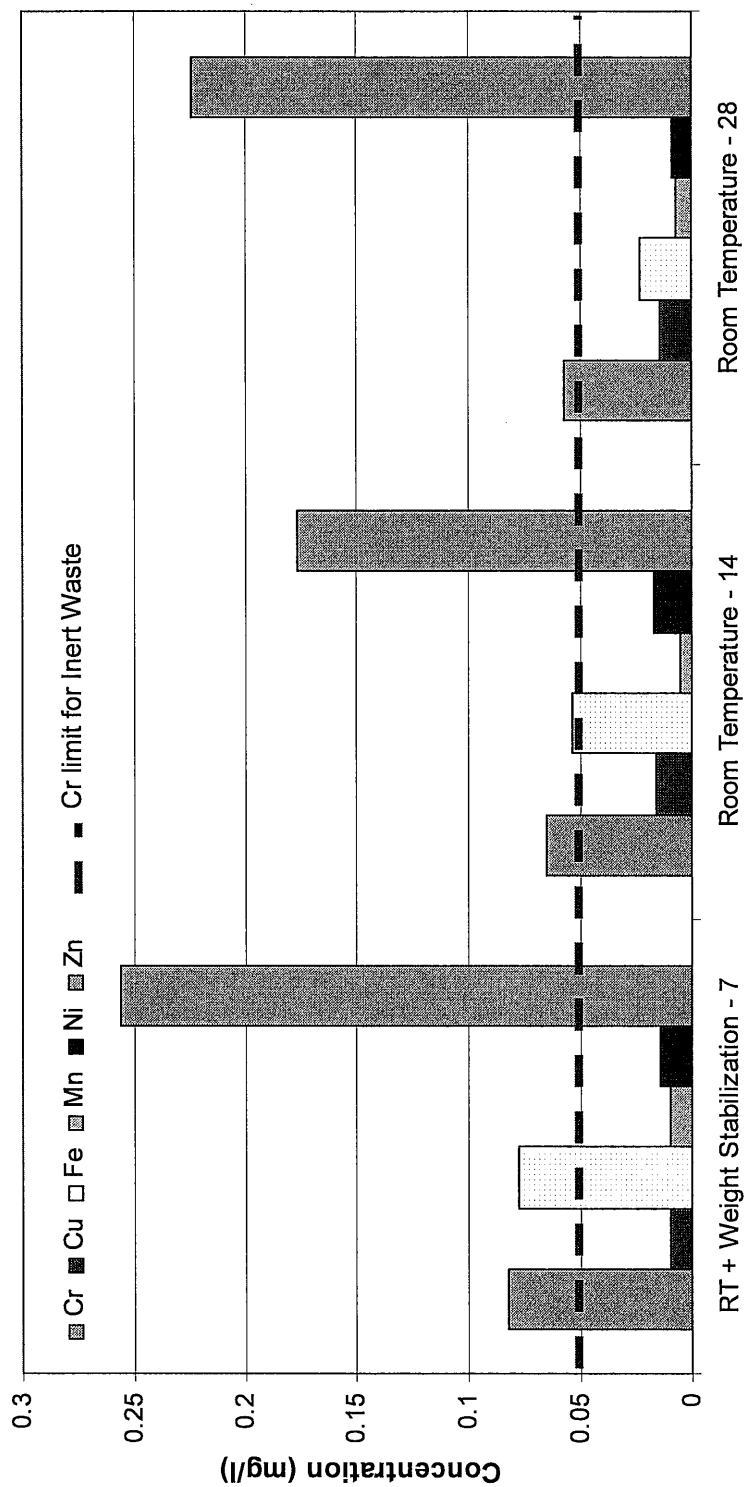

Figure B.10. Leaching results of mixtures prepared with FA1 and P12 perlite