ABSTRACT
Influence of Fly Ash and Chromium Characteristics on Compressive Strength of Mortar and Concrete

by
Lin Wang

The behavior of cement mortar incorporating fly ash varies with chemical and physical characteristics of fly ash. Of many parameters affecting the compressive strength of fly ash mortar, five were investigated in this study. They are the particle size, the particle size distribution, fineness of fly ash, the CaO content and the Fe_2O_3 content.

Fly ashes from two different sources were used in this study. One comes from the Public Service Electric and Gas (PSE&G)'s electrical generation station in Hudson county and the other is from the PSE&G plant in Mercer county. Each was separated into seven different particle size ranges.

The results of the tests indicated that there are direct relationships between the particle size, Blaine fineness, mean diameter of fly ash and the compressive strength.

Fe_2O_3 content of fly ash is not found to have a notable effect on the mortar strength. CaO content of fly ash varying from 2.47% to 6.76% also has no significant effect on the strength of mortar.

Additionally, the effect of chromium on cement mortar and concrete was studied. Trivalent and haxavalent chromium were used in the experiment. The compressive strength of mortar and concrete incorporating Cr(III), as well as mortar and concrete incorporating Cr(VI) were tested up to 180 days according to ASTM C-109. Leaching tests were conducted with different pH extractants.

The results of the tests showed that the leaching characteristic of Cr(III) mortar and Cr(VI) mortar are different. The influence of Cr(III) and Cr(VI) on compressive strength of mortar and concrete is also varied. The results of

leaching tests indicated that cement is very good for immobilizing Cr(III) under field condition, unless the pH is extremely low. However, Cr(VI) can be leached from the mortar at early ages. The compressive strength of Cr(III) mortar and concrete is higher than that of the conventional mortar and concrete at all ages. But the strength of Cr(VI) mortar and concrete is lower than that of the conventional mortar and concrete.

A major finding was the discovery of significant amount of soluble chromium in Mercer fly ashes. The results show that the majority of the chromium in Mercer fly ash is concentrated in the small particles, those in the 0-10 micron range.

INFLUENCE OF FLY ASH AND CHROMIUM CHARACTERISTICS ON COMPRESSIVE STRENGTH OF MORTAR AND CONCRETE

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To my parents
and all parents who spare no pain
to see their children in the path of education

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CHAPTER 1

INTRODUCTION

1.1 General

Coal Fly Ash is the unburned residue resulting from the combustion of coal in utility and industrial boilers. It is a fine, silt-size material consisting largely of spherical, sometimes hollow, glassy particles. In 1988, the electric utility industry generated about 50,900,000 tons of fly ash, 14,300,000 tons of bottom ash, and 5,000,000 tons of boiler slag. Of these amounts, only 22%, 38%, and 56% of fly ash, bottom ash and boiler slag, respectively, were used beneficially with the remaining material placed at great expense in disposal areas [1]. Because of the difficultly locating ash disposal areas and the existence of environmental problems, the disposal of coal ash is being restricted and very costly. In order to cope with the increase in the generation of fly ash, it is necessary to find a utilization method of fly ash that is feasible and more cost effective so that large-volume disposal can be avoided. Over the past few decades fly ash utilization has been found largely in the construction industry [2]. Fly ash is a pozzolan and a considerable amount is used as a concrete additive. It is also used in combination with lime, portland cement and aggregate as road base [3, 5], grout, and as a backfill [4]. Fly ash is also useful as a soil amendment for land reclamation and for subgrade stabilization. Large volumes have also been used as structural fill [5]. It has also been studied for use as an absorbent in waste water treatment as replacement for higher cost absorbents(e.g. ion-exchange resins, activated carbon) [6, 7]. It has also been mixed with cement for the solidification/stabilization of contaminated soil [8, 9].

The handling, use and disposal of large volumes of fly ash are formidable engineering problems. This paper focuses on the influence of the above mentioned physical and chemical properties of fly ash on the compressive strength of cement mortar and, the discovery of the trace soluble chromium in the fly ash used in this study. Also, the effects of chromium on the compressive strength of mortar and concrete will be investigated.

1.2 Literature Review

1.2.1 Application of Fly Ash in Construction

Over the past few decades fly ash emerged as a construction material in its own rights. Fly ash serves two functions in fly ash concrete. The recognition that fly ash exhibits pozzolanic properties had originally lead to its use as a cementitious material, which replaces considerable percentages of cement in concrete. The other function is as a micro aggregate (the part of fly ash that does not completely react with $Ca(OH)_2$), which makes the concrete mixture more workable and impermeable. Regardless of what it substitutes for in concrete, fly ash is known to affect all aspects of concrete properties [10].

Fly ash tends to densify the microstructure, hence improves the durability. This is achieved through improved particle packing between fly ash particles and cement grains at the initial stages of hydration. This improved particle packing lays down the framework for later densification of the paste by the pozzolanic reaction of the fly ash. At the initial stages of cement hydration, most fly ash particles do not react, but merely serve as nuclei for precipitation of $Ca(OH)_2$ and C-S-H gel. The actual pozzolanic reaction usually begins after this "incubation period", when the alkalinity of the pore water has increased sufficiently to break down the glass network. This rising alkalinity results from the release of alkalies from the cement used, from alkali salts deposited on the fly ash surface and, in later stages, from alkalies of the dissolving fly ash glass [11].

The hydration of fly ash in cement-water system is known to occur mostly on the particle surface [12, 13]. Many researchers have observed that it is difficult for fly ash and lime to completely react with each other. This is, in part, because the degree of hydration of fly ash depends on the alkalinity of the cement paste. As the products surrounding the surface of fly ash harden, the diffusion of $(OH)^-$ ions is inhibited. One may predict that the hydration of fly ash will cease when the pH of the cement paste in pores decreases to a certain value.

Since some part of fly ash does not completely react with $Ca(OH)_2$, this part of fly ash works as micro aggregates in concrete. Most of fly ash is composed of spherical particles. When they are mixed into the concrete, they improve the workability of the fresh concrete allowing further reductions in the water/cement ratio. It results in a porosity reduction, and this is so called the packing effect.

Researchers consider two distinct aspects when evaluating fly ash characteristics; direct assessment of material properties and the evaluation of properties of fly ash in concrete or mortar mixes. Attempts are being made to find relations between the physical and chemical properties of fly ash with its behavior in concrete.

Some studies conducted have revealed that chemical composition alone is not the governing criterion for the behavior of fly ash in concrete [14]. However many researchers have observed that there is a direct increase in strength with the increase of the content of CaO in fly ash [15, 16, 17].

Studies conducted so far have revealed that the favorable influence of fly ash on concrete properties is attributable to various factors, with not only the chemical but also the physical effects being of importance [18]. Many investigations have been made of the physical and chemical properties of fly ash and the strength of fly ash concrete [19, 20, 21, 22]. The studies illustrated the dependence of the mortar strength on the fineness of the fly ash. At low median diameter, D_{50} , strengths of fly ash mixtures are higher than those of coarser fly ash mixtures [19]. Similar results have been observed by S. Slanicka [22] in his experiments conducted with fly ashes which have similar chemical and mineralogical composition but different fineness. The utilization of fly ash for the production of concrete can be considerably increased when its finest size fractions are withdrawn separately from the end stages of the retainers. In the cases where researchers have concluded that particle size does not have any notable effect on fly ash concrete strength, it is noted that they have paid no attention to the particles finer than 45 microns [23, 24].

Pozzolanic activity of fly ash is found to increase with the content of CaO of the fly ash. Also, studies conducted have revealed that there is a direct increase in compressive strength with the increase of soluble SiO_2 and soluble Al_2O_3 contents in fly ash [19]. Since the hydration of fly ash occurs between soluble Al_2O_3 and soluble SiO_2 and $Ca(OH)_2$ to get C-S-H gel, the more soluble SiO_2 and Al_2O_3 content in the fly ash, the more the reaction of fly ash with $Ca(OH)_2$ is possible, and the more C-S-H gel will be produced. Thus, the concrete strength is improved.

1.2.2 Application of Fly Ash in Environment

The huge amounts of fly ash produced by thermal power plants create disposal problems. In addition to its utilization for bricks, portland cement, pozzolona etc., it has also been recently used for pollution control.

Researchers have found several ways to utilize fly ash in environmental management. Fly ash has been used as an absorbent in wastewater treatment;

as a cementitious binder in solidification/stabilization of a heavy metal sludge; and as a soil conditioner for land reclamation.

Adsorption at solid-solution interfaces is an important means of controlling the extent of pollution due to metallic species in industrial effluent. The use of activated carbon is not suitable for this use in developing countries due to its high cost. So, fly ash can sometimes be used for this purpose as an inexpensive absorbent. One application using absorbent properties of fly ashes is the inexpensive treatment of leachate generated from industrial waste in landfills. Fly ash can serve as absorbents for heavy metals, toxic anions, and organic substances commonly found in leachates.

Studies conducted have pointed out that coal fly ash is a good adsorbent for mercury(II) and copper(II) from aqueous solutions and it can be utilized for the removal of mercury(II) and copper(II) from wastewater [25, 26]. The hydrolyzed species of Cu(II) are in complexed with surface active sites of fly ash. Low and Batley [27] demonstrated the effective removal of phenolic compounds and PAHs (Polycyclic aromatic hydrocarbons) from aqueous industrial wastes by adsorbing these compound on fly ashes. The adsorption of PAHs on fly ash particles, therefore, can have an important implications for the management of PAHs in the environment. Investigations conducted the adsorption capacity of PAHs on fly ashes [27, 28, 29] indicated the residual carbon content of fly ash is the main regulating parameter. The removal of Omega Chrome Red ME (a popular chrome dye) from aqueous solutions can be accomplished by adsorption on a homogeneous mixture of fly ash and coal. It has been noted that the adsorption capacities increase at low adsorbate concentration, with small particle size of adsorbent, low temperature and acidic medium [30].

Another environmental application of fly ash is that fly ash is used for the solidification/stabilization (S/S) of contaminated soil [31, 32]. Researchers have observed that solidification/stabilization by cementitious binders is the best demonstrated available technology for some wastes and waste forms [33]. The United States Environmental Protection Agency has approved its use for clean-up of certain Superfund sites [34]. Studies conducted by Helmuth,R. [35] revealed that fly ash in solidification/stabilization of heavy metal sludge process affects leaching rates by reducing the permeability of hardened paste. It can also chemically react with the waste and the binder. Microanalyses of the cement/ash mixtures used in S/S of a heavy metal sludge study indicated that fly ash spheres reacted with the ordinary portland cement (OPC) component to form a variety of reaction products including ettrigite and straetlingite [9].

Although past research has helped to establish many parameters that may affect fly ash concrete's behavior and its utility in environmental management, utilization of fly ash in concrete and in the environment are hampered mainly by the lack of understanding of this material. A more detailed knowledge is needed before fly ash can be properly used in structural concrete and for environmental management with effectiveness and confidence.

1.2.3 Effect of Chromium on Concrete Structure

There are numerous kinds of hazardous wastes which may be in solid, liquid, or gaseous forms. Potential source of chromium in industrial waste streams include metal cleaning and chromium plating, encompass pigments, tanning and textile chemicals synthetic rubies for lasers, synthetic emeralds, wood preservatives, catalysts, stainless steels, etc [36]. Chromium can cause serious injuries like burns to the skin, nose, throat; prolonged exposure can cause lung cancer. It can damage the liver and kidneys and has mutated the DNA in the laboratory. Some people think that chromium can also produce serious problems when it is in soil which even damage concrete structure and threaten human health. This problem can be seen in some places in Jersey City, New Jersey where there are failure of buildings and pavements, believed to cause by chromium contamination. The results of analyzing the soil from that site showed the chromium concentration was as high as 53,000 ppm [37]. According to the standard of DEP(the Department of Environmental Protection), all sites contaminated with more than 75 milligrams of chromium per kilogram of soil must be cleaned up [38].

Previously, studies conducted focused on the leaching characteristics of treating sludge or contaminated soil bound into a cement matrix. Little research, however, has been devoted to the effect of chromium itself on the concrete strength. Experimental data [8] show that strength of mortar cast by mixing contaminated soil (containing chromium(III)) with cement is higher than the strength of mortar which cast by mixing uncontaminated soil(no chromium(III)) with cement. This means that certain amount of chromium in cement mortar can increase the strength of mortar.

Studies conducted have revealed that potassium chromate and dichromate can be used in concrete as corrosion inhibitors [39]. Chromium hydroxide from the chromates is adsorbed on the reinforcing sheet and a protective film is formed. If large quantities of chromium inhibitors are used, adverse effects, such as severe localized corrosion or pitting will occur on concrete [40]. For longer curing periods, the splitting tensile strength of concrete decreased with increased percentages of potassium chromate, and there were substantial decreases in compressive strengths. There is ample evidence to suggest that the strength of concrete decreases with increased quantities of potassium chromate [39].

Researches showed that there was significant deterioration of the building and the parking lot which were constructed on fill made up of chromium ore residue mixed with soil. The building was no longer usable because the structural integrity of the building had deteriorated. Bricks had fallen from the walls because the wall was heavily contaminated with chromium residue.

In light of the review, the more knowledge regarding chemical compatibility and the long term effects of a chemical on materials and structures will be required before any definite conclusions can be drawn as to the effect of chromium on concrete.

1.3 Objectives

Review of past work has brought to light many parameters that could affect the behavior of fly ash in concrete and chromium in concrete. If a definite relationship could be established between these parameters and the effects of its application it would enable the use of fly ash and chromium in structural concrete more effectively.

This research consists of three parts. They are:

1.3.1 Effects of Fly Ash on Compressive Strength of Mortar

The parameters selected for investigation are

1. Different particle size with the same chemical and mineralogical composition
2. Fineness of fly ash
3. CaO content of fly ash
4. Fe_2O_3 content of fly ash
5. Particle size distribution

Each of the two fly ash types, Hudson and Mercer, was separated into seven different particle size range. Investigations are made to find a relationship between the compressive strength of fly ash-cement mortars and different particle size ranges of fly ashes which have the same chemical and mineralogical composition at various ages up to 180 days. The particle size distribution are also studied and used in the evaluation of this study.

Specific surface area of selected fly ash types are analyzed. Attention is given to the effects of fineness on compressive strength of mortar.

Chemical composition of fly ash are analyzed and attempt is made to determine if chemical composition, especially CaO and Fe_2O_3 contents, of fly ash with same particle size range have any effect on the compressive strength of mortar.

1.3.2 Effects of Cr(III) and Cr(VI) on Compressive Strength of Mortar and Concrete

The parameters selected in the investigations are

(1) Chromium (III)
(2) Chromium (VI)
(3) Leaching in the deionized water
(4) Leaching in the acetic acid

Investigations are made to discover whether the chromium-hazardous heavy metal in soil will destroy the concrete structures or not. In addition, the leaching of chromium mortar in deionized water and acetic acid (0.5N) have been studied.

1.3.3 Determination of Soluble Chromium in Fly Ash

The surface layers on coal fly ash particles are of special environmental interest in that concentration enrichments of trace elements may occur, thereby enhancing the potential bioavailability of toxic species. Little research, however, has been devoted to the analytical characterization of intraparticle and interparticle distributions of trace elements[41].

In this experiment, chromium concentrations were determined for all kinds of fly ashes used.

CHAPTER 2

EXPERIMENTAL PROGRAM

Experiments were set up in three series with the objectives of investigating: (1) the influence of selected parameters on the unconfined compressive strength of fly ash concrete and mortar; (2) the influence of chromium(III) and chromium(VI) on the compressive strength of concrete and mortar; (3) determining the concentration of chromium in fly ash.

2.1 Test Series 1

In this study, experimental programs were conducted for the purpose of studying the influence of selected parameters on the unconfined compressive strength of fly ash.

The standard 2"x2"x2" cube mortar specimen and 3"x6" concrete cylinder were used. The compression tests were conducted using an MTS closed-loop testing machine. Details of these tests are discussed below.

2.1.1 Materials

Materials used in the mortar and concrete of this study consisted of standard portland cement type I, siliceous sand (river sand), fly ash, and tap water.

Cement throughout the experiment the same type of cement Portland Cement Type I was used.

Crushed limestone

Sand local siliceous sand (river sand) passing through sieve No.8 (opening size 3.36mm) was used in this experiment.

Fly Ash Fly ash from two different types of coal-fired boilers were selected in this study. The first was the dry bottom boiler with direct fired burn located on opposite walls. The second type, was wet bottom boiler. The difference of these two boilers is that the dry bottom boiler is designed to have flame being below the fluid temperature of the coal ash, 2600 F, while the wet bottom boiler is designed to have a flame being higher than the fluid temperature of the coal ash. Dry bottom ash was collected from the Hudson plant while the wet bottom ash was from the Mercer plant. Each was separated into seven different particle size range. Using the Micro-Sizer Air Classification System of Progressive Industries Inc. The ranges fractionated are as follows:

Hudson fly ash: 11C(94.4%-88 microns)
11F(94.4%-44 microns)
10F(99.4%-31 microns)
7F(93.6%-16 microns)
6F(94.6%-11 microns)
5F(95.4%-7.8 microns)
3F(91.5%-5.5 microns)

Mercer Fly Ash: 18C(96.7%-88 microns)
18F(93.7%-22 microns)
17F(97%-22 microns)
16F(99.5%-22 microns)
15F(97.6%-11 microns)
14F(96.5%-7.8 microns)
13F(94.6%-5.5 microns)

Note: 11C(94.4%-88) indicates that 94.4% of the particles of 11C Hudson fly ash was smaller than 88 micron. The others are similar.

Fig. A.1 and **Fig. A.2** in Appendix A show the particle size distributions of Hudson fly ash and Mercer fly ash respectively.

2.1.2 Test Program

Fly Ash Mortar

Fly ash from Hudson and Mercer power plants with different particle sizes were mixed with cement and sand. 35% by weight of cement in the mix was replaced by fly ash. The specimens were mixed and cast in accordance with ASTM C-109. All specimens were cured in lime saturated water and tested at the ages of 1, 3, 7, 14, 28, 56, 90, and 180 days. The type of test specimen used is 2"x2"x2" cube.

Fly Ash Concrete

Fly ash from Hudson and Mercer power plants with different particle size were mixed with cement, sand, and coarse aggregate following a standard mixing procedure. 35% by weight of cement was replaced by fly ash. The specimens were mixed and cast in accordance with ASTM C-109. All specimens were mixed and cured in lime saturated water and test at the ages of 1, 3, 7, 14, 28, 56, 90, and 180 days. The test specimen used for evaluating the concrete strength is the 3"x6" cylinder.

2.1.3 Test Procedure and Setup for Compressive Strength

The compressive strength of mortar and concrete specimen was tested in a 100 kips MTS servo-controlled closed-loop hydraulic testing machine. The closed-loop control system provides very accurate control of the loading rate.

The 2"x2"x2" cube and 3"x6" specimens were tested in uniaxial compression under closed-loop stroke control. All tests were conducted at the displacement rate of 0.0008 in./sec.. The observed parameter from this testing was the ultimate load. The compressive strength was then calculated. The data used in the strength analysis was obtained from the average of three specimens.

2.1.4 Mix Proportion

In this experiment, fly ash replacement is 35% of cement, the ratio of water to cementitious material is 0.5, and the ratio of sand to cementitious material is 2.75 in every mix proportion. Tables 2.1, 2.2, 2.3, and 2.4 show the mix proportions used in test series 1.

2.1.5 Specific Gravity and Fineness

The specific gravities of fly ashes and cement used in the experiments were determined according to the standard procedures of ASTM C 188.

The fineness of fly ashes and cement conducted in the experiments were determined according to the standard procedures of ASTM C 204.

2.2 Test Series 2

Experiments were set up with the objective of investigating the influence of chromium on the unconfined compressive strength of mortar and concrete. The standard 2"x2"x2" cube mortar specimen and 3"x6" cylinder concrete specimen were used for the compression test of mortar and concrete in an MTS closed-loop testing machine.

Leaching test was set up with the objective of checking whether the chromium in the mixture of mortar can be fixed without leaching.

Table 2.1 Mix Proportion of Hudson Fly Ash Mortar

Sample	Cement(gm)	Sand(gm)	Fly ash(gm)	Water(ml)
CMC	500	1375	0	250
3F35	325	1375	175	250
5F35	325	1375	175	250
6F35	325	1375	175	250
10F35	325	1375	175	250
11F35	325	1375	175	250
1C35	325	1375	175	250
HO35	325	1375	175	250

Table 2.2 Mix Proportion of Mercer Fly Ash Mortar

Sample	Cement(gm)	Sand(gm)	Fly Ash(gm)	Water(ml)
CMC	500	1375	0	250
13F35	325	1375	175	250
14F35	325	1375	175	250
15F35	325	1375	175	250
16F35	325	1375	175	250
18F35	325	1375	175	250
18C35	325	1375	175	250
MO35	325	1375	175	250

Table 2.3 Mix Proportion for Studying the Effect of CaO content on Compressive Strength

Sample	Cement(gm)	Fly Ash(gm)	Lime(gm)	Sand(gm)	Water(ml)
CMC	500	0	0	1375	250
HCA35	325	166.58	8.42	1375	250
MCA35	325	175	0	1375	250
5CA35	325	168.3	6.7	1375	250
14CA35	325	175	0	1375	250
6CA35	325	168.1	6.9	1375	250
16CA35	325	175	0	1375	250

Notes: Fly ashes used are:

HCA35	Hudson feed fly ash CaO% = 6.89% *
MCA35	Mercer feed fly ash CaO% = 6.89%
5CA35	Hudson(95.4%-7.8) CaO% = 6.71% *
14CA35	Mercer(96.5%-7.8) CaO% = 6.71%
6CA35	Hudson(94.6%-11) CaO% = 6.55% *
16CA35	Mercer(99.5%-22) CaO% = 6.55%

* Free lime (CaO) is added in order to provide the same CaO content in both Hudson and Mercer fly ash concrete mixes.

Table 2.4 Mix Proportion of Studying Effects of Fe_2O_3 Content on Compressive Strength

Sample	Cement(gm)	Fly Ash(gm)	Fe_2O_3(gm)	Sand(gm)	Water(ml)
CMC	500	0	0	1375	250
6FE35	325	160.39	14.61	1375	250
16FE35	325	175	0	1375	250
5FE35	325	159.46	15.54	1375	250
4FE35	325	175	0	1375	250

Notes: Fly ashes used are:

5FE35	Hudson(95.4%-7.8)	Fe_2O_3% = 13.02%	*
14FE35	Mercer(96.5%-7.8)	Fe_2O_3% = 13.02%	
6FE35	Hudson(94.6%-11)	Fe_2O_3% = 13.26%	*
16FE35	Mercer(99.5%-22)	Fe_2O_3% = 13.26%	

* Additional Fe_2O_3 is added to keep the same Fe_2O_3 content in the fly ash concrete mixes.

2.2.1 Materials

Material used in the mortar and concrete of this study are standard portland cement type I, siliceous sand(river sand), chromium(III) and chromium(VI).

Cement and Sand are the same as those used in SERIES 1

Coarse Aggregate max. size is 3/8"

Chromium Two kinds of valences chromium were used.

chromium(III) comes from $CrCl_3 .6H_2 O$

chromium(VI) comes from $K_2 Cr_2 O_7$

2.2.2 Test Program

For the 2"x2"x2" mortar cubes, the chromium was mixed with cement and river sand. The amount of chromium as ClCr $_3$6H $_2$O (Cr(III)) and as $K_2Cr_2O_7$ (Cr(VI)) used was 5% by weight of cement. The ratio of water to cement is 0.5. The chromium is first added into the water in the bowl and allowed it to dissolve completely. The mixer was set at a slow speed and cement and sand were added. The specimen were mixed and cast in accordance with ASTM. C-109. All the specimens were cured in tap water and tested at the ages of 1, 3, 7, 14, 28, 56, 90, and 180 days.

For the 3"x6" concrete cylinder, the chromium was mixed with cement river sand, and coarse aggregate. The amount of chromium as ClCr .6$_3$H O_2(Cr(III)) and as $K_2Cr_2O_7$ (Cr(VI)) used was also 5% of cement by weight. The ratio of water to cement is 0.5625. All the specimens were cured in tap water and tested at the ages of 1, 3, 14, 28, 56, 90, and 180 days.

2.2.3 Mix Proportion

In this test chromium(III) and chromium(VI) were mixed in the cement mortar and concrete. Chromium content added as $ClCr_3.6H_2O$ (Cr(III)) and as $K_2Cr_2O_7$ (Cr(VI)) was 5% by weight of cement. The mix proportion is shown in Table 2.5 and Table 2.6.

Table 2.5 Mix Proportion of Chromium Mortar

Sample	Cement(gm)	Sand(gm)	Chromium(gm)	Water(ml)
CMC	500	1375	0	250
CMC3	500	1375	25 [Cr(III)]	250
CMC6	500	1375	25 [Cr(VI)]	250

Note: The ratio of water to cement is 0.5.

Table 2.6 Mix Proportion of Chromium Concrete

Sample	Cement(lb)	Sand(lb)	Coarse Agg.(lb)	Cr(lb.)	Water(lb)
CMY	16	32	48	0	9
CMY3	16	32	48	0.8[CrIII)]	9
CMY6	16	32	48	0.8[Cr(VI)]	9

Note: The ratio of water to cement is 0.5625.

2.2.4 Leaching Test Pricedure

The 2"x2"x2" blocks were suspended separately in the 500 ml deionized water and 500 ml acetic acid (0.5N) extractant and gently stirred by means of magnetic stirrers for 24 hours. The leachates were filtered through 0.45 um membranes for analyses. The process repeated for 1, 3, 7, 14, 28, 56 days of age.

2.2.5 Test of Leachates with AAS

Method AA Direct Aspiration

Flame Conditions:

Element: Cr
HCL: 6 ma(sig)
Nitrous Oxide/Acetylene
Reducing: (Fuel Rich, Yellow)
Wavelength: 357.9 nm-UV
Band Width 0.5

PROCEDURE The test procedure of Atomic Absorption Spectrometer is given in Appendix D.

2.2.6 Test Procedure and Set up for Compressive Strength

The compressive strength of mortar and concrete specimen was tested using the procedure described in 2.1.3.

2.3 Test Series 3

2.3.1 Materials

Two kinds of fly ash were used in this study. They are Hudson fly ash and Mercer fly ash of different particle size.

2.3.2 Test Procedure

The experiment was carried out by soaking 50 gram of fly ash sample in 100 ml tap water for 24 hours. The concentration of chromium was determined by filtering the solution then analyzing the solution with AAS. Blanks without fly ash were also prepared to correct for any trace metal chromium in the tap water.

CHAPTER 3

EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Experimental Results of Test Series 1

3.1.1 Chemical Compositions of Fly Ash

The chemical compositions of fly ashes used in this experimental program were analyzed by X-Ray Fluorescence according to ASTM Method D 4326: Major and Minor Elements Content of Coal/coke Ash. The results are given in Appendix A. There is no significant variation in the chemical compositions apparent among different particle size of Hudson fly ashes and among different particle size of Mercer fly ashes.

The values of loss on ignition (LOI) of both Hudson and Mercer fly ashes with different particle size vary a little, range from 1.46% to 4.97% by weight. The moisture contents of all fly ashes were found to be very close and also very small. All fly ashes have moisture content as little as 0.11% by dry weight.

There is little variation in the minor element composition between Hudson and Mercer fly ashes. Among major elements, the average of calcium oxide(CaO) contents of Hudson fly ashes is about 2.47% by weight while the average of calcium oxide contents of Mercer fly ashes is about 6.76% by weight. It is obvious that Mercer fly ashes have higher calcium oxide content than Hudson fly ashes. The iron oxide (Fe_2O_3) content varies considerably between Hudson and Mercer fly ashes. The average of iron oxide content of Hudson fly ashes and Mercer fly ashes are about 5.03% and 14.01% by weight respectively.

3.1.2 Compressive Strength Development

In this experiment, Hudson and Mercer fly ash were used as 35% replacement of cement by weight of cement. The mix proportions are given in Table 2.1 and Table 2.2.

The tabulated results for the compressive strength and the percentage compressive strength of Hudson and Mercer fly ash mortars compared to conventional (with no fly ash) mortar strength are given in Appendix B.

The results of the tests show that the compressive strength development and the rate of strength gain vary with the different particle size of fly ash incorporated in the mortar mixture for same ages.

The difference in compressive strength can be observed in Fig.3.1, Fig. 3.2, Fig. 3.3 and Fig. 3.4, which show that incorporation of different particle size of Hudson fly ash in the mortar gave a wide range of strengths for the same mix proportions. The finer the particle size fly ash incorporated in mortar, the higher the compressive strength obtained. A similar relationship was also found using Mercer fly ash mortar with different particle size of fly ash.

In Fig.3.1 and Fig. 3.2, all the strengths of Hudson fly ash mortar are lower than the conventional mortar strength before 28 days age except 3F (91.5%-5.5) fly ash mortar. Similarly, all the compressive strength of Mercer fly ash mortar are lower than the conventional mortar strength before 28 days age except 13F(94.6%-5.5) fly ash mortar.

It is interesting to note that 3F Hudson fly ash mortar and 13F Mercer fly ash mortar have higher compressive strength than the conventional mortar even at an early 14 days age. At 28 days, the strengths of 3F35 and 13F35 have increased to more than the conventional mortar by about 15.27% and 6.5% respectively. After 28 days age, however, the rate of strength gain for both 3F35 and 13F35 diminish similar to the conventional mortars.

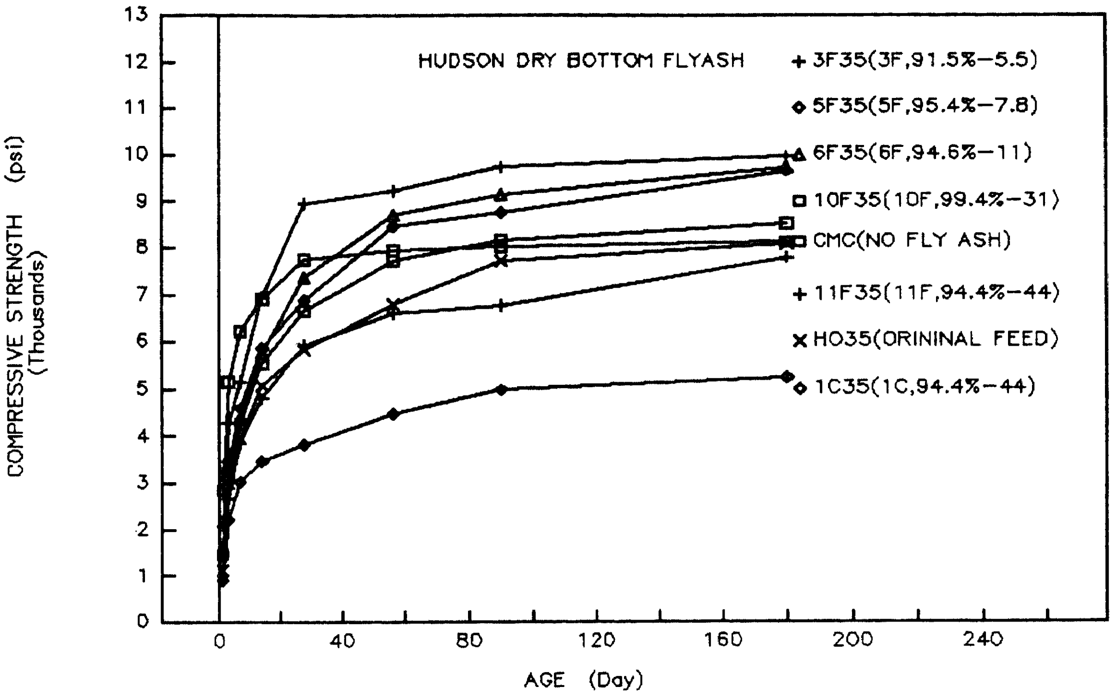

Fig. 3.1 Compressive strength development of Hudson fly ash mortars

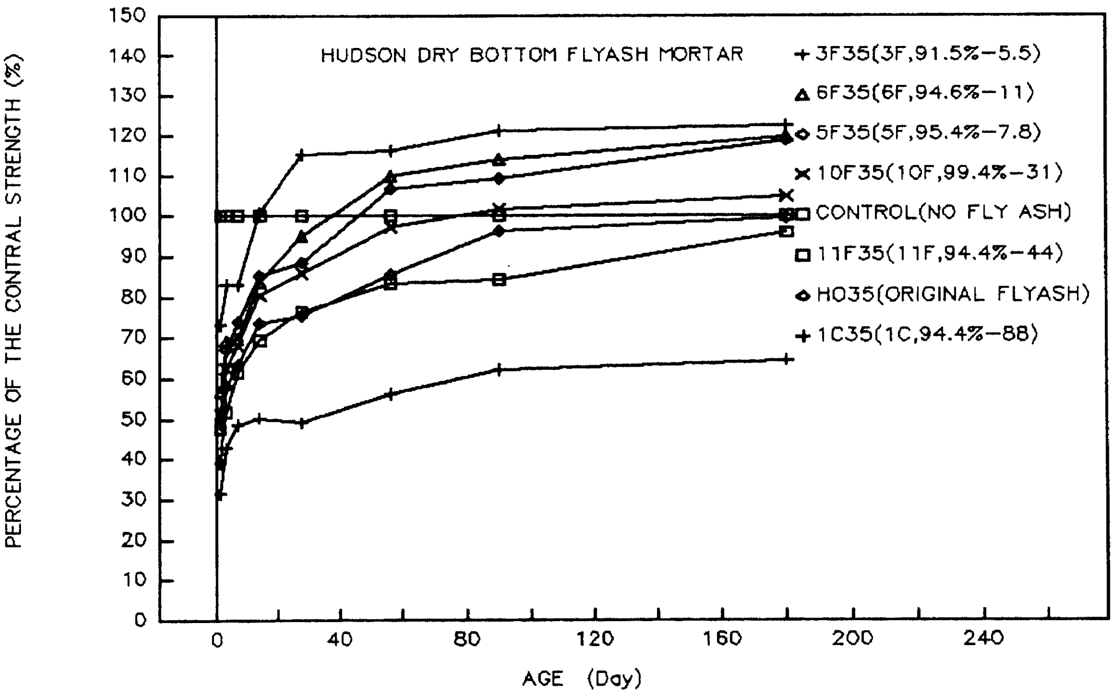

Fig. 3.2 Compressive strength of Hudson fly ash mortars as a percentage of control strength

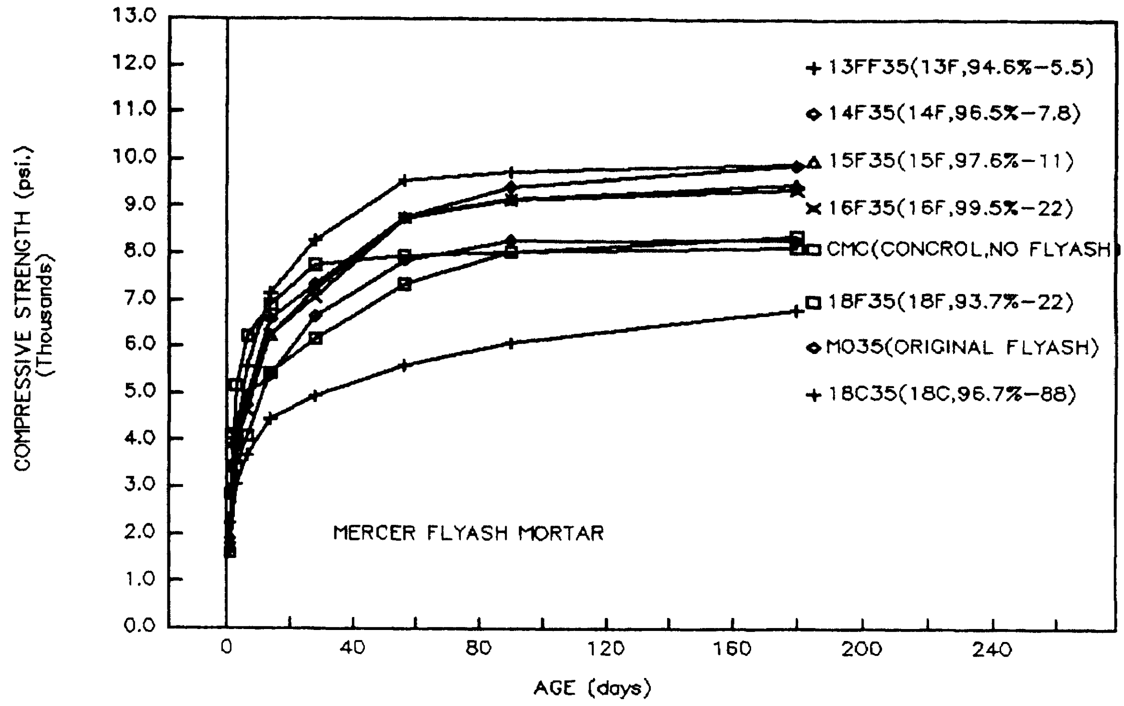

Fig. 3.3 Compressive strength development of Mercer fly ash mortars

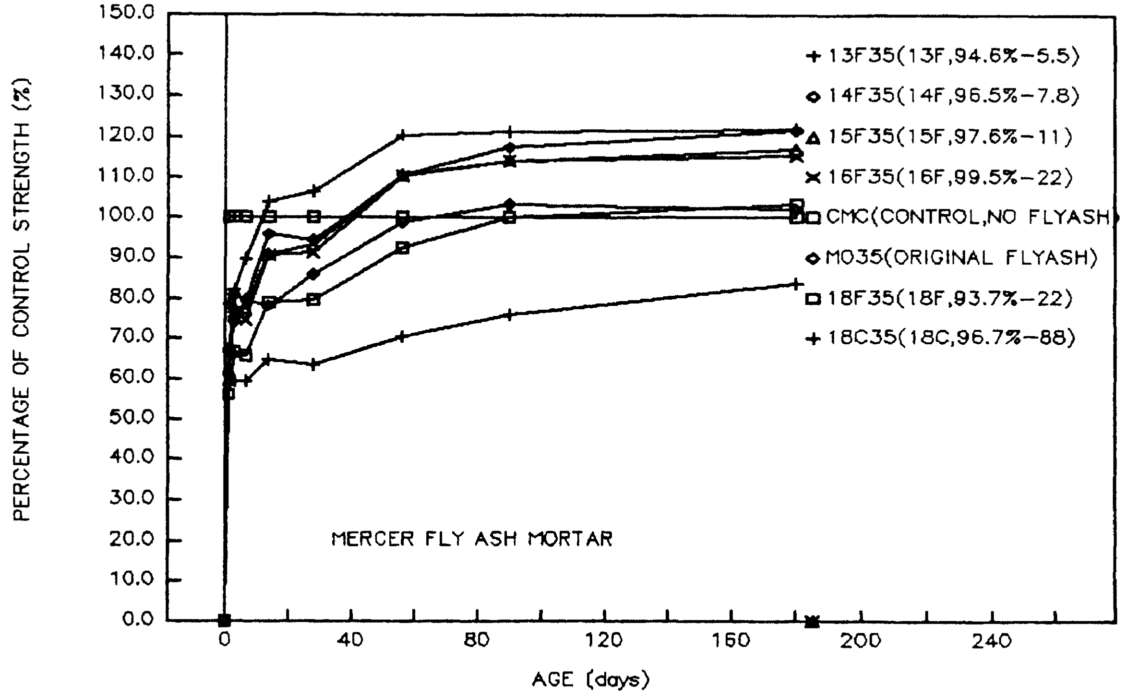

Fig. 3.4 Compressive strength of Mercer fly ash mortars as a percentage of control strength

For other Hudson fly ash mortar, such as 5F35, 6F35, 10F35, 11F35, 1C35, and the original Hudson fly ash mortar HO35, the rate of strength gain continues to increase steadily up to 180 days age. But their strengths are lower than that of the conventional mortar before 28 days age. So far, the experiments conducted up to 180 days age show that the strength of 10F35, 6F35, 5F35 14F35 15F35, 16F35 and MO35 surpass the conventional mortar strength at 180 days. Moreover, the strength of 5F35, 6F35, 14F35, 15F35, and 16F35 already surpass the conventional mortar strength at 56 days. On the other hand, 11F35, 1C35, HO35, and 18C35 mortars still show compressive strengths lower than the conventional mortar strength at the age of 180 days.

3.2 Influence of Selected Parameters on the Unconfined Compressive Strength of Mortar (Test Series 1)

3.2.1 Influence of Particle Size

In spite of these large differences in particle size, little variation in bulk chemical composition is observed for the same kind of fly ash.

It is evident from the results of these test that the finer the particle size of fly ash incorporated into mortar, the higher the mortar compressive strength for both Hudson and Mercer fly ash mortar. The past research work shows that fly ash mortar has a lower compressive strength at early age(up to 28 days), compared to conventional mortar. The reaction of fly ash in cement is initiated only after one or more weeks. In this period the fly ash behaves as a more or less inert material and serve as a precipitation nucleus for $Ca(OH)_2$and C-S-H gel originating from cement hydration [48]. The 3F35 and 13F35 mortars, however, exhibited noted increase in compressive strength at 14 days age compared to the conventional mortar as shown in the following figures: Fig. 3.5 and Fig. 3.6. This indicated that for 3F and 13F fly ashes the hydration reaction occurs at an early age.

The cause, in part, is that finer particles contain a higher glass content [42], and are thus more reactive. More C-S-H gel is produced to fill the pore space in the mortar or in the concrete and therefore yield a higher compressive strength. Another part of the reason is its "shape" function. The finer particles are generally spherical in shape which permits large water reductions in mortar or in concrete mixes while maintaining good workability. Water reduction is an important contribution to a strength gain. The last reason is that the 0-5.5 micron particle size fly ash have a very large specific surface area, and the specific surface area of 0-5.5 micron fly ash is more than twice as that of cement used. This will be further discussed later.

The above discussion concludes that fly ash with particle size 0-5.5 micron range not only has a cementitious effect as good as cement, but also gives a good workability which the cement itself does not have. Therefore, cement incorporating this kind of fly ash can give a higher compressive strength than conventional mortar. A similar trend in long-term strength development can be observed with 3F35 and 13F35 compared to the conventional mortar. They show that the strength increase very little beyond 28 days age.

For the fly ashes in which more than 30% of the particles are larger than 45 micron, such as 1C Hudson fly ash (particles >45 micron = 42%) and 18C Mercer fly ash(particles >45 micron = 30%), their mortar strengths are much lower than fly ash mortars made with smaller particles. They are even weaker than conventional mortar at the age of 180 days. This is because, in part, the large particles contain less glass and thus are less reactive. This agrees with the observations reported by the past researchers [43]. Also, the coarse fly ashes require an increase of the W/(C+F) ratio [44]. Since every mix proportion has the same W/(C+F), the coarse fly ashes result in lower workability of the mixes and therefore reduces the compressive strength. ASTM and CSA specify that no more than 34% by weight of a given ash be coarser than 45 microns(um) if the ash is proposed for use as a pozzolan in concrete. More severe are British standards which restrict the amount of +45 um fraction to 12% [45].

It is evident from the results of tests and analyses that particle size of fly ash larger than 45 micron have little contribution, even negative contribution, to the compressive strength. The variations in the amount of glassy phase has a direct influence on the reactivity of the fly ash.

3.2.2 Influence of Particle Size Distribution

Compressive strengths plotted against mean particle size, D_{50} which is the mean diameter of particles in a sample, show that there is a relationship between D_{50} and the compressive strength (Fig. 3.7, Fig. 3.8, and Fig. 3.9). The mean diameter D_{50} can be identified on the particle size distribution curve. Different types of fly ash has different particle size distribution curves and give different D_{50}. The D_{50} is an important index expressing particle size distribution.

It is important to note that the compressive strength development of fly ash mortar changes with the change of mean diameter of fly ash particles. The smaller the D_{50} of the fly ash, the higher the compressive strength of fly ash mortar. This relation is more apparent observing for long-term strength (after 14 days). However, it is not quite significant for strength development at early age.

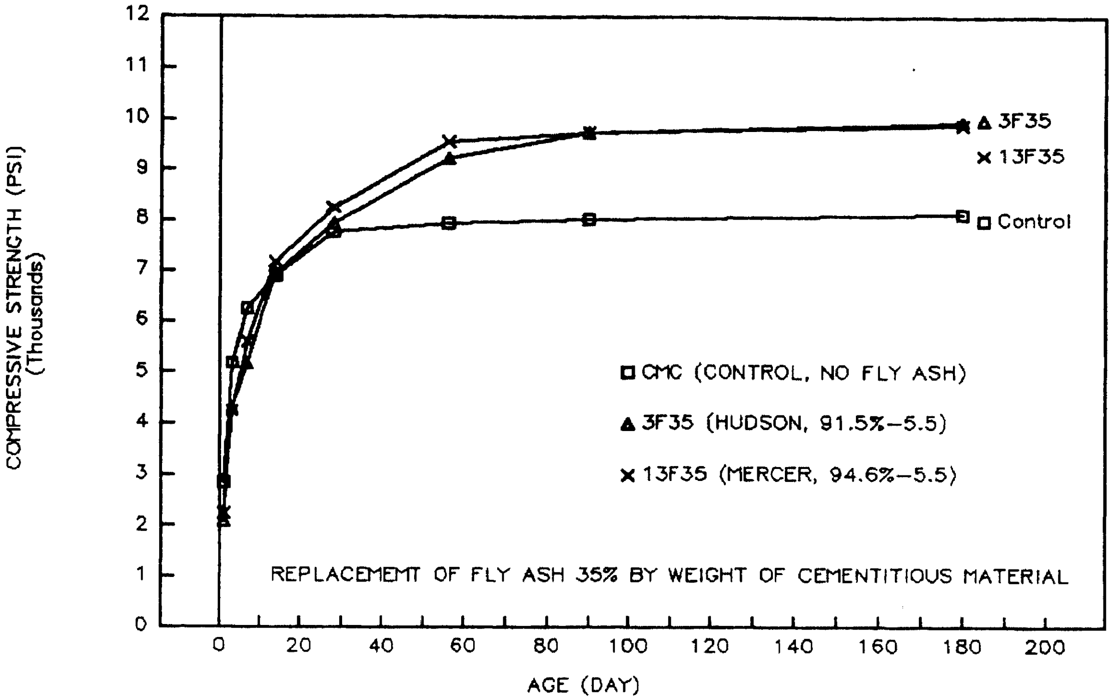

Fig. 3.5 Compressive strength of 3F35 and 13F35 mortars

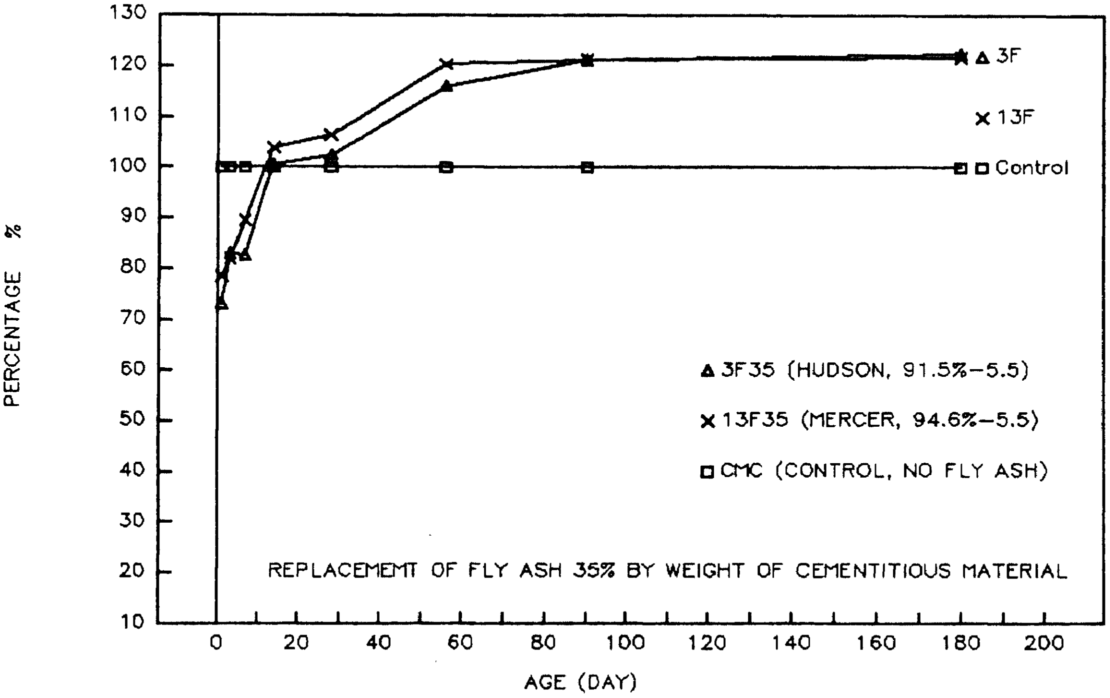

Fig. 3.6 Compressive strength of 3F35 and 13F35 mortars as a percentage of control test strength

The graphs presented in Fig. 3.10 and Fig. 3.11 show that the percentage of the compressive strength of fractionated types of Hudson and Mercer fly ash mortars compared to the original Hudson and Mercer original fly ash mortars respectively. The results of tests revealed that particle size of fly ashes between 11-44 micron have an amphoteric effect depending on the particle size distribution. Although the original Hudson fly ash often includes particles which are larger than 45 um, mortar made with this fly ash still has higher strength than 11F35 mortar which does not contain fly ash particles larger than 44 um. Since the mean diameter of 11F Hudson fly ash is slightly larger than that of the original Hudson fly ash, so its mortar strength is lower.

There is a notable difference in the strength of 16F35 mortar and 18F35 mortar regardless of their particle size range, chemical and mineralogical composition, and mix proportion. The graph Fig. 3.12 shows that 16F35 mortar has higher compressive strength than 18F35 mortar. The higher mean particle size of 16F Mercer fly ash is part of explanation. Another reason can be seen in Fig.3.13. It shows that 16F Mercer fly ash contains more 0-5.5 um and 5.5-10 um particles, and fewer 10-22 um particles than 18F fly ash. This confirmed that 0-5.5 um and 5.5-10 um particles always induce strength gain.

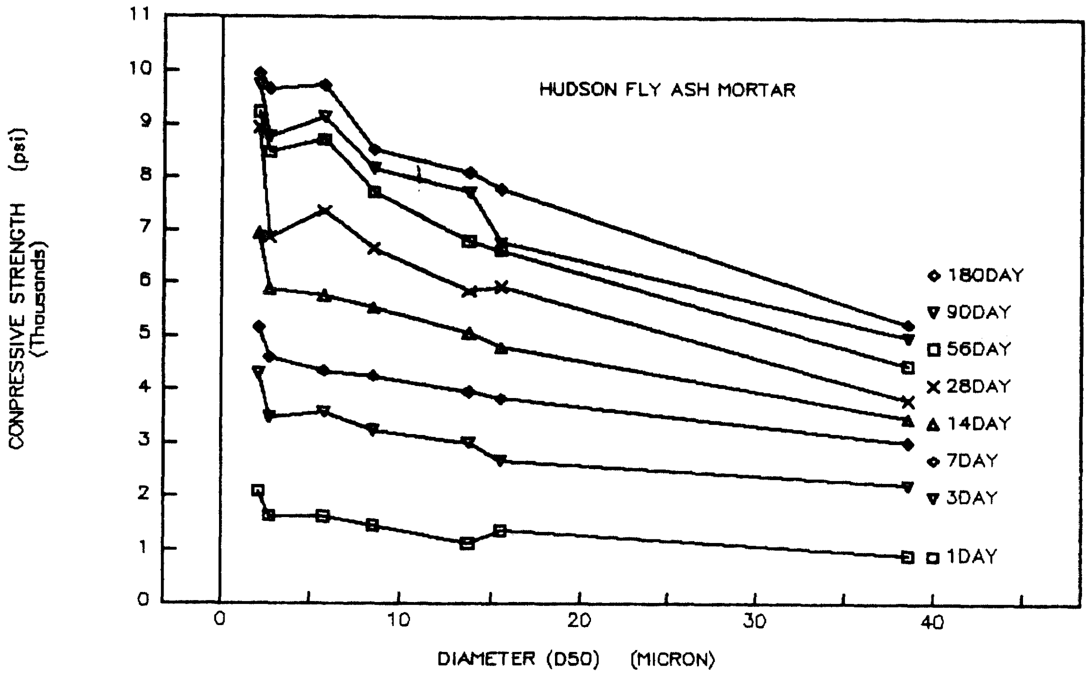

Fig. 3.7 Effect of mean particle size on compressive strength of Hudson fly ash mortars

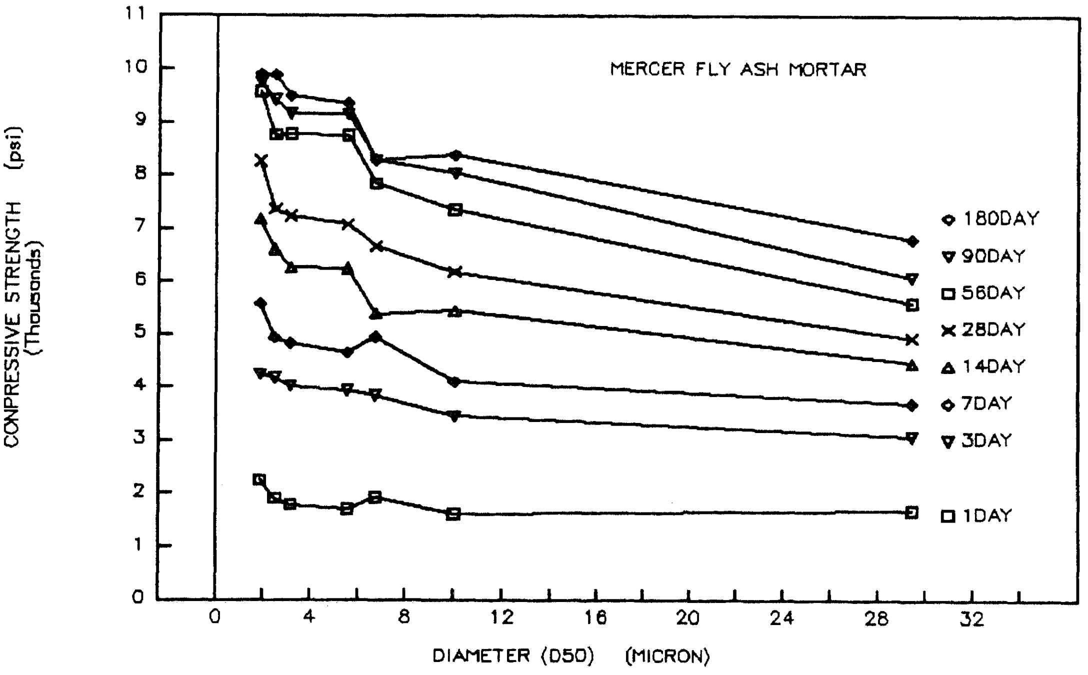

Fig. 3.8 Effect of mean particle size on compressive strength of Mercer fly ash mortars

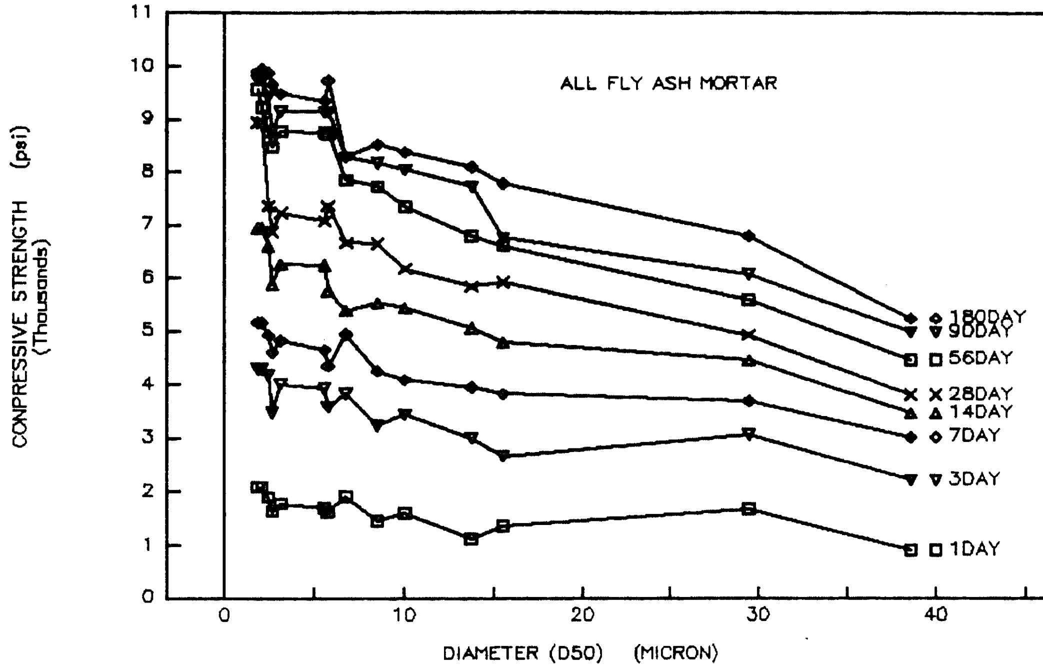

Fig. 3.9 Effect of mean particle size on compressive strength of Hudson and Mercer fly ash mortars

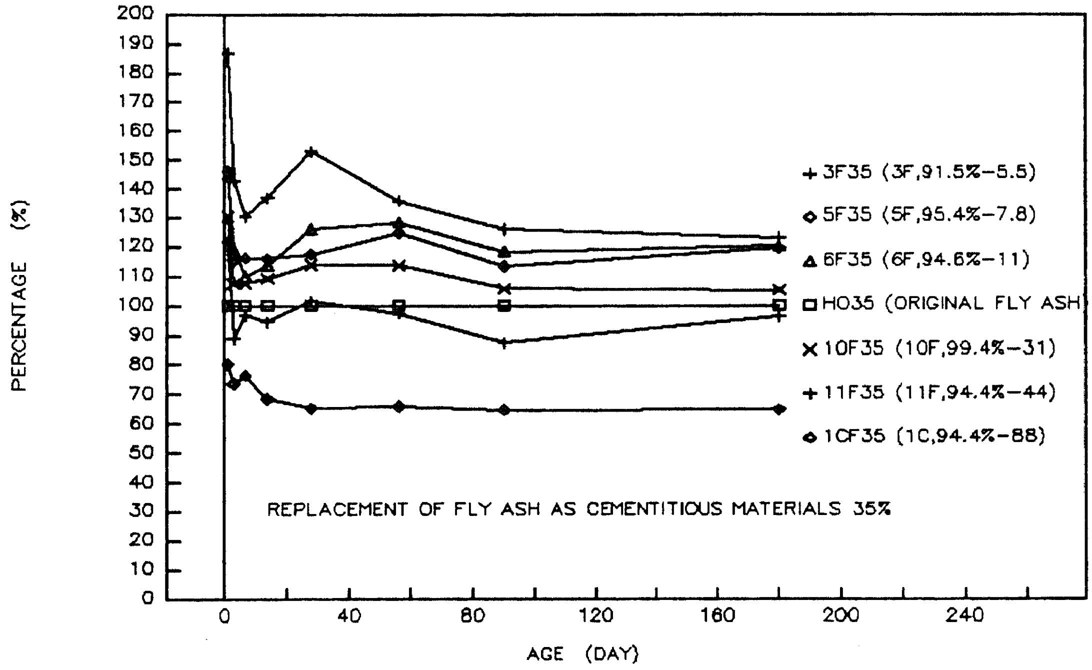

Fig. 3.10 Compressive strength of fractionated Hudson fly ash mortars as a percentage of original Hudson fly ash mortar strength

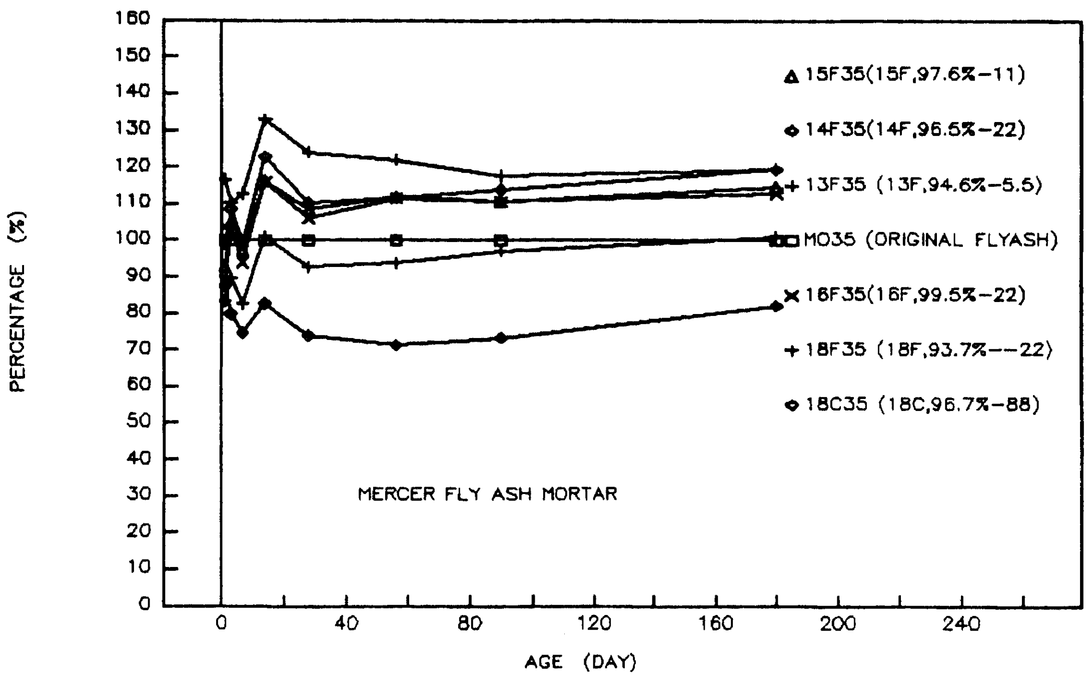

Fig. 3.11 Compressive strength of fractionated Mercer fly ash mortars as a percentage of original Mercer fly ash mortar strength

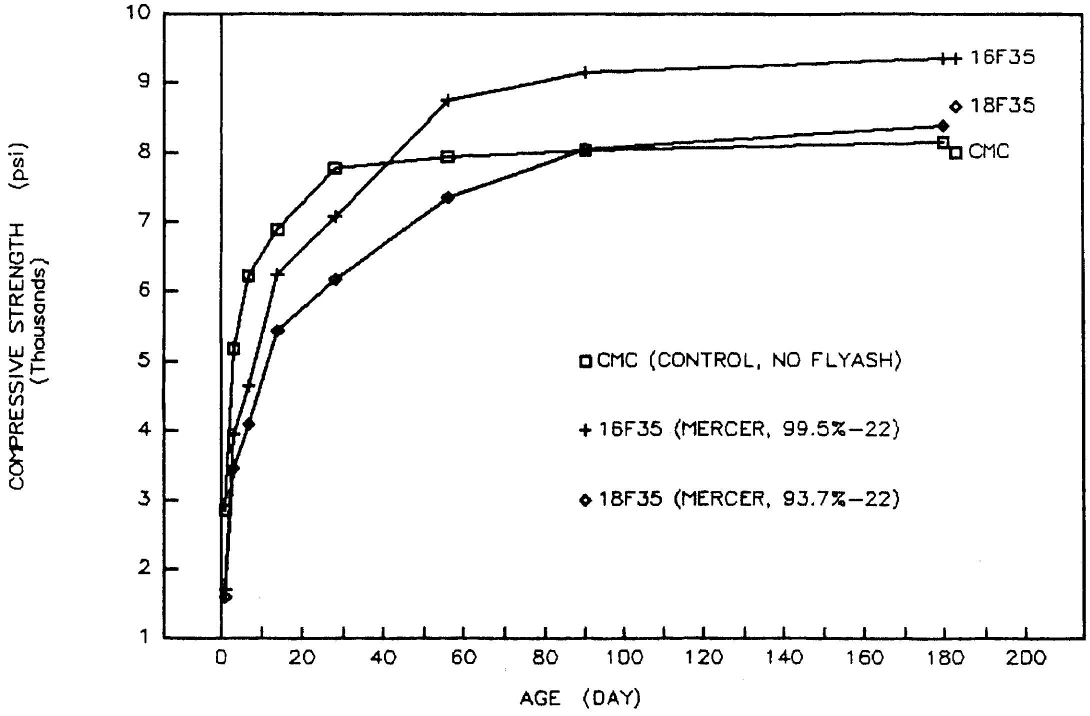

Fig. 3.12 Compressive strength of 16F35 and 18F35 mortars

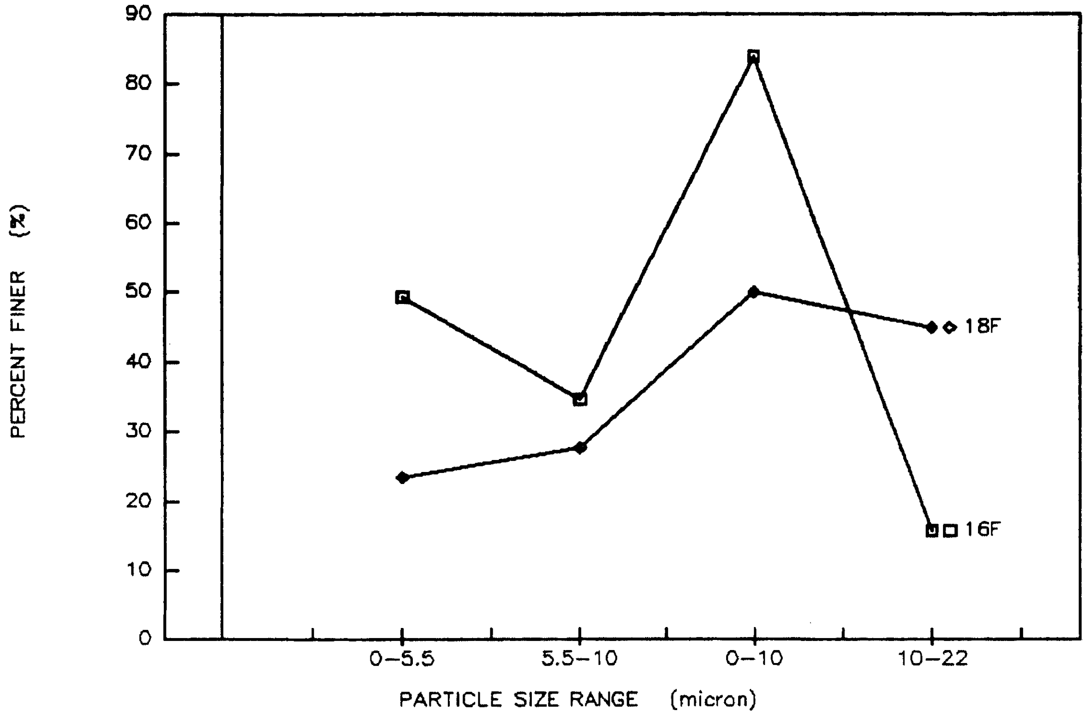

Fig. 3.13 **Dominant particle size range of 16F and 18F fly ashes**

3.2.3 Influence of Blaine Fineness

Specific Gravity

Specific gravity is one parameter that is frequently determined when analyzing fly ash for chemical properties and for use as an additive in concrete. It is also of interest in understanding the engineering properties of fly ash. The specific gravities of fly ashes and cement were determined by Le Chatelier flask according to ASTM C 188. The results of those tests, given in Appendix B and Appendix C, show that there is a slight variation (from 2.279 to 2.748) in the specific gravity with these large differences in particle size. Specific Gravities plotted against mean particle size D_{50}, given in Appendix C, show that generally the smaller the D_{50} , the higher the specific gravity.

Blaine fineness

Fineness of fly ashes and cement were determined by Blaine Air Permeability Apparatus according to ASTM C204. The results of tests in Appendix B and Appendix C exhibit a significant difference in fineness with different particle size fly ashes.

The graph Fig. 3.14 illustrates the dependence of the compressive strength on the fineness of the fly ash. The larger the specific surface area, the higher the strength. 3F and 13F fly ashes have very large specific surface areas. The most significant influence of large specific surface of fly ashes on fly ash mortar is at early stage strength development. The large specific surface area of fly ashes support a fast reaction between fly ash and lime which results in higher compressive strength at early ages. It is very evident from the results of tests that 3F35 and 13F35 mortar have higher early strength. At 7 days, their strength was 85% and 90% of the strength of conventional mortar. At 28 days, they had a higher or equal strength compared to the conventional mortar. After 28 days, their strengths are generally higher than that of the conventional mortar.

The hydration rates of 3F and 13F fly ashes are much faster than that for other fly ashes from 1 to 28 days. Therefore, their early strengths are higher than other fly ash mortars. After 28 days, however, their hydration rates diminish and are slower than other fly ashes. This is because the surface of fly ashes particles were surrounded by the hydration products, which almost stop the hydration process after 28 days. This explains why the compressive strengths of 3F35 and 13F35 mortars increase very little after 28 days.

The figure in Appendix C shows a relationship between mean particle size D_{50} and Blaine fineness. It indicates that the smaller the D_{50} , the larger the Blaine fineness.

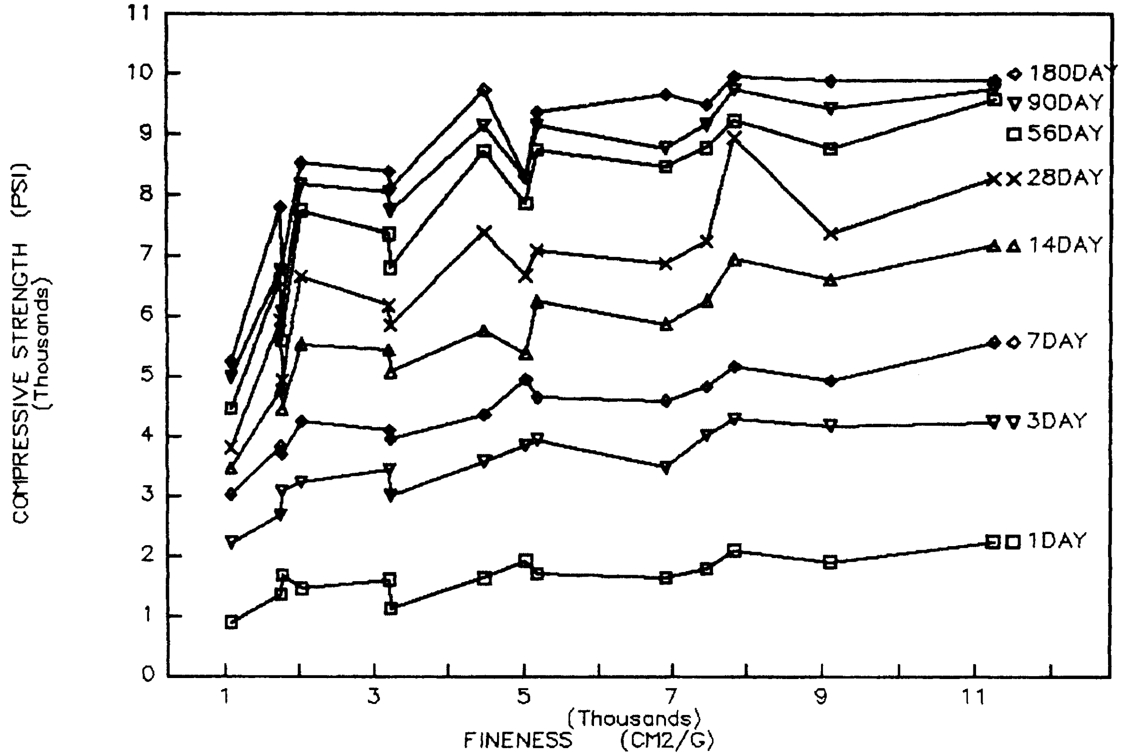

Fig. 3.14 Effect of fineness of fly ash on compressive strength

3.2.4 Influence of CaO and Fe $_2$O $_3$ Content

Hudson and Mercer fly ash mortars which have same particle size range like 3F and 13F, 5F and 14F, as well as 6F and 16F fly ashes, still have notable differences in their compressive strengths. Usually Mercer fly ash mortar has a higher strength than Hudson fly ash mortar for the same particle size range. See Fig. 3.5, Fig. 3.6 and Appendix C.

The results of chemical analyses, found in Appendix A, show that Mercer fly ash has higher CaO and Fe $_2$O $_3$content than Hudson fly ash. The average difference of CaO content between Mercer fly ash and Hudson fly ash is about 4.29% by weight and the difference of Fe_2O_3 content is about 8.98% by weight.

In order to determine if the differences in CaO and Fe_2O_3 content of fly ash caused the difference in strength of mortar, CaO and Fe_2O_3 were added to Hudson fly ash to achieve the same content as in Mercer fly ash. The mix proportions are given in Table 2.3 and Table 2.4.

The experiments to investigate the effect of CaO content were conducted using original Hudson fly ash and original Mercer fly ash, 6F and 16F fly ash, as well as 5F and 14F fly ash. The graphs, given in Appendix C, show that even by adding additional amount of CaO to Hudson fly ash mortars, the resultant strength was still lower than for the related Mercer fly ash mortars.

Past research [16] reveals that additives based on calcium compounds contribute to early and long-term strength of fly ash concrete. Calcium-enriched fly ashes also improve carbonation resistance of fly ash concrete. The reason for this was generally attributed to the CaO content of up to 10% by weight of fly ash (Class C). The variation of CaO content of fly ash in our experiments conducted in test series 1 is from 2.47% to 6.76%. This still is in the low CaO content fly ash (Class F) range. Thus, there is no significant effect of CaO content change on the strength.

The experiments for studying the influence of Fe_2O_3 content were conducted using 5F and 14F fly ash, and 6F and 16F fly ash. The mix proportions are given in Table 2.4. The graphs, presented in Appendix C, show that Hudson fly ash mortars with additional Fe_2O_3 still yield a lower strength than the related Mercer fly ash mortars. The Fe_2O_3 content varying from 5.03% to 14.01% has no notable influence on the compressive strength of mortar. This is because that Fe_2O_3 in fly ashes does not react with $Ca(OH)_2$ directly.

In conclusion, the particle size and its distribution and the fineness of fly ashes have significant influence on the strength of fly ash mortar. CaO content varying in the range below 6% of CaO content has no notable effect on the mortar strength. Fe_2O_3 content of fly ashes also does not have any notable effect on the mortar strength.

3.3 Experimental Results of Test Series 2 - Effects of Chromium on Mortar and Concrete Strength

In the Test Series 2, chromium(III) and chromium(VI) were mixed in the cement mortar and concrete. The addition of chromium(III) as $CrCl_3.6H_2O$ and chromium(VI) as $K_2Cr_2O_7$ was 5% of the cement by weight. In addition, leaching tests were conducted with the mortars using deionized water and acetic acid (0.5 N) as extractants separately.

3.3.1 Chemistry of Chromium

The inorganic chemistry of chromium is not only rich in its variety of colors, but also in its many oxidation states and the geometries of its many compounds. The oxidation states of chromium can go from -2 to +6. In aqueous solution the +3 state is most stable, followed by the +2 state. The +6 state is unstable in acid solution and goes to the +3 state. Further more, chromium in the +2 state is a good reducing agent, while in +6 state it is a powerful oxidizing agent.

There are differences in toxicity and carcinogenicity of trivalent and hexavalent chromium. Hexavalent chromium is a potent carcinogen while trivalent chromium is an essential trace element [46]. Available data show trivalent chromium compounds to be less toxic than those of hexavalent chromium. It should be noted that at low pH, the +3 state, $Cr(H_2O)_6^{+3}$, is the predominant or stable species, and the +6 state, CrO_4^{-2}, is the predominant species at high pH. It is believed that the +3 oxidation state is the most stable oxidation state of chromium, and it is represented by thousands of compounds. The oxidation states of +3 and +6 are most commonly encountered in the environment [47].

3.3.2 Development of Compressive Strength

The tabulated results for the compressive strength and the percentage of control compressive strength of chromium mortar and chromium concrete are shown in Appendix B. Strength relationships are graphically illustrated in Fig. 3.15, Fig. 3.16, Fig. 3.17 and Fig. 3.18.

The difference in compressive strength can be observed through out the test. The results of tests indicate that different valences of chromium in mortar have different strengths for the same mix proportions. Up to the age of 180 days, the chromium(III) mortar has a higher compressive strength as compared to the conventional mortar. The compressive strength of chromium(VI) mortar, however, is less than that of the conventional mortar up to the age of 90 days. Similar results can be observed in chromium concrete.

It is evident from the results of these tests that the compressive strength gain of chromium of chromium(VI) mortar is very small after 14 days. And, the strength of chromium(VI) mortar concrete even decreases a little after 28 days age. On the other hand, the compressive strengths of chromium(III) mortar and chromium(III) concrete still increase after 14 days. The rate of strength gain is higher than those for conventional mortar and concrete.

3.3.3 Leaching Test with Deionized Water Extractant

The significant differences in the leaching characteristics of chromium(III) and chromium(VI) mortar can be seen. With deionized water as extractant, there is no detectable leaching of chromium from the chromium(III) mortar specimen determined by Atomic Adsorption Spectrometer. But leaching of chromium from the chromium(VI) mortar specimens was clearly observed. Fig. 3.19 graphically indicates that chromium(VI) concentration in the leachates decreased with the development of strength. Before 14 days, the concentration of chromium(VI) was higher than the EPA standard of 5ppm. After 14 days, it is lower than the EPA standard of 5 ppm.

3.3.4 Leaching Test with Acetic Acid (0.5N) Extractant

The leaching test result of Cr(III) and Cr(VI) mortar using acetic acid (0.5N) as an extractant is given in Fig. 3.20.

There is considerably chromium leaching from both Cr(III) mortar and Cr(VI) mortar when using acetic acid as an extractant. The concentrations of both Cr(III) and Cr(VI) in leachates decreased with the development of strength. Chromium leaching from Cr(VI) mortar was much higher than that of Cr(III) mortar at all ages. This may be due to the fact that the strength of Cr(VI) mortar is lower than that of Cr(III) mortar at any ages. The maximum chromium concentration in the leachates of Chromium(VI) mortar is 420 ppm while those from chromium(III) is only 130 ppm.

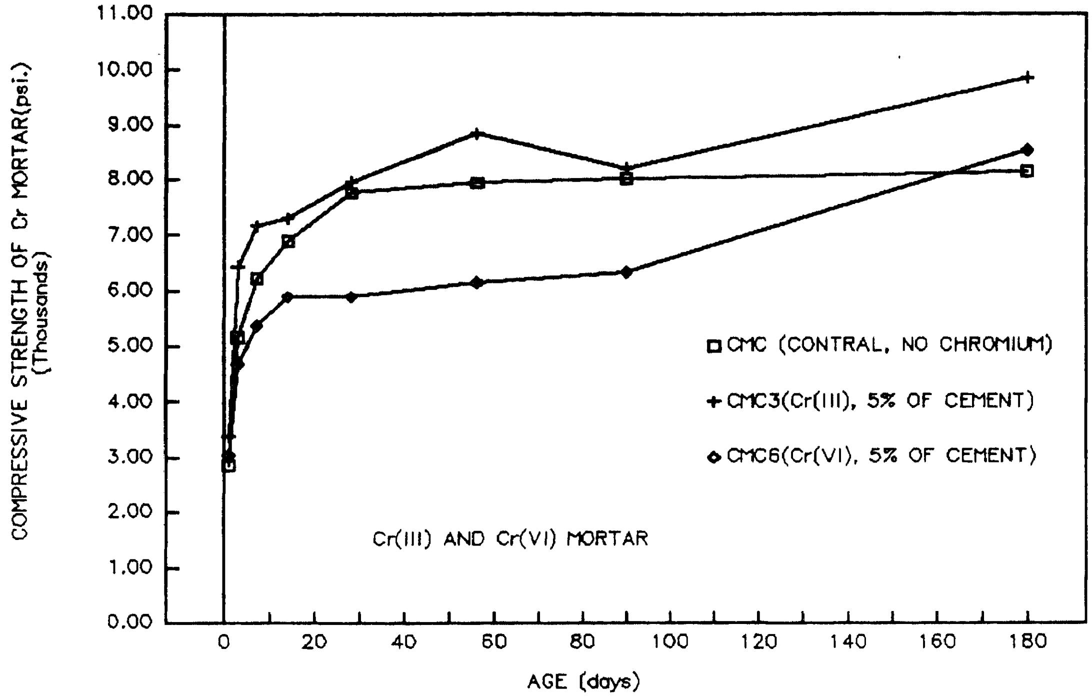

Fig. 3.15 Compressive strength development of chromium mortar

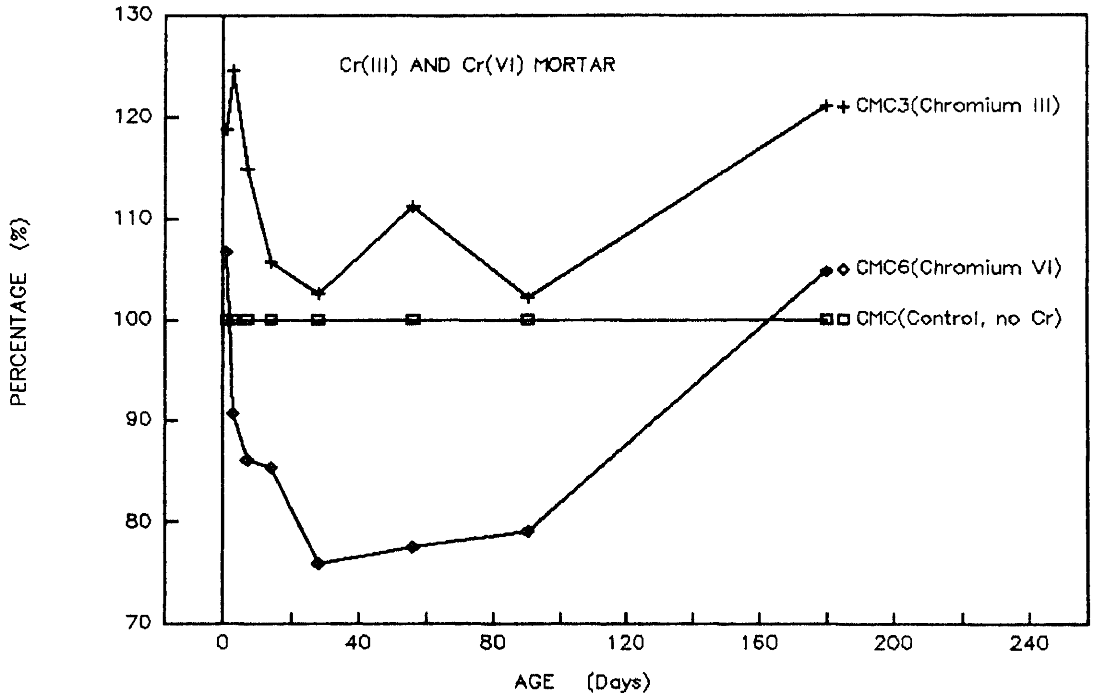

Fig. 3.16 Compressive strength of chromium mortar as a percentage of control test strength

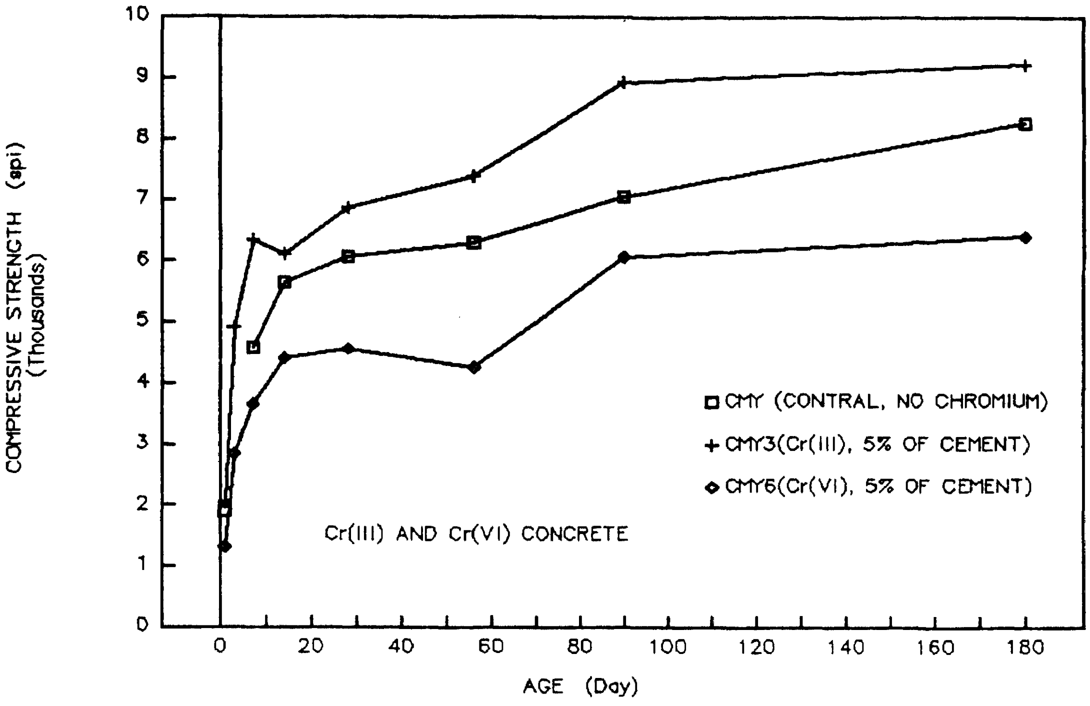

Fig. 3.17 Compressive strength development of chromium concrete

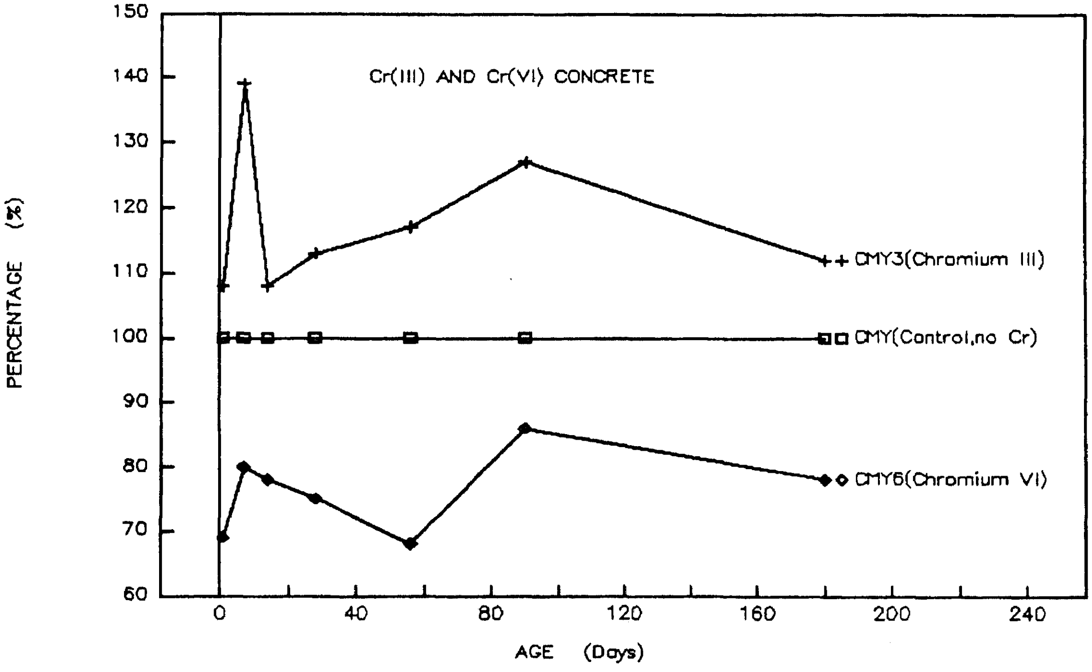

Fig. 3.18 Compressive strength of chromium concrete as a percentage of control test strength

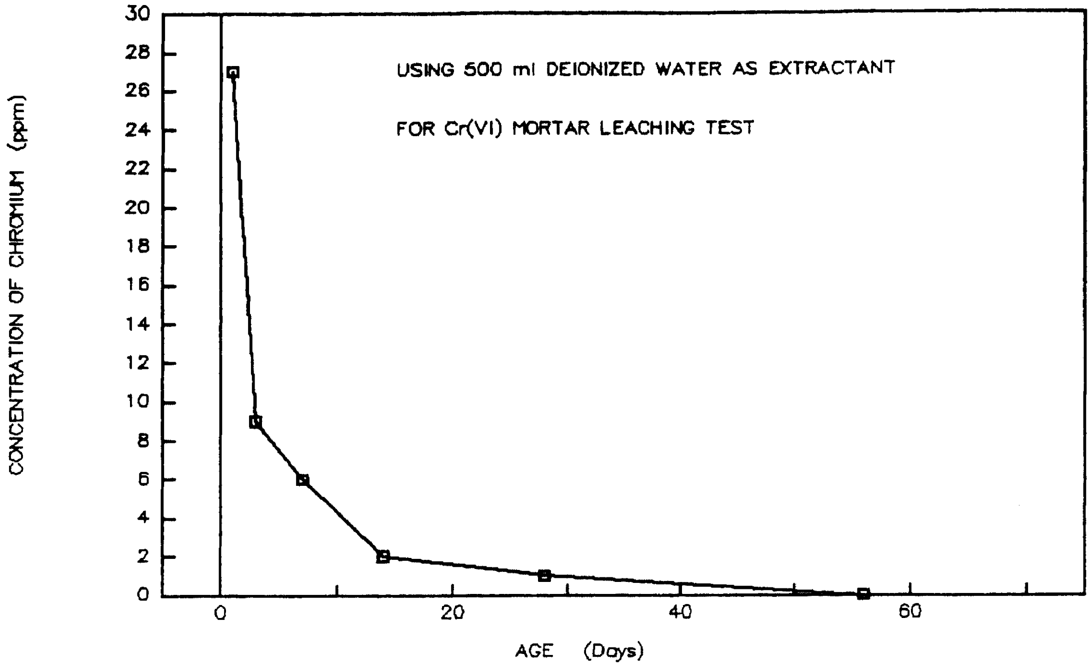

Fig. 3.19 Relationship between chromium concentration in leachates and ages

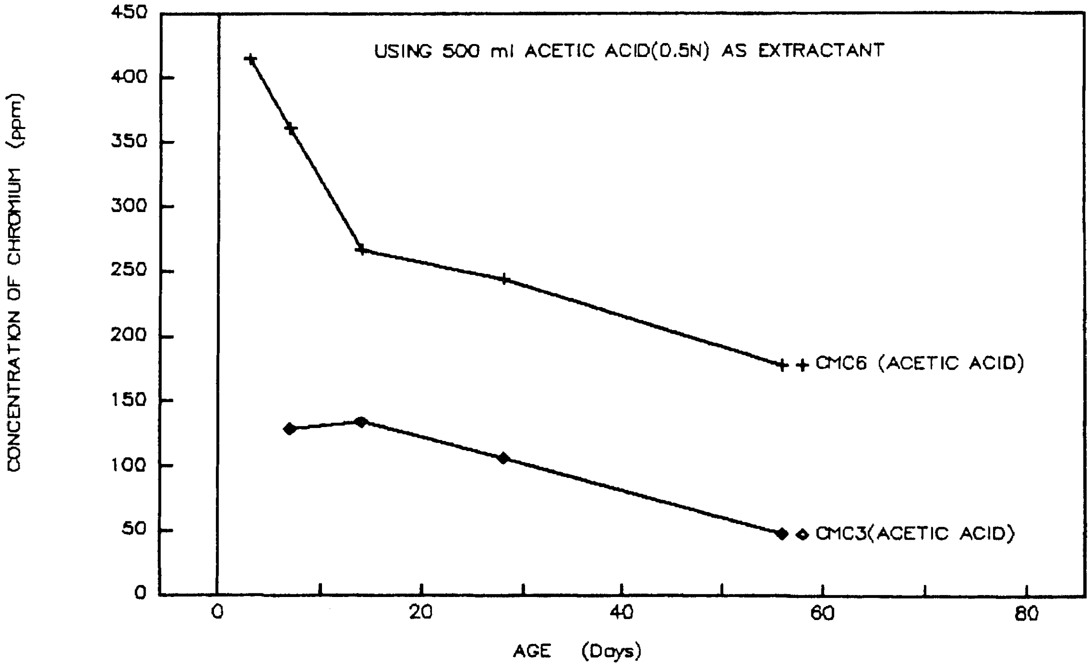

Fig. 3.20 Relationship between chromium concentration in leachates and ages

3.4 Influence of Chromium on Compressive Strength of Mortar and Conctete

In the presence of lime most heavy metals will be combined to form colloidal metal hydroxides. The metal hydroxides become an intimate constituent of the cement matrix. The reaction is divided into two steps. The first is that cement reacts with water to form calcium-silicate-hydrate gel(C-S-H). Along with this gel formation comes the formation of various crystalline hydration products such as calcium hydroxide and various heavy metal hydroxides. In the second step, the C-S-H gel swells to the point where particle overlap occurs and silica fibrils develop. During the gel development, crystals of hydration by-products, which have a layered structure, have grown to their maximum size. They might be either overlapped by fibrils or have grown into the particle gel themselves. If there is room which is suitable for crystal growth, the interlocking of the fibrils and the formation of various hydration products bind the cement and other component of the mixture into a rigid mass. It is evident from the results of the tests that the compressive strengths of Cr(III) mortar and concrete are higher than for conventional mortar and concrete. This is because chromium hydroxide crystals have formed in such a way that it tends to lock the concrete paste together in a tighter way than before.

Tests indicated that this amount of chromium(III) in mortar and concrete (5% by weight of cement) has a positive effect on the compressive strength up to 180 days of age. Attention should be given to the fact that the strength gains of the Cr(III) mortar and concrete are small after 28 days. The experimental data [8] revealed that the compressive strength of Cr(III), cement and soil mixtures decreased when Cr(III) content increased from 2% by weight of cement to 6% by weight of cement.

The results of the tests show that the effect of chromium (VI) in mortar and concrete on the strength is very different from those of chromium(III). The strengths of chromium(VI) mortar and concrete are much lower than the conventional mortar and concrete.

The reason may be that if the heavy metal hydroxide crystals grow too big, it swells the C-S-H gel structure and destroys or looses the structure of the C-S-H gel. That is, the crystallization of salts from supersaturated solutions produces pressures which may cause cracking in the concrete thereby reducing the concrete strength. Also, because Cr(VI) in cement mixture may form CaCr O_2 ,7 Cr(VI) is leached from cement mixtures readily and results in a decrease in strength of the cement matrix. The strengths decreased. Laboratory tests indicate that chromium migrates into the pores filled by capillary action over a period of time and causes swelling to occur, resulting in damage to slabs, parking lots, and other structures [39]. Part of the reason is that the degree of hydration of chromium phases in mortar is low as compared to conventional mortar as indicated by the amount of unhydrated calcium silicate grains in the former group. It has been reported that the presence of heavy metals tends to retard hydration of the calcium silicates [9].

3.5 Influence of Cr(III) and Cr(VI) on the Leaching Results

Leaching tests using deionized water as an extractant on cement mixtures containing Cr(III) show that cement is very good for immobilizing Cr(III) as a result of the formation of $Cr(OH)_3$. Because chromium hydroxides are quite insoluble under field conditions, unless the pH is extremely low. However, Cr(VI), on the contrary, readily leached from the cement matrix. The release of the Cr(VI) is similar to the release of Ca^{2+} and may be related to the formation of $CaCr_2O_7$ within the cement mixture.

It is evident from the results of the test that both trivalent and hexavalent chromium leached more readily in low pH extractant (in acetic acid, 0.5 N). And, it is also evident that chromium leached from Cr(VI) mortar at a relatively high concentrations.

The reason is that the hydroxyl ions from calcium hydroxide combine with heavy metals to form complexes, the pH, and therefore the concentration of hydroxyl ions, has a significant effect on the stability of the heavy metal. In the absence of calcium hydroxide, the pH of the system would be even lower, perhaps affecting the solubility of the heavy metals in a manner unlike a system containing calcium hydroxide. The research verified that the calcium hydroxide in heavy metal(including chromium) cement mixtures is lower than that of conventional mortar [9].

3.6 Experomental Results of Test Series 3

In Test Series 3, the soluble chromium concentration were determined for both Hudson fly ashes and Mercer fly ashes by soaking in the tap water. The results of tests are given in Appendix D.

The absence of soluble chromium in all Hudson fly ashes was observed. However, a significant amount of soluble chromium was found in Mercer fly ashes. The highest concentration of chromium is 21.75ppm or 2262 mg/Kg. The chromium concentration varied with the different particle size of Mercer fly ashes. Instead of having the usually gray color of fly ash, Mercer fly ash has an orangish color. Fig. 3.21 and Fig. 3.22 show the relationship between chromium concentration and different particle size. The result of test shows that the heavy metal chromium is more concentrated in the small particles than among larger particles. Enrichment of trace metals in the finer particles has been also reported by a number of investigators [42].

In terms of glass inhomogeneity, it has been suggested that as the fly ash particle cools from a droplet of an homogeneous aluminosilicate melt, trace elements (e.g. As, Be, Cd, Cr, Mn, Ni, Pb, Sb, Se, Tl, V and Zn) may migrate to the surface from within the molten particle to decrease surface free-energy by an increase in chemical potential of solute. This would lead to a concentration gradient across the diameter of the particle with "impurities" enriched in the outer regions. This phenomena has also been associated with an energy barrier to inter-particle coalescence as a rationale for the greater enrichment of trace elements in the smaller particles [48].

Fig. 3.22 shows that the effect of 0-10 micron particles content on chromium concentration. It is evident from the result that the chromium is mainly concentrated on the 0-10 micron Mercer fly ash particles. Attention should be given to the fact that the chromium concentration of original Mercer fly ash (6.56 ppm) is also higher than the EPA leaching test standard of 5ppm. This small amount of chromium may contribute to the variation of the concrete strength.

It should be noted that the general chemical composition analyses often do not pay much attention to these key trace elements.

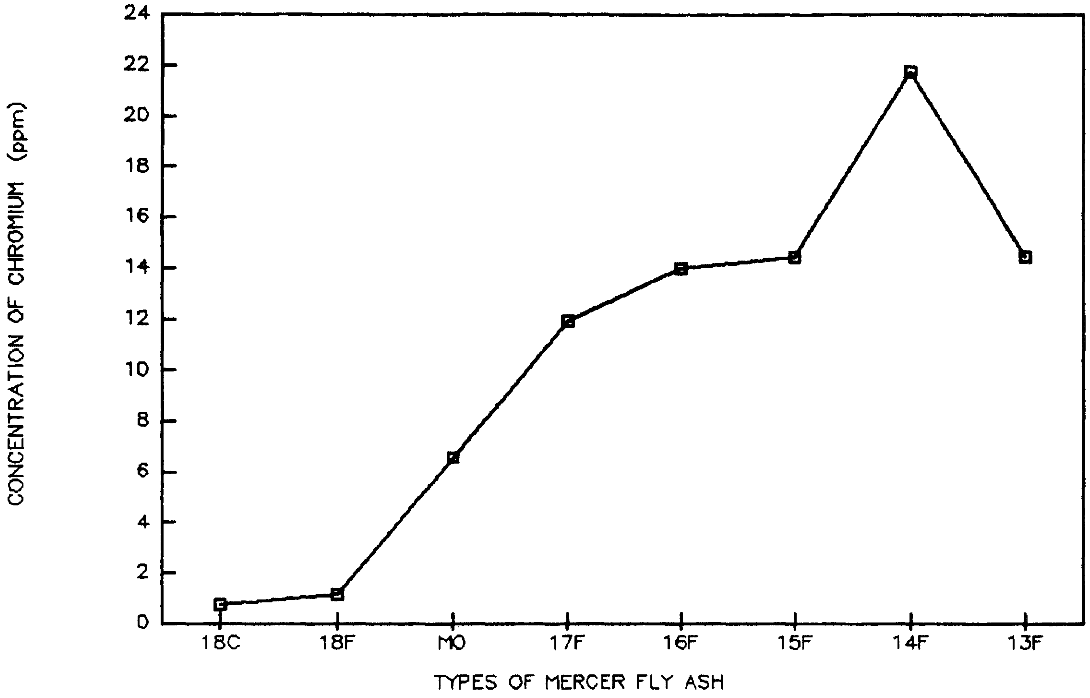

Fig. 3.21 Determination of chromium concentration of Mercer fly ash

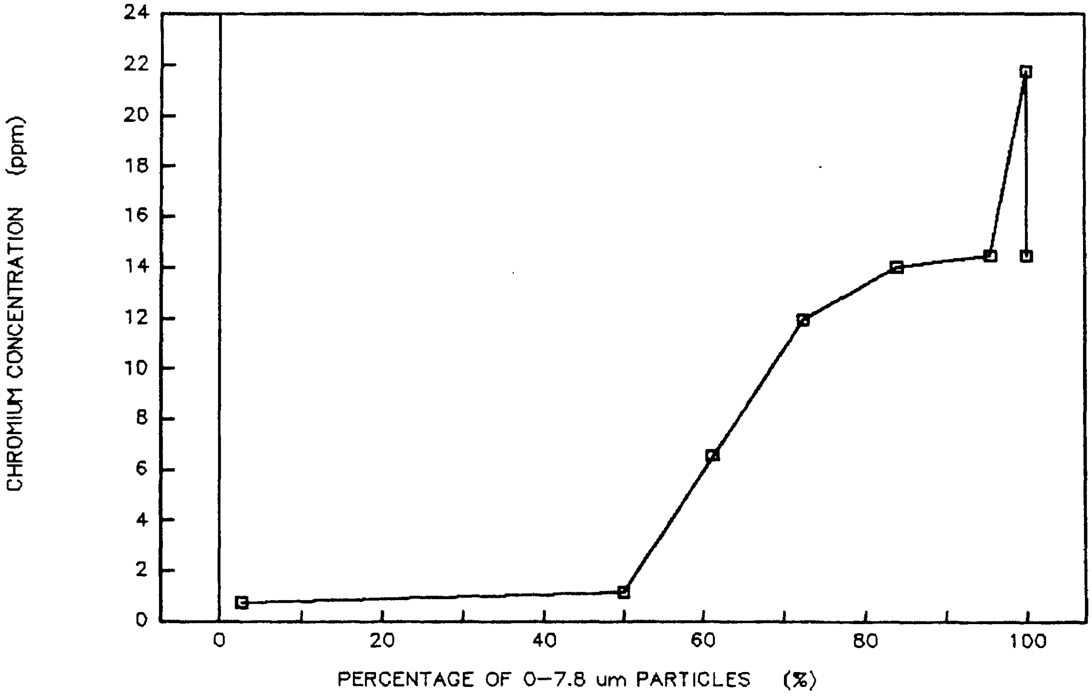

Fig. 3.22 Effect of 0-10 micron fly ash particles content on chromium concentration.

CHAPTER 4

CONCLUSION

The results of the experiments conducted in this study lead to the following conclusions.

The chemical compositions and chemical contents do not show any significant difference among different particle size of same kind of fly ash except that Mercer fly ash contains trace amount of chromium. Specific gravity of fly ash of different particle size and from different sources has slight variation. The finer the particle size, the larger is the specific gravity of fly ash.

CaO content varying from 2.47% to 6.76% has no notable effect on the mortar strength. The reason may be that the CaO content presents in the fly ash is still far below the range of CaO content needed.

Fe_2O_3 content of fly ash is not found to have a notable effect on the mortar strength. This is because Fe_2O_3in the fly ash does not react with $Ca(OH)_2$ directly.

It is quite evident from the results of the tests conducted that there is a direct relationship between particle size and its distribution and the compressive strength development of fly ash mortar.

The effect of particle size range of fly ash from 0-5.5 um, 0-7.8 um, 0-11 um, 0-22 um, 0-31 um, 0-44 um to 0-88 um on the compressive strength of fly ash concrete were studied. It is found that the finer the particle size of fly ash incorporated into mortar, the higher the compressive strength of the cement matrix.

Unlike past research, which indicated that the compressive strength of fly ash mortar at early ages (up to 28) is lower than conventional mortar, fly ash mortars that use the finest particle size range, 0 to 5.5 um, exhibited a notable increase in compressive strength even at an early (14 days) age. The causes may be: (1) the finer particles contain a higher glass content; (2) the finer particles are generally spherical in shape, which improves workability of mortars, and permit large water reductions in mortar or in concrete mixes; and (3) the specific surface area of 0-5.5 um fly ash is very large, and is about twice that of cement type I. The finest particles fly ash mortars, however, have very little strength gain beyond 28 days.

Fly ash particles larger than 45 micron contribute little to the compressive strength of mortar and concrete.

The mean diameter, D_{50}, is an important index expressing particle size distribution. The strength development of the fly ash mortar changes with the change of mean diameter D_{50} of fly ash particles. The smaller the D_{50} of the fly ash, the higher the compressive strength. This relationship is obvious for long-term strength (after 14 days). Additionally, there is a relationship between the mean diameter and the Blaine fineness. The smaller the D_{50}, the larger the Blaine fineness.

It is evident from the results of the tests that there is direct relationship between Blaine fineness and the compressive strength. The larger the fineness, the higher the strength. In particular, very large Blaine fineness of fly ash results in a fast hydration rate and induces high strength at an early age.

The leaching characteristic of Cr(III) mortar and Cr(VI) are very different. They have different behaviors with changes in pH and type of extractants.

With deionized water as an extractant, no chromium leached from Cr(III) mortar specimens. But chromium was clearly leached from Cr(VI) mortar specimens and the leaching amount of chromium decreased with the age of the specimens.

When acetic acid(0.5N) was used as an extractant, both Cr(III) mortar and Cr(VI) mortar have a great deal of leaching. The chromium leached from Cr(VI) mortar at a relatively high concentration and with a maximum concentration of chromium up to 420ppm.

The effect of chromium(III) and chromium(VI) on mortar and concrete strength is quite different. The strength of Cr(VI) mortar and concrete is lower than that of the conventional mortar while the strength of Cr(III) mortar and concrete is higher.

Because chromium hydroxides are quite insoluble under field conditions, the cement mixtures containing Cr(III) show that cement is very good for immobilizing Cr(III) as a result of formation of $Cr(OH)_3$ unless the pH is extremely low. However, Cr(VI) readily leached from the cement mortar. The release of the Cr(VI) may be related to the formation of $CaCr_2O_7$ within the cement mixture.

It is suggested that future research is needed to identify different mechanisms involving Cr(III) and Cr(VI) in cement hydration through micro-structural analyses of cement mortar.

It is interesting to find that there is soluble chromium in Mercer fly ashes. The chromium is more concentrated in the small particles, i.e. those in the 0-10 micron range.

APPENDIX A

PROPERTIES OF MATERIALS

Table A.1 Chemical Composition of Hudson Fly Ashes

Parameter	Composition in Percentage			
	3F	5F	6F	7F
Loss on Ignition	4.97	4.10	3.12	2.56
Moisture	0.22	0.13	0.15	0.25
Sulfur Trioxide	1.69	1.53	1.09	0.86
Silicon Dioxide	49.89	50.27	51.40	51.95
Aluminum Oxide	26.94	26.74	26.54	26.27
Iron Oxide	5.43	5.30	4.91	4.63
Calcium Oxide	2.99	2.95	2.72	2.51
Potassium Oxide	1.76	1.74	1.71	1.67
Phosphorous Anhydride	0.60	0.55	0.37	0.25
Magnesium Oxide	0.99	0.93	0.74	0.63
Barium Oxide	0.17	0.16	0.14	0.12
Sodium Oxide	0.33	0.33	0.31	0.30
Manganese Oxide	0.04	0.04	0.03	0.03
Titanium Dioxide	1.91	1.88	1.76	1.68
Strontium Oxide	0.20	0.20	0.19	0.17

Table A.1 Continue

Parameter	Composition in Percentage			
	10F	11F	1C	HO
Loss on Ignition	2.52	2.04	1.46	2.75
Moisture	0.20	0.10	0.10	0.02
Sulfur Trioxide	0.72	0.53	0.39	0.98
Silicon Dioxide	51.98	51.27	53.01	52.25
Aluminum Oxide	26.23	26.28	26.50	26.72
Iron Oxide	4.44	4.42	5.66	5.43
Calcium Oxide	2.28	2.02	1.90	2.41
Potassium Oxide	1.60	1.55	1.61	1.67
Phosphorous Anhydride	0.17	0.11	0.05	0.28
Magnesium Oxide	0.54	0.49	0.56	0.69
Barium Oxide	0.12	0.10	0.09	0.11
Sodium Oxide	0.29	0.26	0.24	0.28
Manganese Oxide	0.02	0.02	0.03	0.03
Titanium Dioxide	1.60	1.54	1.42	1.62
Strontium Oxide	0.16	0.14	0.11	0.15

Table A.2 Chemical Composition of Mercer Fly ashes

Parameter	Composition in Percentage			
	13F	14F	15F	16F
Loss on Ignition	2.67	1.94	1.88	2.06
Moisture	0.18	0.09	0.21	0.15
Sulfur Trioxide	3.81	3.47	3.33	3.05
Silicon Dioxide	38.93	39.72	40.25	40.65
Aluminum Oxide	24.91	25.08	25.02	24.92
Iron Oxide	12.89	13.02	13.12	13.26
Calcium Oxide	6.85	6.71	6.60	6.55
Potassium Oxide	2.10	2.11	2.11	2.09
Phosphorous Anhydride	0.07	0.04	0.01	<0.01
agnesium Oxide	1.55	1.50	1.47	1.41
Barium Oxide	0.61	0.55	0.51	0.44
Sodium Oxide	1.31	1.31	1.30	1.26
Manganese Oxide	0.05	0.04	0.04	0.04
Titanium Dioxide	1.57	1.51	1.44	1.36
Strontium Oxide	0.34	0.31	0.28	0.24

Tabble A.2 Continue

Parameter	Composition in Percentage			
	17F	18F	18C	MO
Loss on Ignition	2.30	1.94	2.55	2.05
Moisture	0.10	0.10	0.02	0.09
Sulfur Trioxide	3.01	2.94	2.40	3.13
Silicon Dioxide	40.89	41.56	43.25	41.54
Aluminum Oxide	24.81	24.47	23.31	24.74
Iron Oxide	13.56	14.21	17.19	14.83
Calcium Oxide	6.54	6.58	7.38	6.89
Potassium Oxide	2.06	2.01	2.00	2.07
Phosphorous Anhydride	<0.01	<0.01	<0.01	<0.01
Magnesium Oxide	1.40	1.40	1.30	1.43
Barium Oxide	0.41	0.35	0.23	0.40
Sodium Oxide	1.22	1.17	0.88	1.17
Manganese Oxide	0.04	0.04	0.04	0.04
Titanium Dioxide	1.34	1.29	1.21	1.36
Strontium Oxide	0.23	0.20	0.14	0.23

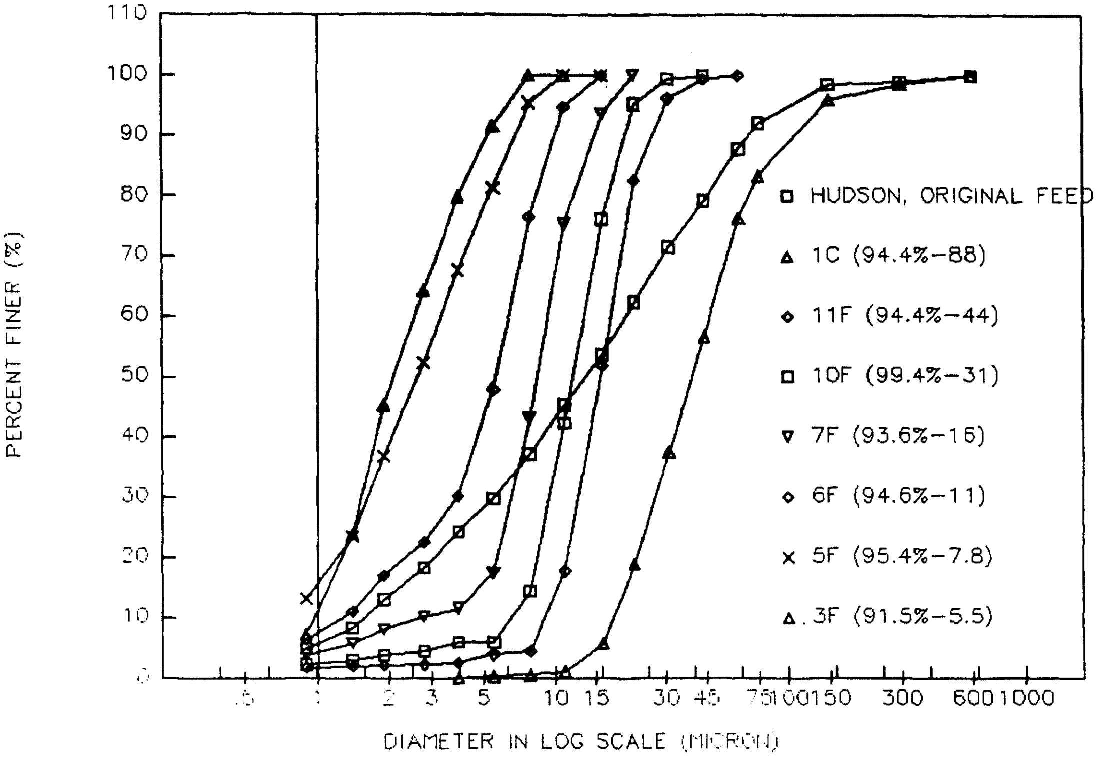

Fig. A.1 Particle Size Distribution of Hudson Fly Ash

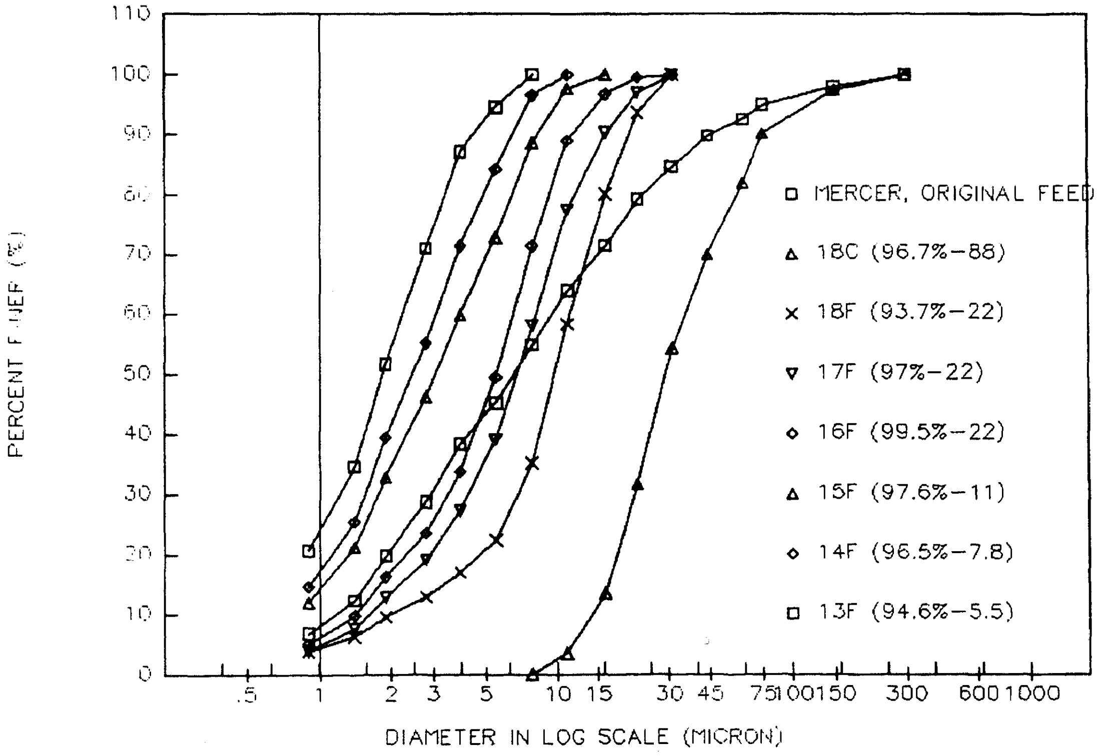

Fig. A.2 Particle Size Distribution of Mercer Fly Ash

APPENDIX B

EXPERIMENTAL RESULTS OF TESTS

Table B.1 Compressive Strength of Hudson Fly Ashes Mortar

Sample no.	Compressive Strength of Cube (psi.)							
	1day	3day	7day	14day	28day	56day	90day	180day
CMC	2850	5170	6233	6898	7763	7946	8032.5	8131
3F35	2088	4296	5163	6944	8949	9229	9740	9956
5F35	1634	3477	4600.8	5882	6872	8475	8772	9656
6F35	1620	3580	4355	5768	7374	8719	9146	9729
10F35	1458	3233	4257	5539	6661	7728	8174	8518
11F35	1358	2670	3835	4792	5931	6618	6767	7791
1C35	896	2213	3025	3470	3813	4467	4989	5243
HO35	117	3008	3961	5073	5850	6794	7729	8094

Table B.2 Compressive Strength of Mercer Fly Ashes Mortar

Sample no.	Compressive Strength of Cube (psi.)							
	1day	3day	7day	14day	28day	56day	90day	180day
CMC	2850	5170	6233	6898	7763	7946	8032.5	8131
13F35	2238	4241	5583	7165	8271	9566	9740	9898
14F35	1898	4175	4933	6611.7	7358	8763	9424	9884
15F35	1781	4018	482	6265	7228	8778	9163	9488
16F35	1701	3941	4648	6246	7078	8750	9151	9358
18F35	1597	3445	4095	5441	6180	7353	8042	8379
18C35	1674	3069	3694	4458	4932	5600	6080	6805
MO35	1918	3843	4953	5390	6668	7848	8284	8293

Table B.3 Compressive Strength of Fly Ash Mortar for Studying the Effect of CaO Content

Sample no.	Compressive Strength of Cube (psi.)						
	1-day	3-day	7-day	14-day	28-day	56-day	90-day
CMC	2850	5170	6233	6869	7763	7946	8032.5
HCA35	1355	2863	3827	4547	5479	6627	7060
MCA35	1597	3381	4517	5191	6097	7249	7613
5CA35	1520	3734	4912	5693	6874	8373	8675
14CA35	1701	4103	5208	5943	7503	8955	9075
6CA35	1222	3178	4155	5426	6546	7418	8014
16CA35	1255	3285	4422	5518	6743	7750	8201

Note: Replacement of Fly Ash 35% by Weight of Cement
CaO = 6.55%(16F, 6F) CaO=6.71% (5F,14F)
CaO=6.89% (original fly ash)
Water/(Cement+Fly Ash) Ratio = 0.5

Table B.4 Compressive Strength of Fly Ash Mortar for Studying the Effect of Fe_2O_3 Content

Sample no	Compressive Strength of Cube (psi.)						
	1-day	3-day	7-day	14-day	28-day	56-day	90-day
CMC	2850	5170	6233	6869	7763	7946	8032.5
6FE35	1454	3842	4568	5082	6348	7704	
16FE35	1680	4018	5303	5762	6767	8360	
5FE35	1684	3859	4800	5272	6380	7736.7	
14FE35	2062	4284	5393	5772	7133	8522	

Note: Replacement of Fly Ash 35% by Weight of Cement
Fe_2O_3 = 8.35%(16F, 6F) Fe_2O_3 =7.72% (5F,14F)
Water/(Cement+Fly Ash) Ratio = 0.5

Table B.5 Compressive Strength of Chromium Mortar and Concrete

Sample no.	Compressive Strength (psi.)							
	1day	3day	7day	14day	28day	56day	90day	180day
CHROMIUM MORTAR								
CMC	2850	5170	6233	6898	7763	7946	8032.5	8131
CMC3	3388	6445	7160	7298	7963	8843	8207	9848
CMC6	3044	4690	5369	5891	5895	6163	6349	8525
CHROMIUM CONCRETE								
CMY	1899		4575	5645	6076	6299	7056	8263
CMY3	2049	4917	6348	6112	6866	7389	8941	9221
CMY6	1308	2842	3671	4414	4573	4273	6078	6410

Note: Chromium (III) :$CrCl_3 .6H_2 O$
Chromium (VI) :$K_2 Cr_2 O_7$

Table B.6 Specific Gravity, Mean Particle Size and Blaine Fineness of Hudson and Mercer Fly Ash

Sample No.	Specific Gravity	Blaine Fineness (cm2/g)	Mean Particle Size D_{50} (um)
CEMENT	3.122	3815	
HUDSON FLY ASH			
3F	2.535	7844	2.126
5F	2.529	6919	2.698
6F	2.488	4478	5.736
10F	2.424	2028	8.498
11F	2.400	1744	15.476
1C	2.279	1079	38.566
ORIGINAL	2.343	3235	13.738
MERCER FLY ASH			
13F	2.748	11241	1.88
14F	2.729	9106	2.492
15F	2.641	7471	3.15
16F	2.609	5171	5.557
18F	2.512	3216	10
18C	2.416	1760	29.442
ORIGINAL	2.500	5017	6.723

Table B.7 Chromium Concentration of Mercer Fly Ash Soaking in Tap Water

Sample no.	Concentration of Chromium	
	(ppm)	(mg/Kg)
18C	0.764	79.456
18F	1.136	118.144
Original	6.56	682.24
17F	11.93	1240.74
16F	14.0	1456
15F	14.45	1473.9
14F	21.75	2262
13F	14.46	1503.84

APPENDIX C

GRAPHS DEVELOPED FROM THE EXPERIMENTAL RESULTS

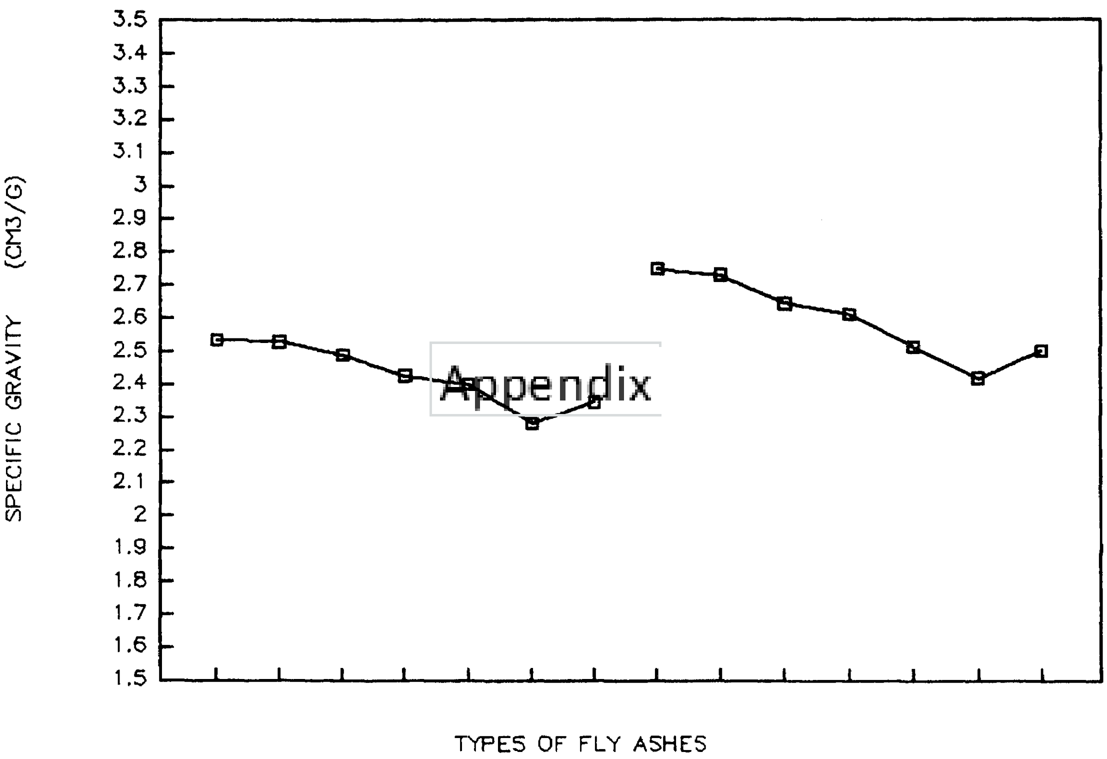

Fig. C.1 Specific Gravity of Hudson and Mercer Fly Ash

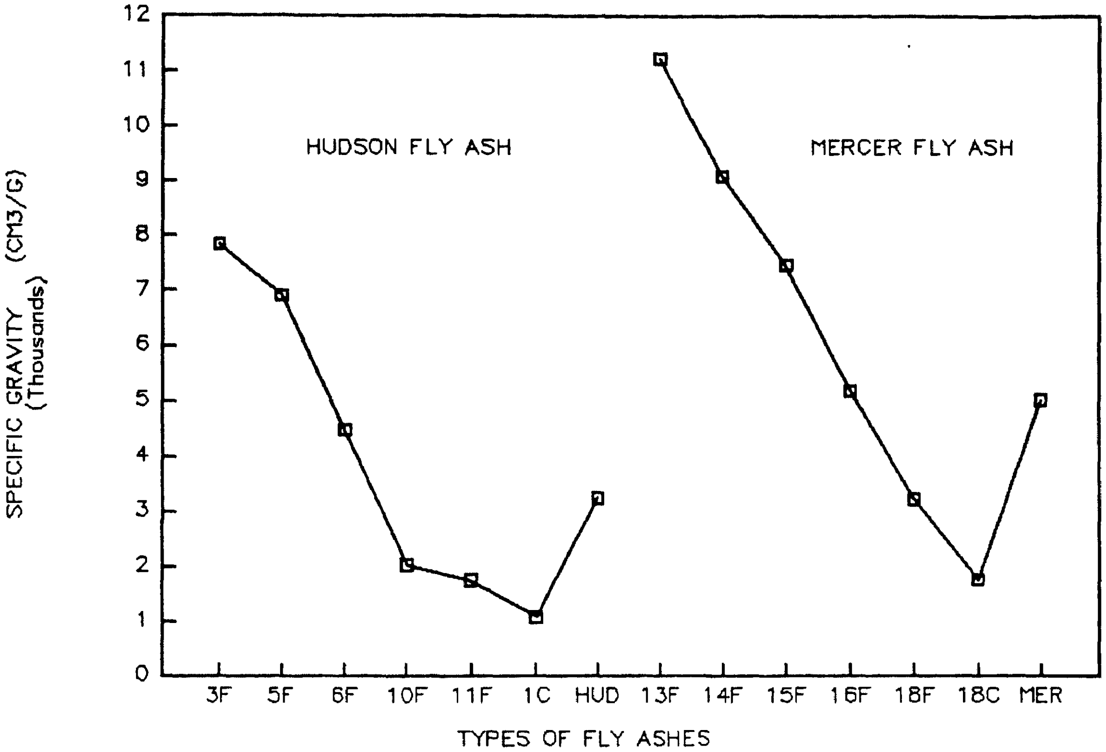

Fig. C.2 Blaine Fineness of Hudson and Mercer Fly Ash

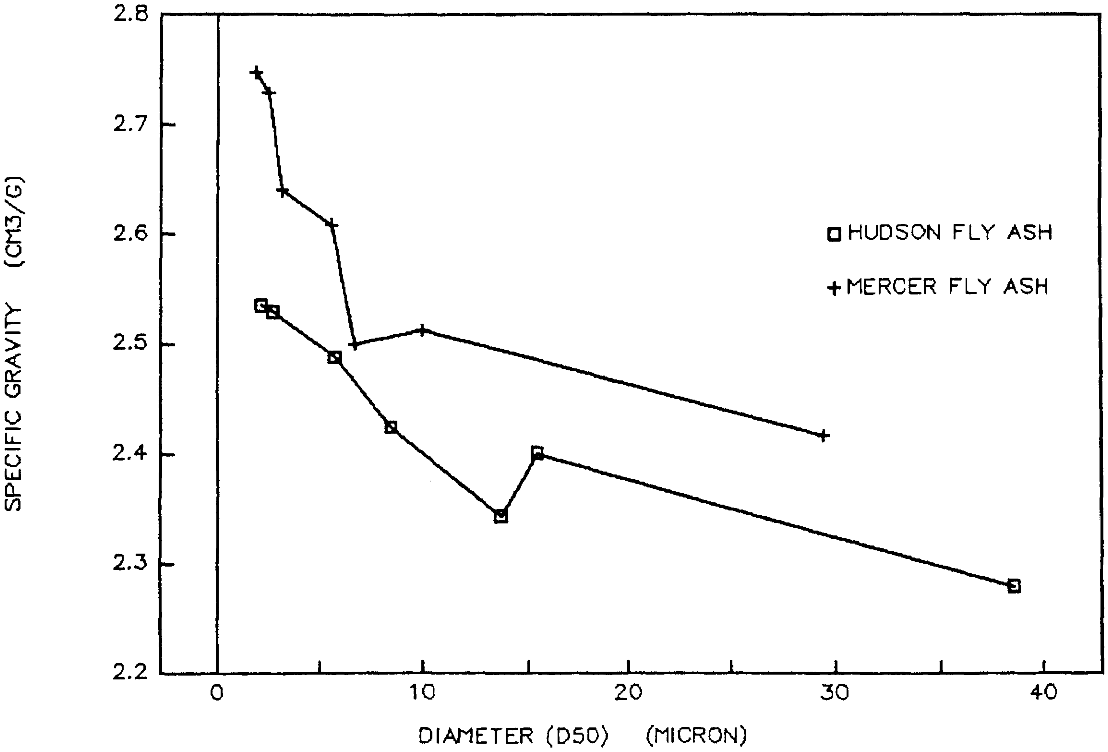

Fig. C.3 Relationship Between Specific Gravity and Mean Particle Size

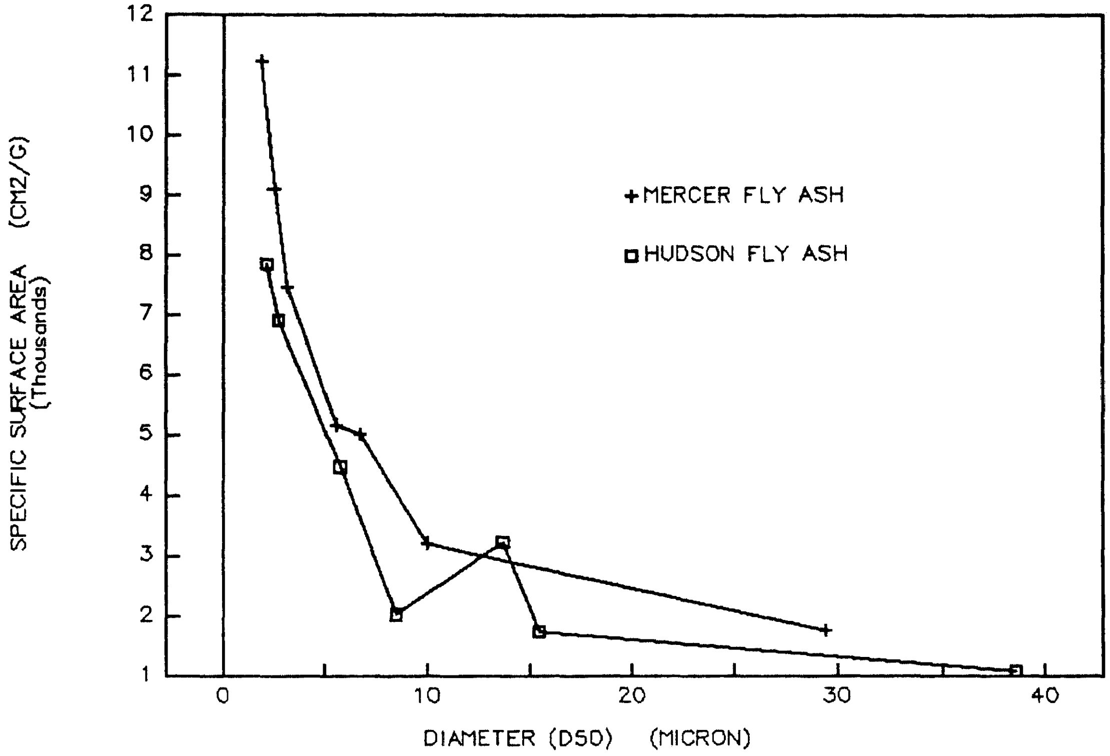

Fig. C.4 Relationship Between Blaine Fineness and Mean Particle Size

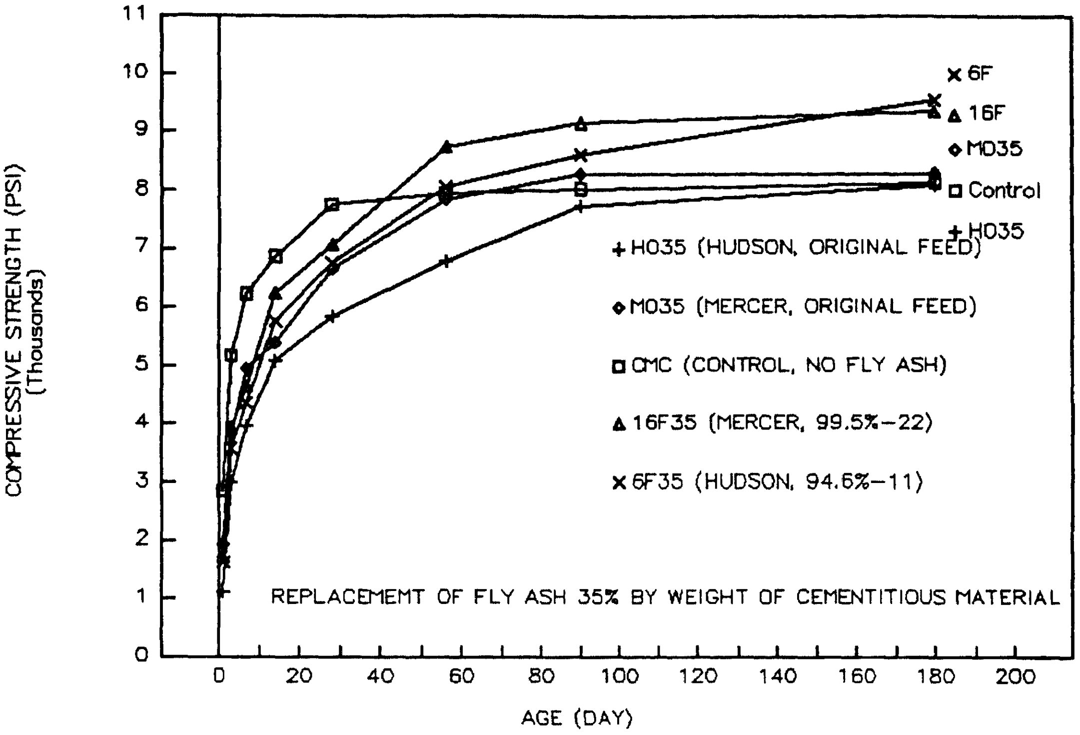

Fig. C.5 Compressive Strength of 6F35 and 16F35 Mortar

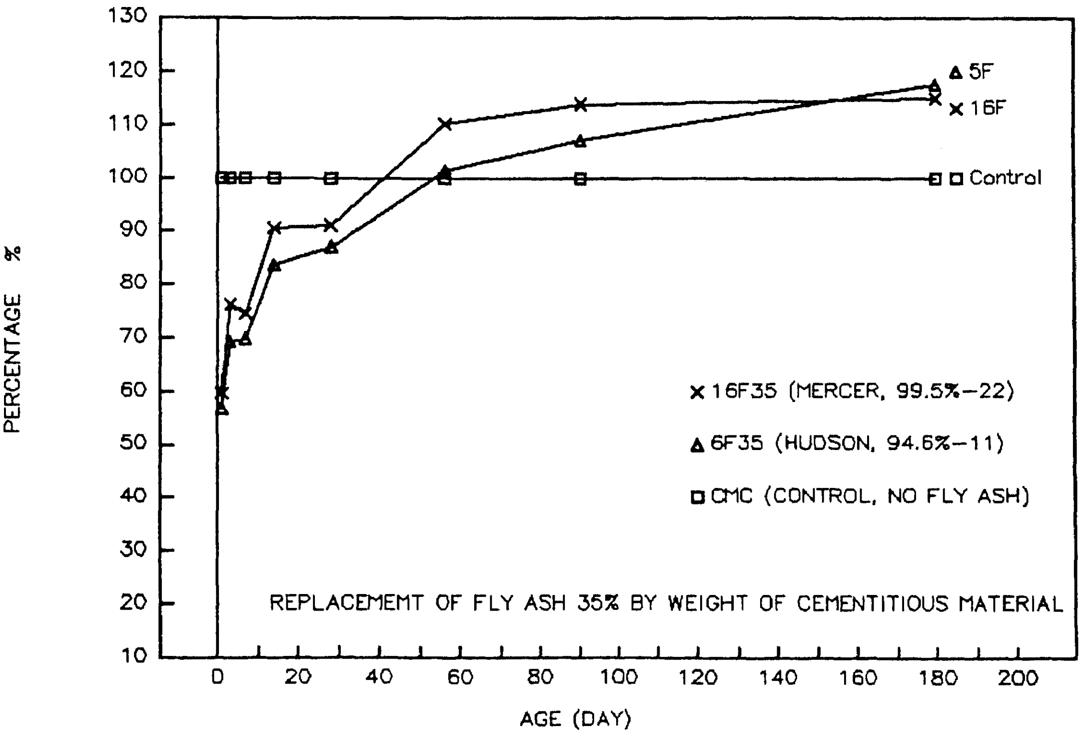

Fig. C.6 Compressive Strength of 6F35 and 16F35 Mortar as a Percentage of Control Test Strength

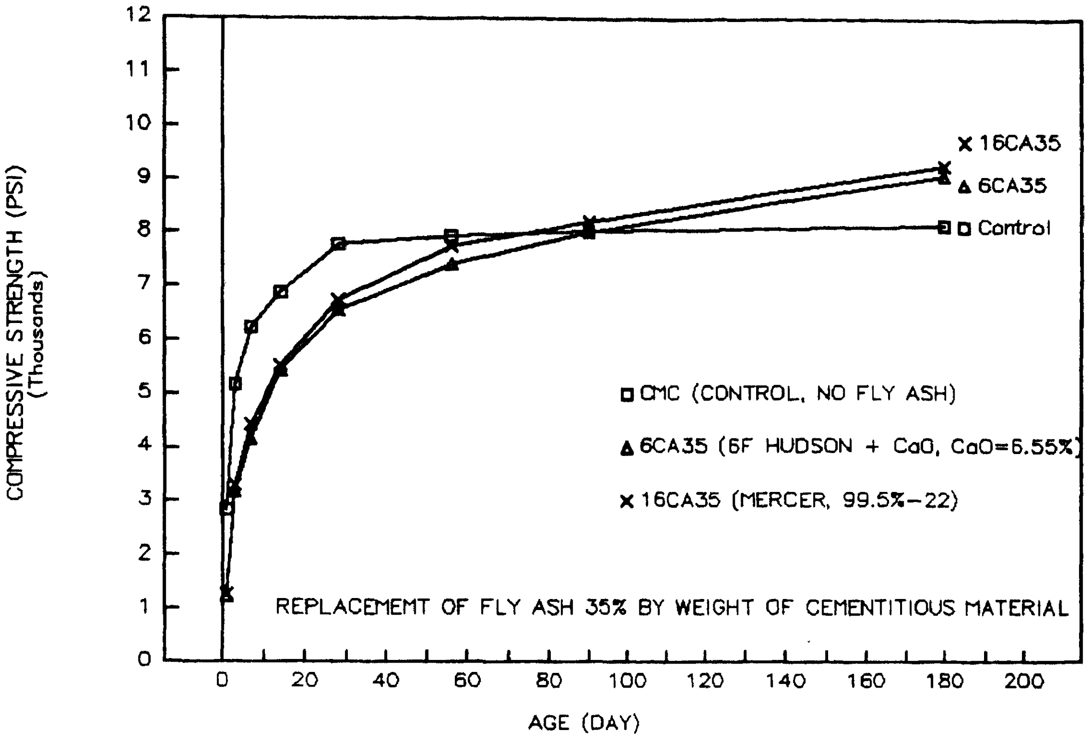

Fig. C.7 Compressive Strength of 6CA35 and 16CA35 Mortar

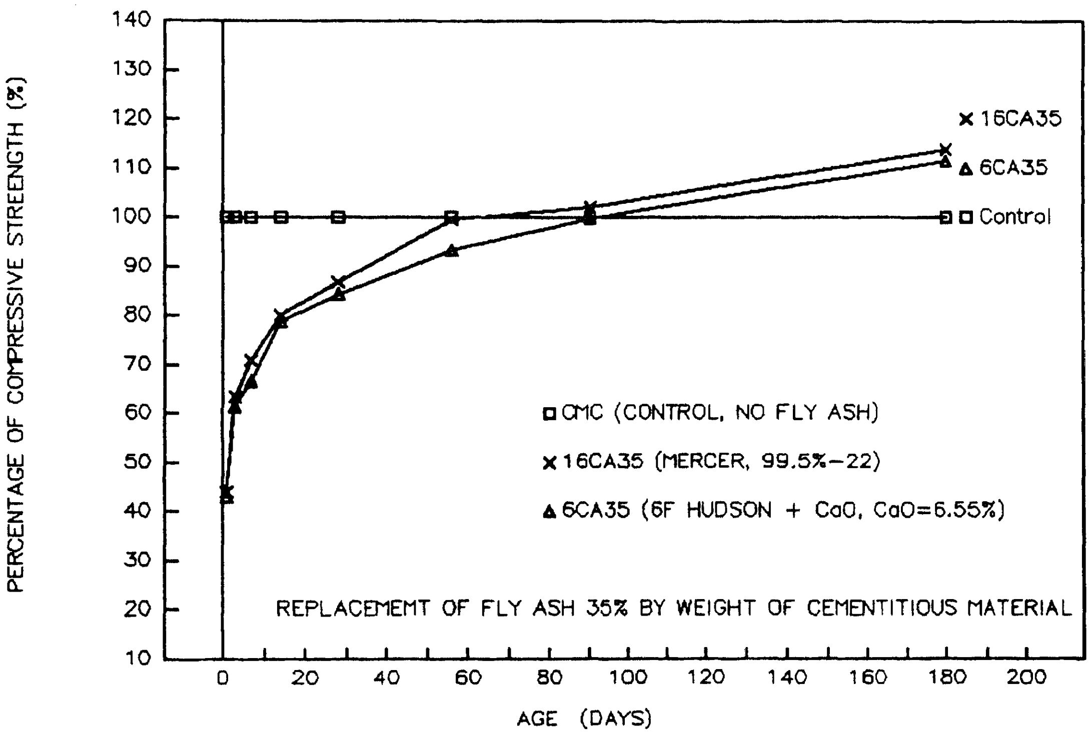

Fig. C.8 Compressive Strength of 6CA35 and 16CA35 Mortar as a Percentage of Control Test Strength

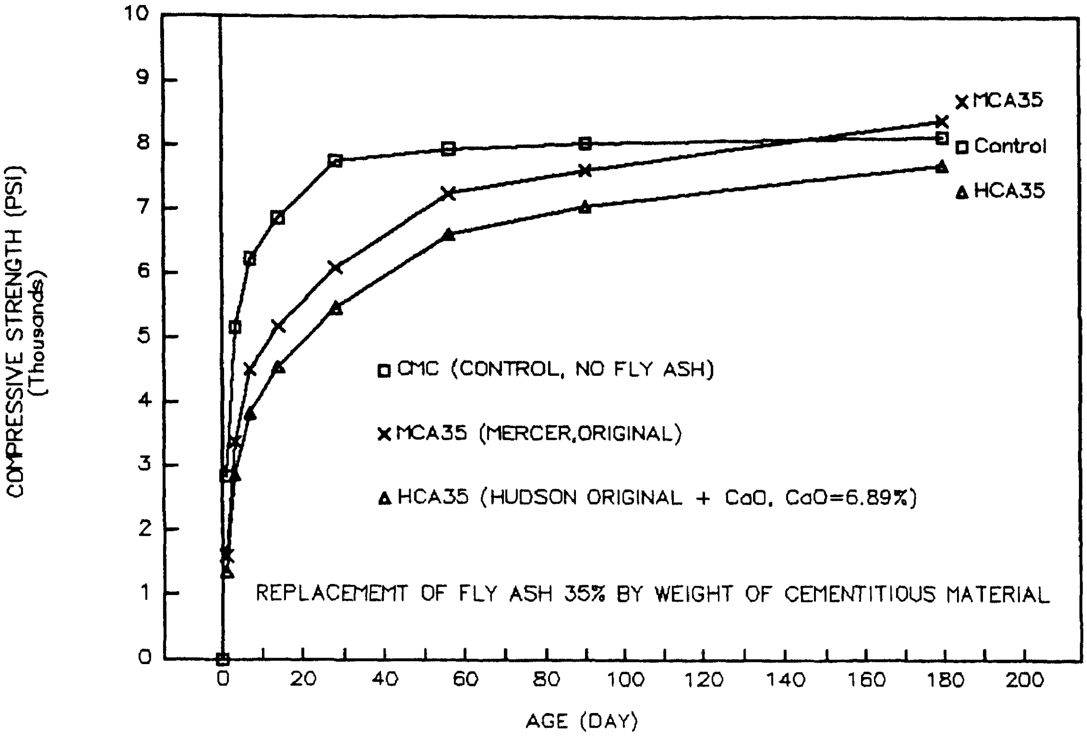

Fig. C.9 Compressive Strength of HCA35 and MCA35 Mortar

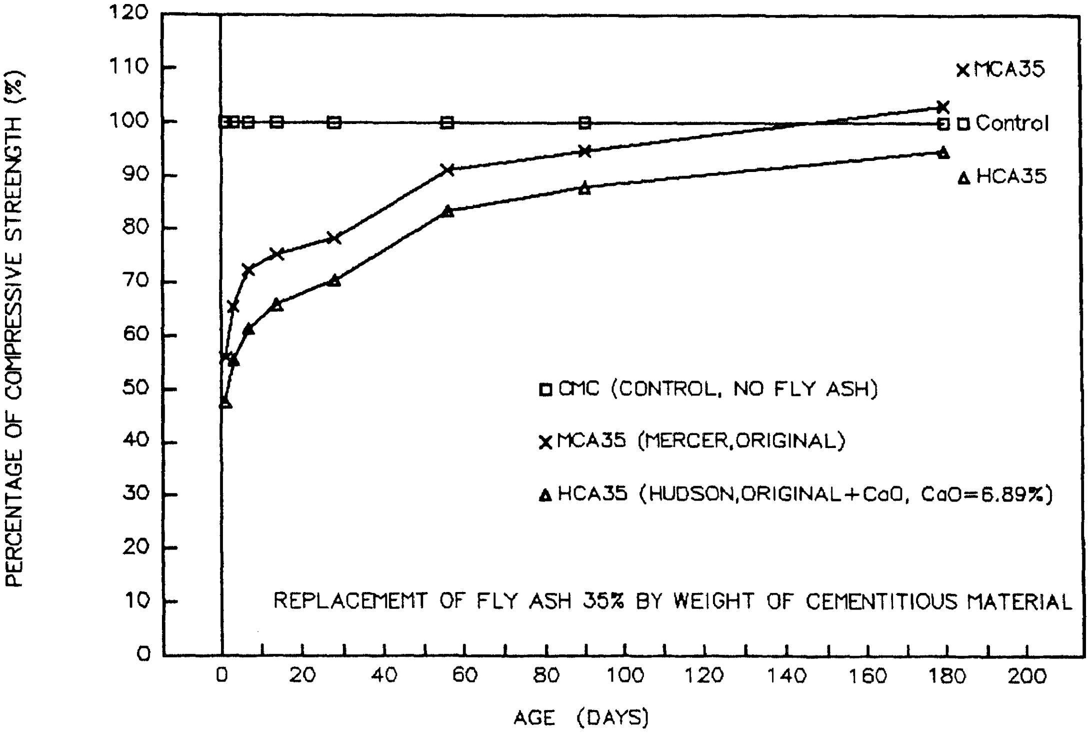

Fig. C.10 Compressive Strength of HCA35 and MCA35 Mortar as a Percentage of Control Test Strength

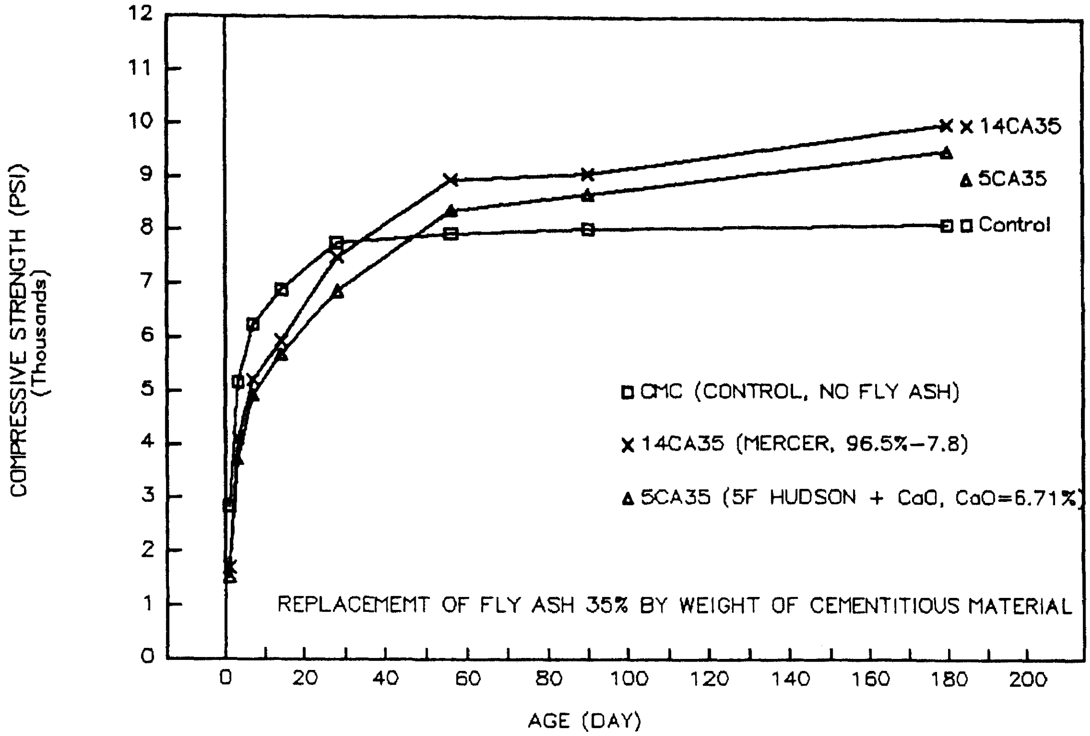

Fig. C.11 Compressive Strength of 5CA35 and 14CA35 Mortar

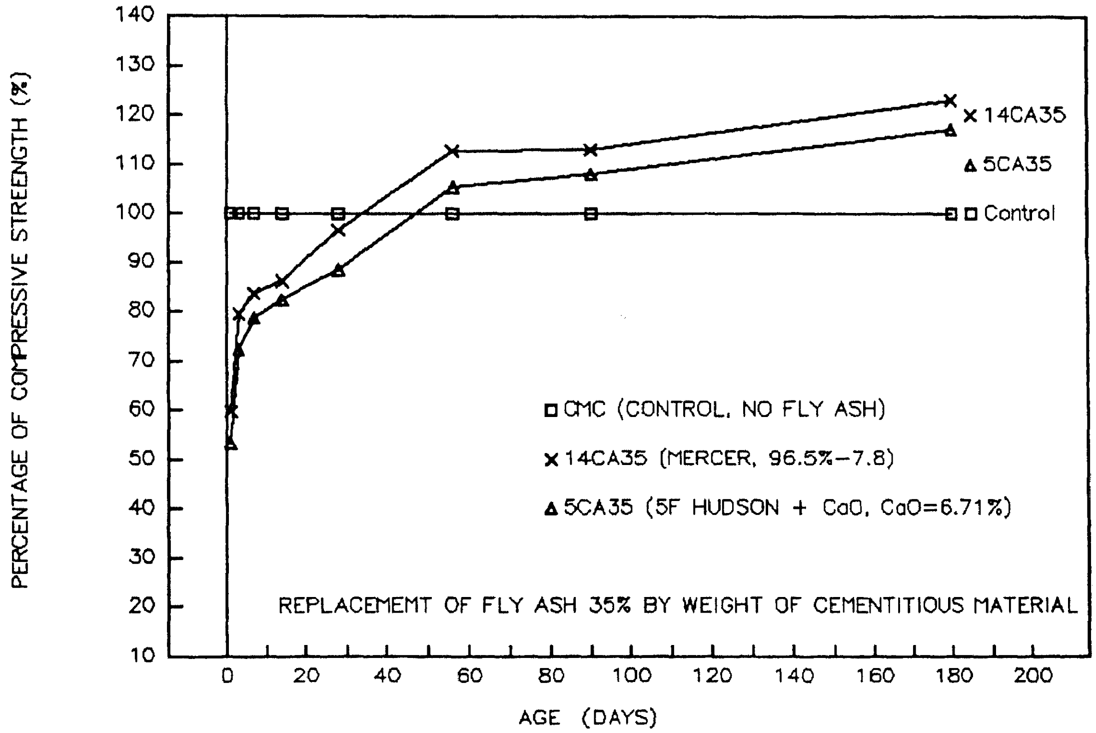

Fig. C.12 Compressive Strength of 5CA35 and 14CA35 Mortar as a Percentage of Control Test Strength

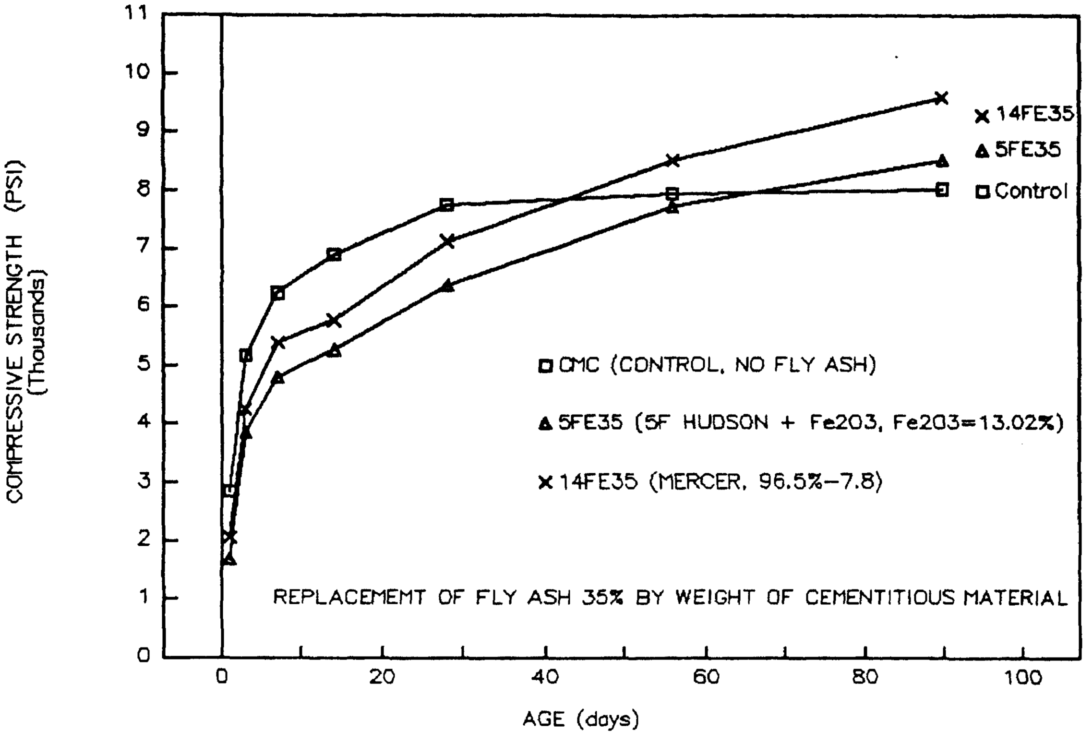

Fig. C.13 Compressive Strength of 5FE35 and 14FE35 Mortar

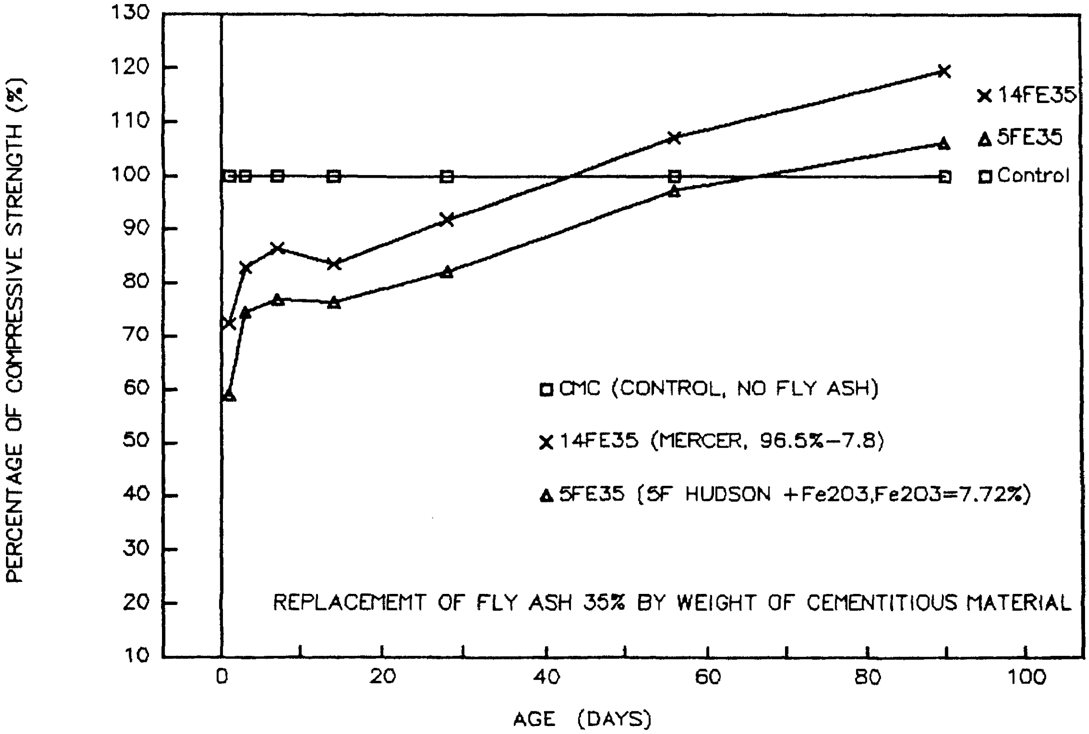

Fig. C.14 Compressive Strength of 5FE35 and 14FE35 Mortar as a Percentage of Control Test Strength

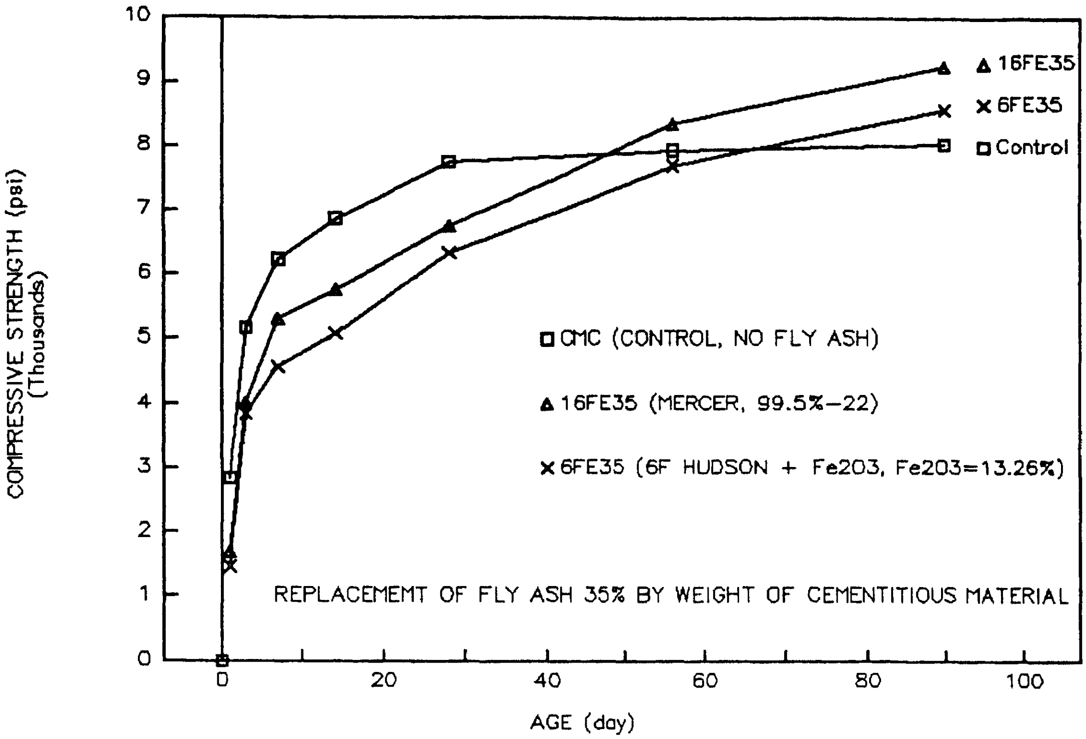

Fig. C.15 Compressive Strength of 6FE35 and 16FE35 Mortar

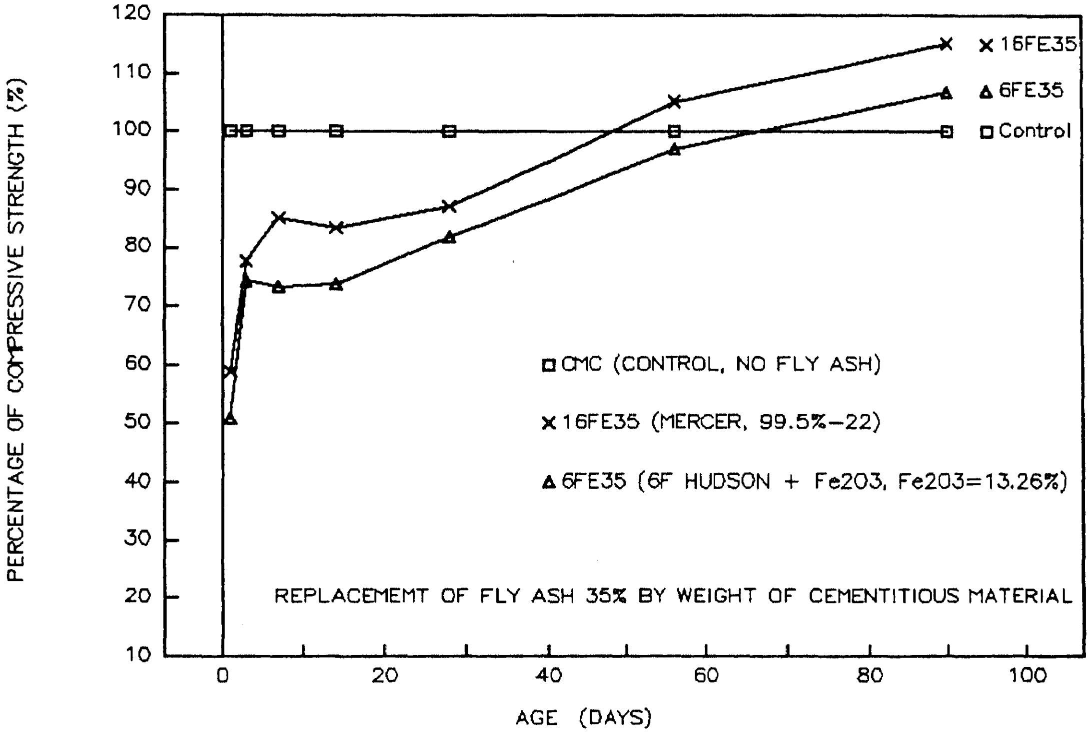

Fig. C.16 Compressive Strength of 6FE35 and 16FE35 Mortar as a Percentage of Control Test Strength

APPENDIX D

TEST PROCEDURE OF AAS

1. Turn on the exhaust fan and install chromium hollow cathode lamp.

2. Turn on instrument and adjust lamp current as necessary and adjust lamp position(back and forth) to set the ENERGY to the maximum reading on the green range.

3. Chosse and adjust the wavelength in order to let the ENERGY at the maximum reading on the green range.

4. Adjust the height of the flame in order to set the absorbance at zero when there is no samples to be aspirated.

5. Turn on the air and acetylene, check the fuel flow rate(usually about 4.5) and air flow rate(usually about 10). Ignite flame by pressing the PILOT button for 5-10 sec.

6. Adjust the fuel flow rate to get the yellow flame over the blue flame.

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