SUBSTITUTION OF A CEMENT SOURCE WITHIN A MIX DESIGN

FINAL REPORT

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EXECUTIVE SUMMARY

Scope

The purpose of this investigation was to study the effects of substituting a cement source within a mix design on the fresh and hardened concrete properties. Towards satisfying the above objective, all approved Florida Department of Transportation cement suppliers were contacted for material collection. Seven cements and their matching clinkers were collected from approved sources. A Class IV concrete mix design was selected and batched under hot weather conditions.

The as-received material was subjected to several characterization tests that include: mineralogical x-ray diffraction analysis, x-ray fluorescence for oxide chemical analysis, Blaine fineness and particle size distribution using laser analysis. In addition, clinker morphology was assessed through optical microscopy. In assessing fresh and hardened concrete properties, three mixes per cement were prepared using a Class IV concrete mix design. The same mix design proportioning was maintained constant for all the as-received cements, including constant air-entraining and water-reducer admixtures' dosages. Fresh properties that were measured in this study include: air content, initial and final set, slump and slump loss, unit weight and temperature. The hardened concrete properties that were assessed include: concrete compressive strength at 1, 3, 7, 14 and 28 days in addition to rapid chloride permeability. Sulfate durability was also examined in this study using mortar bars exposed to sulfate solution.

Results:

The findings in this study indicate that there was variation in fresh concrete properties under hot mixing conditions. The slump loss over a period of 90 minutes was reported between 1 and 2 inches for cements' mixes . In addition, variation in the initial set among Type II cements was as high as 84 minutes on varying cements sources. However, air content variation was not significant [less than 1%]. Variation in compressive strength was approximately 700 psi at 28 days among the cements examined

here. In addition, results from rapid chloride permeability tests indicate variation in the durability rating from moderate to high chloride permeability among the cements included in this study. For sulfate durability, variation in mortar expansion, for an exposure period of 480 days, was between 0.14% to 1% expansion for the Type II cements studied in this investigation.

Recommendations:

Since the findings of this study indicate that substitution of Type II cement in a concrete mixture affects its plastic and hardened properties, it is recommended that the laboratory or field trial batches be performed prior to permitting cement substitution in a mixture.

CHAPTER I
INTRODUCTION

OBJECTIVE:

The objective of this investigation is to study the material parameters in cements obtained from different sources that would affect fresh and hardened concrete properties. In addition to identifying those parameters and their impact on concrete durability, a third objective is to make recommendations based on the findings to whether the current FDOT standards need to be modified.

SCOPE:

Currently, FDOT standards do not allow substitution of a cement source within a mix design that contains the proposed cement, prior to reverification of the mix design. The current study presents data that can verify such a requirement in the current standards. Towards achieving this objective, the scope of work was divided into several stages. The first stage was focused on studying and characterizing the as-received materials. The properties studied here include:

1. Cement inorganic oxide content
2. Fineness and particle size distribution of cements
3. Mineralogical characterization of cement phases through chemical analysis and x-ray diffraction

In the second stage, a Class IV mix was used to prepare concrete mixes in order to assess the effect of variable cement source on the fresh and hardened concrete properties. Fresh properties that were examined in this study are: setting time, slump and slump loss and air content. Hardened concrete properties included strength and rapid chloride permeability tests. Concrete durability in sulfate environments was also addressed through monitoring mortar bar expansion.

Finally, data generated from the tests conducted on the as-received material and concrete and mortar mixes were analyzed and interpreted to identify the properties of cement that will affect fresh and hardened concrete properties.

Report:

The report documents the results of the tests, provide interpretation of results and recommendations as to what is needed to be done in order to ensure better concrete quality.

CHAPTER II

LITERATURE REVIEW

Portland cement clinker is made up of four main compounds: tricalcium silicate ($3CaO\ SiO_2$), dicalcium silicate ($2CaO\ SiO_2$), tricalcium aluminate ($3CaO\ Al_2O_3$), and a tetra-calcium aluminoferrite ($4CaO\ Al_2O_3Fe_2O_3$). In an abbreviated notation differing from the normal atomic symbols, these compounds are designated as C_3S, C_2S, C_3A, and C_4AF respectively, where C stands for CaO (lime), S for SiO_2, A for Al_2O_3, and F for Fe_2O_3. Small amounts of uncombined lime and magnesia also are present, along with alkalies and minor amounts of other elements. Portland cement is produced through grinding clinker with calcium sulfate. Calcium sulfate in Portland cements can exist in several forms; namely, anhydrite, hemihydrate and gypsum.

The most important hydraulic constituents are the calcium silicates, C_2S and C_3S. Upon mixing with water, the calcium silicates react with water molecules to form calcium silicate hydrate ($3CaO\ 2SiO_2\ 3H_2O$) and calcium hydroxide ($Ca[OH]_2$). These compounds are given the shorthand notations C-S-H (represented by the average formula $C_3S_2H_3$) and CH, and the hydration reaction can be crudely represented by the following reactions:

$$2C_3S + 6H = C_3S_2H_3 + 3CH$$

$$2C_2S + 4H = C_3S_2H_3 + CH$$

During the initial stage of hydration, the parent compounds dissolve, and the dissolution of their chemical bonds generates a significant amount of heat. Then, for reasons that are not fully understood, hydration ceases. This quiescent, or dormant, period is extremely important in the placement of concrete. Without a dormant period, there would be no reason for cement trucks; pouring would have to be done immediately upon mixing.

Following the dormant period (which can last several hours), the cement begins to harden, as CH and C-S-H are produced. This cementitious material (hydrated paste) binds concrete together. As hydration proceeds, water and cement are continuously consumed. Fortunately, the C-S-H and CH products occupy almost the same volume as the original cement and water; volume is approximately conserved, and shrinkage is manageable. Although the formulas above treat C-S-H as a specific stoichiometry, with the formula $C_3S_2H_3$, it does not at all form an ordered structure of uniform composition. C-S-H is actually an amorphous gel with a highly variable stoichiometry. The ratio of C to S, for example, can range from 1:1 to 2:1, depending on mix design and curing conditions.

The strength developed by portland cement depends on its composition, fineness, calcium silicates content and to a lesser extent tricalcium aluminate content. Tricalcium silicate (C_3S) is mainly responsible for the strength development in the early stages of hydration while the C_2S is responsible for the ultimate strength. The alumina and iron compounds that are present only in lesser amounts make little direct contribution to strength, but significant contributions to concrete durability. However, the contribution of tricalcium aluminate to 1 day strength has been documented.

The morphological properties of the four main components of clinker (C_3S, C_2S, C_3A, and C_4AF) have their significance. Clinker morphology reveals information on the compound reactivity. Clinker particle morphology is affected by the time and temperature of the clinkering process in addition to the cooling process. As fresh and hardened concrete properties depend on cement hydration they would inadvertently depend on the reactivity of cement phases.

In addition to the significance of cement properties on concrete properties, environmental factors, such as hot weather, affect concrete performance in the fresh and hardened state[1]. Since concrete properties are additionally related to the rate of hydration of cement, the speed of the latter rate depends upon reactivity, quantity, and morphology of cement compound composition, therefore making it undoubtedly important to elaborate on its components.

It has been proven that rate of hydration of cement is dependent of the chemical composition and particle size distribution of the cement, and on the temperature of concrete [2]. Focusing on type II cements, their relative low fineness has shown to provide little help to strength development at early ages [3]. Variation on the particle size distribution within the same type of cement is likely to be observed when changing cement source, and it is due to the different raw materials, clinkering and grinding processes adopted for each cement producer [4]. Moreover, it has been demonstrated that variability in time, temperature and kiln rotation when clinkering may retard or accelerate the chemical interaction of the materials, resulting in a change of phase distribution in clinker particles [3].

Tricalcium silicate (C_3S) particles surface morphology impact cement reactivity and therefore the setting time and early strength of concrete[5]. Moreover, variation of C_3S content may be related to the setting behavior of the mixture, and may be responsible for the rate of strength development at early ages. Likewise, when hot weather extended mixing procedures are applied to the mixture, hydration rate of cement is then accelerated –by increasing the reactivity of C_3S– reducing setting times and increases early strength.

Morphology of C_3S phases –defined as the size, shape, and texture of the compound– is of importance when analyzing the behavior of a concrete mixture. The most frequently occurring forms of C_3S are compact, prismatic crystals that often exhibit and hexagonal section. This shape is designated as idiomorphic (well-developed crystals). In addition, when the alite hexagonal shape is barely discernible, it is the named xenomorphic (without crystal faces). All possible variations, which occur between the two extremes idiomorphic and xenomorphic shapes of alite, are designated as hypidiomorphic (partly developed crystal outlines). Reactivity of C_3S depends upon its crystal faces and exposed surface area, therefore idiomorphic, small alite compounds represent its ideal morphology, yielding higher hydration rates.

Dicalcium silicate (C_2S) is responsible for the later-age strength of concrete; therefore, reduction of ultimate strength may be related to its content and reactivity [4]. C_2S hydrates much slower than C_3S, therefore liberating less heat when hydrating. When the morphology of C_2S is studied, it is possible to visualize factors for which variation in its hydration rate is taking place. Round crystal form is characteristic of belite –shorthand name for C_2S– but variation in its shape and internal structure may affect its reactivity, therefore diminishing its contribution to later-age strength gain. There are three possible transformations that belite particle can suffer through the process of clinkering. Moreover, these transformations take place during the genesis of clinker and often depend on temperature, time and cooling rate [6].

Calcium silicates in general –C_3S and C_2S– may transform into one another depending upon the process of clinkering, mixing temperatures, cooling rates applied, quenching, and silica and calcium oxide content. For alite in clinker, there is a certain range of temperature, when clinkering, in which the compound becomes unstable, transforming into belite and calcium oxide (the latter in the form of free lime) [6]. This decomposition starts at the surface of the primary alite particle, and in some cases, it does not proceed fully, creating uncertainty in the resulting reactivity and behavior of the particle. Decomposition of alite into belite affects reactivity and compound content, by reducing alite content, therefore having an impact on early strength of concrete. Now, for belite in clinker, transformation of belite into alite is most likely to be observed. Belite particles usually form first during clinkering –depending on CaO and SiO_2 content–, then alite particles grow from them and on the matrix surrounding the belite particle. These changes occur at certain temperatures and vary depending on the raw mix of the forming clinker. Like alite decomposition, sometimes belite does not decompose completely, forming small alite crystals around it, crystal whose reactivity and influence on cement hydration processes have not been fully understood to the date. Ideally, these small-sized alite crystals may increase initial hydration rates of cement following the surface area principle, but their reactivity might be dependent of factors other that just morphology [6].

Tricalcium aluminate (C_3A) is reported to be detrimental to the mixture for a variety of reasons. When in contact with water, cement sulfates ions and aluminates phases begin to react producing ettringite, which does not damage concrete while the mixture is at its plastic stage [3]. Moreover, lack of sulfate ions in the media promotes the production of monosulfoaluminates. After concrete stiffens, hydration reactions are still taking place within the mixture. In the case that monosulfoaluminates are formed early in the mixture, it may undergo secondary transformations into ettringite if a source of sulfate ions is provided. This transformation comes along with an increase in volume of the final element (ettringite), thereupon creating internal stresses in the concrete matrix, and possible further cracking on concrete. These secondary transformations are responsible for deficient durability characteristics of concrete. Moreover, this detrimental effect can be studied through the expansion of elements often made of cement mortars cured in sulfate solution, which accelerates the transformation processes [4,7,8].

Morphology of the aluminate facets (C_3A) is another important parameter to look at when analyzing its detrimental effect on concrete. Aluminates in clinker are frequently fine-grained, which represents more surfaces available for reactions at the plastic state of concrete, promoting early and therefore harmless ettringite formation. Moreover, it has been demonstrated that aluminates can incorporate alkalis in the lattice, due to partial substitution of *sodium* and *potassium*. The alkali aluminate in clinker exhibits an elongated tubular form, which represent a less reactive compound. This lack of reactivity may adversely affect concrete, given that more aluminate faces will be available for secondary transformations after concrete has hardened, bringing along detrimental expansion and cracking [6].

Since cement hydration involves chemical reactions, it is sensitive to temperature. During hydration of the calcium silicates, this temperature dependence is only effective when the reaction is chemically controlled (which determines initial set, final set and rate of early strength gain). Once the reaction becomes diffusion-controlled (which determines the rate of later strength gain) it is significantly less sensitive to temperature [4]. C_2S reactivity appears not to be considerably affected by high mixing temperature [9].

High mixing temperatures and extended mixing periods is found to accelerate the rate of slump loss. Since the mixture proportioning does not consider the loss of mixing water by reactions other than cement hydration, hot mixing involves a loss of moisture even in the most controlled mixing process. In conditions when slump is allowed to drop, so that the mix is not retempered, extended mixing periods are detrimental to the workability of the mixture. Furthermore, for extended mixing at temperatures above 90 F, the highest rate of slump loss has shown to be between 0 to 30 minutes (30 % - 40% loss), after which slump keeps dropping but in a slower rate (10 % - 20 % loss) [10, 11]. In addition, alite content and its morphology may influence the rate at which cement hydrates and therefore concrete workability, due to compound reactivity and its interaction with the hydration process.

Water required to achieve a certain slump increases dramatically with temperature; a 20°F increase in temperature correlates to approximately 1 inch of slump loss. However, it was observed that percent change in water content for one inch change in slump is 2 ½ % at 73°F while percent change in water content at 120°F was 4 ½ %, thus indicating an exponential increase of water requirement at higher temperatures. Mixes below 73°F showed low strengths at early ages. It was also concluded that increasing the initial and curing temperature results in considerably lower strengths at 3 months and 1 year. Strengths of concretes made with the three cement types used in this study were generally influenced in a like manner by temperature. Test results indicate that there is a temperature at the early age of concrete, which may be considered optimum with regard to strength at later ages. The optimum temperature was found to be dependent on cement composition.

The literature review indicated that fresh and hardened concrete properties are primarily affected by the cement phase reactivity and content. The nature of interaction is further complicated by hot mixing conditions. Increasing the mixing temperature may affect cement phases in different ways. The objective of the current investigation is to identify the parameters that would affect fresh and hardened concrete properties prepared from different sources of cement. In addition to identifying those parameters, the effect of those parameters on concrete durability needs to be addressed. The results and conclusions of this investigation will be presented in the next chapters.

CHAPTER III
EXPERIMENTAL RESULTS AND DISCUSSION

In order to assess the impact of cement substitution from different sources within a mix design, all of the approved and current FDOT suppliers for Type II cement were contacted. Seven cements with their matching clinkers were received. Characterization tests were run on the as-received material. In addition concrete mixes and mortar mixes were prepared in order to address the impact of variation in cement source on the properties of fresh and hardened concrete. The results will be presented in the following sections.

3.1 As-Received Material

3.1.1 Cements

3.1.1.1 Cement Chemistry

The seven as-received cements labeled A, B, LA, LJ, M, X and Y were tested for oxide chemical composition and compound content, so that variation of the latter among cements may aid to define the impact of variable cement source on the properties of fresh and hardened concrete. The chemical composition using x-ray fluorescence spectrometry and x-ray diffraction. In addition, cements' main compounds were calculated following the ASTM C 150-97 (Bogue calculation). The results are depicted in Table 3.1 through Table 3.3.

From the results depicted in Tables 3.1 and 3.2, it can be seen that all of the cements satisfy ASTM Type II classification. In addition, three of the as-received cements adhere to the AASHTO Type II cement classification; they are, A, B and X cements. In addition, it is observed that LA cement had the highest tricalcium silicate content while X cement has the highest tricalcium aluminate content of 8 % and a marginal SO_3 content of 3.09%. However, X-ray diffraction analysis reveals that all of the as-received cements can be classified as AASHTO Type II cements except LA and M cements. The discrepancy between the compound content as determined from Bogue calculations and x-ray diffraction is due to the fact that the Bogue compound calculation represents an approximation that does not take into account the presence of impurities in cements.

Due to the fact that the oxide chemical analysis does not identify the forms of calcium sulfate present in cements, x-ray diffraction was performed in order to identify the compound form of calcium sulfate present. The results presented in Table 3.4 show that in addition to the variation in the total calcium sulfate content in the cements examined here, there is also a variation in the calcium sulfate form. Though most of the cements have calcium sulfate predominately in the hemihydrate form, LA cement and X cement had significant anhydrite content. Actually most of the calcium sulfate in the X cement was in the anhydrite form. Different forms of calcium sulfates have different solubilities. The effect of the various forms of calcium sulfate is expected to affect fresh and hardened concrete properties as will be discussed later.

Table 3.1: **As-Received Cement Oxide Chemical Composition [X-Ray Fluorescence]**

	M Cement	**B Cement**	**A Cement**	**LA Cement**	**LJ Cement**	**X Cement**	**Y Cement**
Analite	**w/o**	**w/o**	**w/o**	**w/o**	**w/o**	**W/o**	**w/o**
SiO_2	20.69	22.17	20.11	19.98	20.01	20.69	20.68
Al_2O_3	4.78	4.36	4.83	4.72	4.83	5.15	4.6
Fe_2O_3	3.31	3.36	1.63	3.55	4.62	3.42	3.68
CaO	64.43	63.89	63.94	64.53	63.97	63.72	64.64
MgO	1.54	0.93	0.79	1.91	0.79	1.02	0.92
SO_3	2.9	2.47	2.81	2.91	2.82	3.09	2.59
Na_2O	0.12	0.11	0.08	<.02	0.08	<.02	0.07
K_2O	0.45	0.34	0.41	0.41	0.41	0.39	0.54
TiO_2	0.25	0.22	0.18	0.25	0.18	0.35	0.25
P_2O_5	0.13	0.09	0.58	0.03	0.58	0.09	0.16
Mn_2O_3	0.03	0.02	0.03	0.04	0.03	0.07	0.03
SrO_3	0.05	0.13	0.1	0.04	0.1	0.07	0.17
L.O.I. (950 C)	1.19	2.02	1.05	1.65	1.2	1.9	1.29
Total	**99.87**	**100.11**	**96.54**	**100.02**	**99.62**	**99.96**	**99.62**

Table 3.2: Cement Compound Composition [Bogue Calculation]

	Compound Composition (w/o)			
Cement	C_3S	C_2S	C_3A	C_4AF
M	60	14	7	10
B	50	26	6	10
A	53	22	6	10
LA	66	8	7	11
LJ	61	11	5	14
X	54	19	8	10
Y	62	12	6	11

Table 3.3: Tricalcium Silicate Content [XRD]

Cement	C_3S (w/o)
M	60
B	51
A	52
LA	63
LJ	56
X	51
Y	58

Table 3.4: Calcium Sulfate Phases' Content [XRD]

	Compound Composition (w/o)			
Cement	**Anhydrite**	**Hemihydrate**	**Gypsum**	**Total Calcium Sulfate Content**
M	0.0	3.9	0.8	4.7
B	0.0	2.0	2.5	4.5
A	0.0	4.2	0.2	4.4
LA	1.9	2.7	0.1	4.7
LJ	0.0	3.6	1.1	4.7
X	3.2	1.3	0.6	5.1
Y	0.0	3.1	0.5	3.5

3.1.1.2 Cement Fineness and Particle Size Distribution

Due to the significance of cement fineness and particle size distribution on concrete fresh and hardened properties, Blaine cement fineness and particle size distribution were performed on the as-received cements. The results are presented in Table 3.5 and Figures 3.1 through 3.7. The Blaine fineness test results, Table 3.4, indicate that A cement has the lowest fineness while M cement has the highest.

Table 3.5: **Cements Blaine Fineness [cm^2/g]]**

Cement	Fineness
M	4220
B	4010
A	3760
LA	4070
LJ	3920
X	3930
Y	3850

Particle size distribution analysis revealed that both X and Y cements have coarse reflect on the properties of fresh and hardened concrete particles present as large as 600 microns. Though A cement has the lowest Blaine among the cements examined here, its particle size distribution did not show the presence of such coarse particles. Higher cement fineness and finer particle size distribution is expected to reflect on the properties of fresh and hardened concrete.

Figure 3.1 : **Particle Size Distribution [Cement M]**

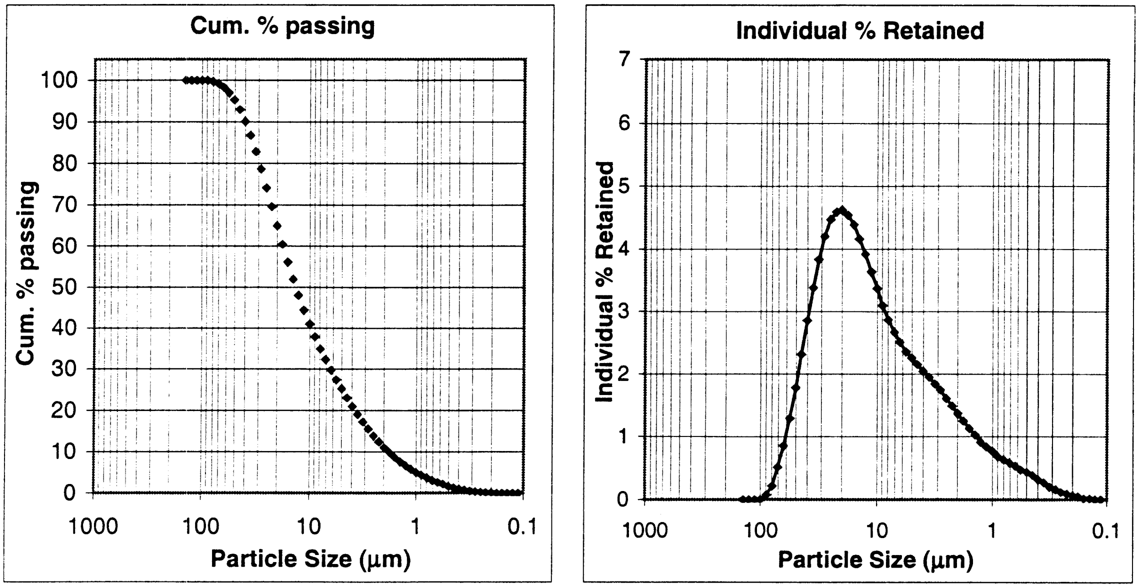


Figure 3.2 : **Particle Size Distribution [Cement B]**

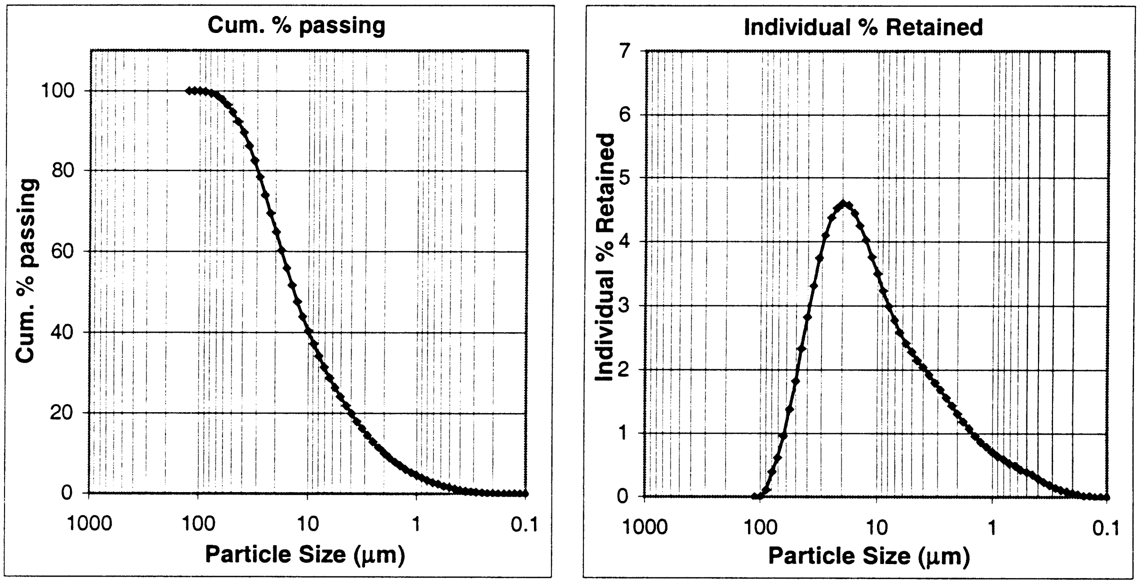


Figure 3.3 : **Particle Size Distribution [Cement A]**

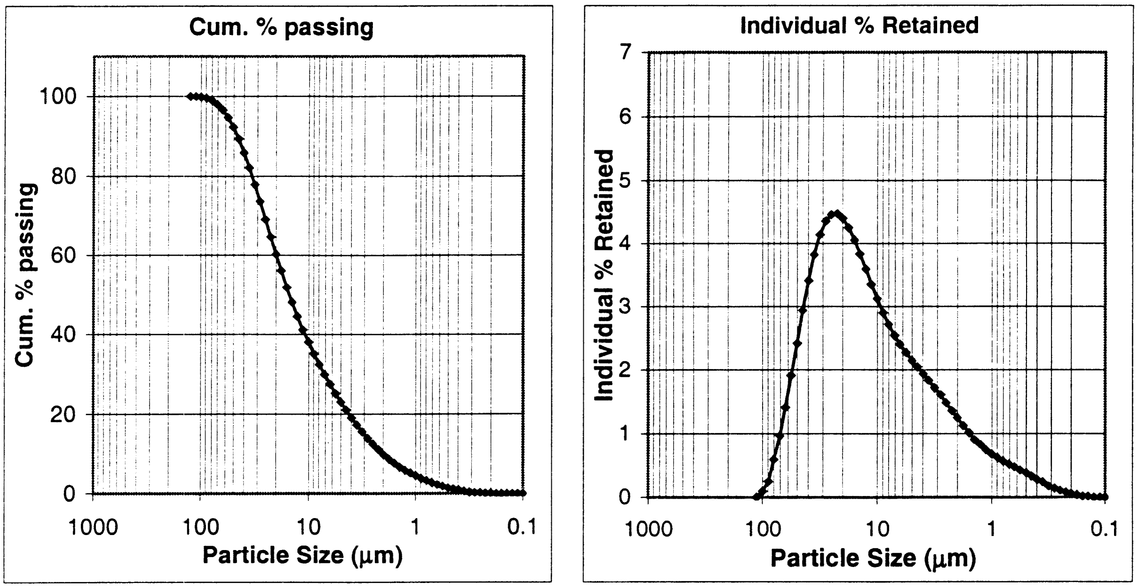


Figure 3.4 : **Particle Size Distribution [Cement LA]**

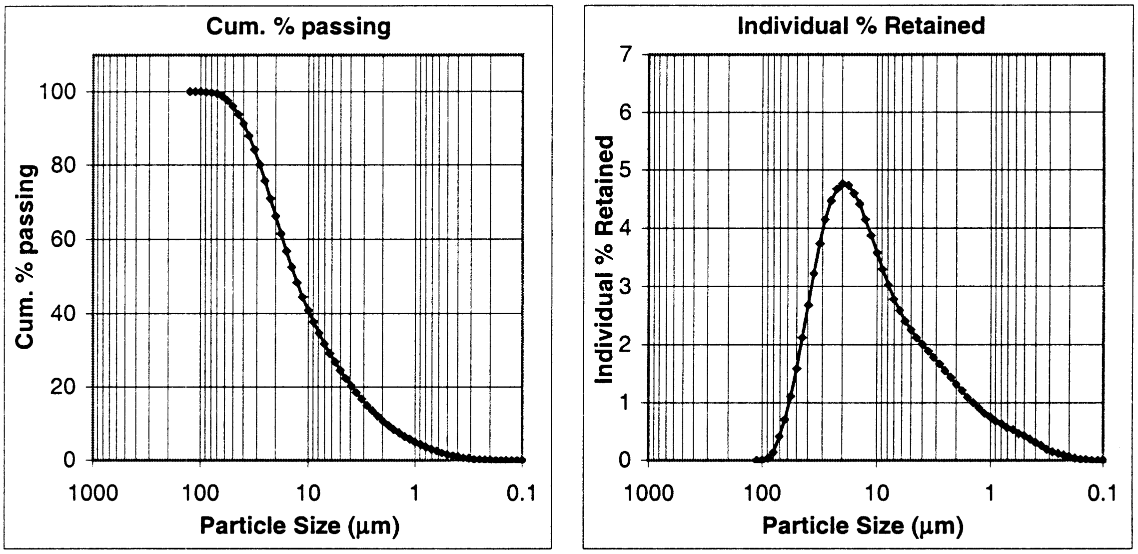


Figure 3.5 : **Particle Size Distribution [Cement LJ]**

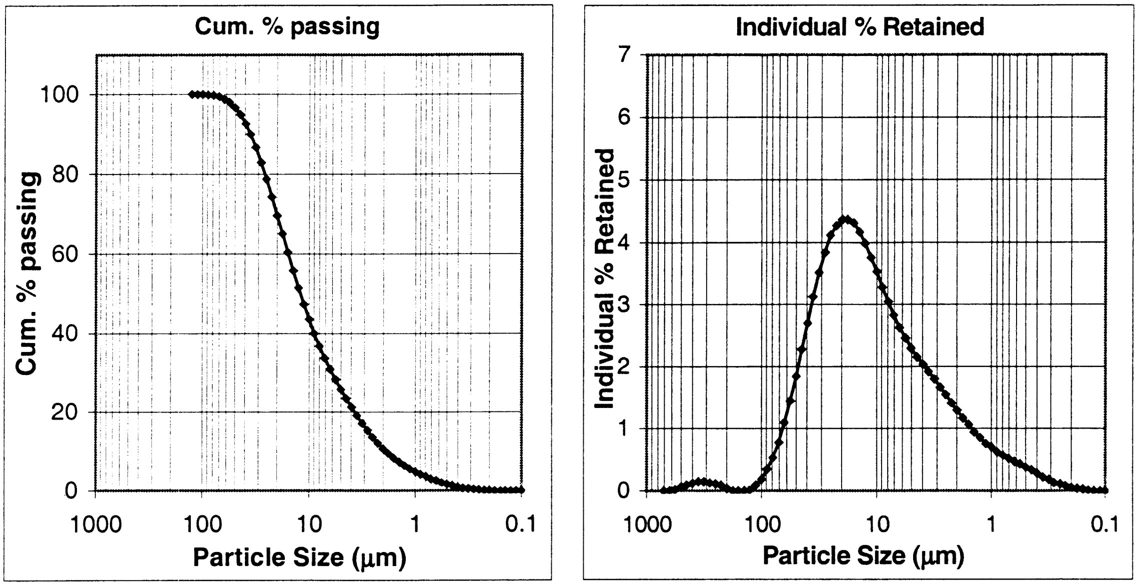


Figure 3.6 : **Particle Size Distribution [Cement X]**

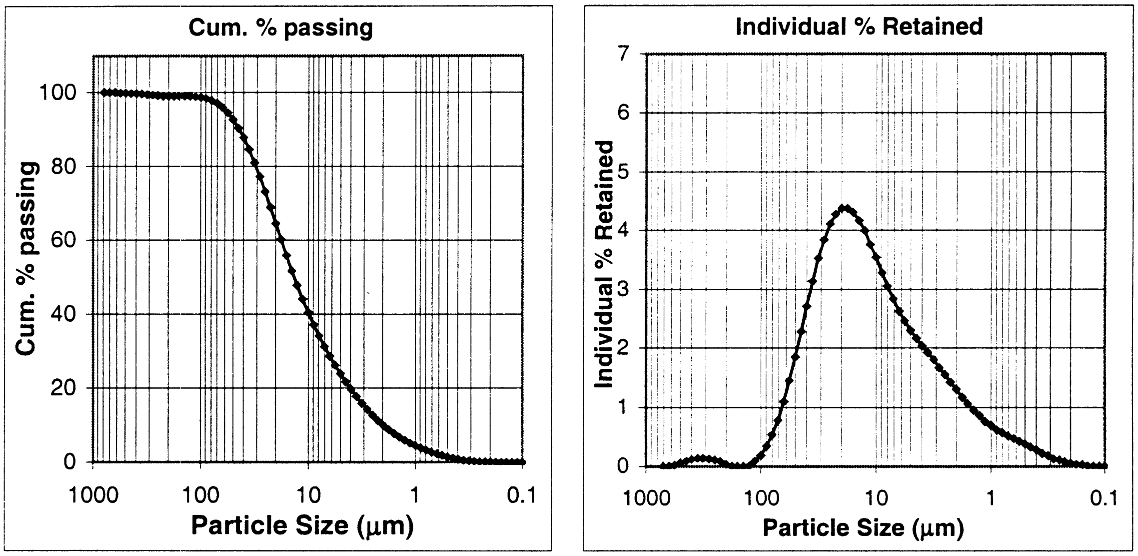
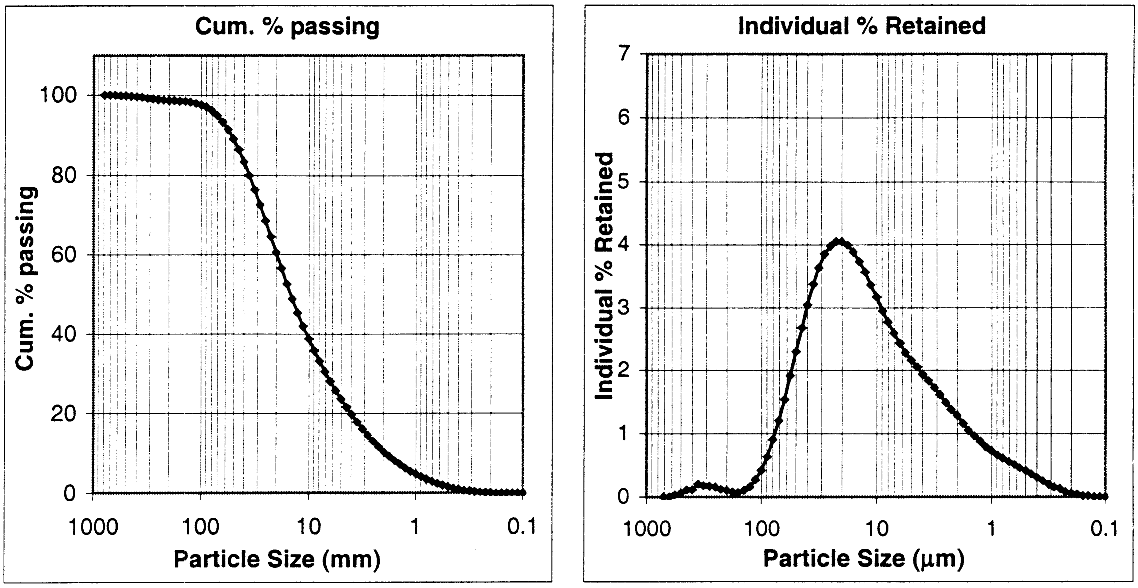


Figure 3.7 **: Particle Size Distribution [Cement Y]**



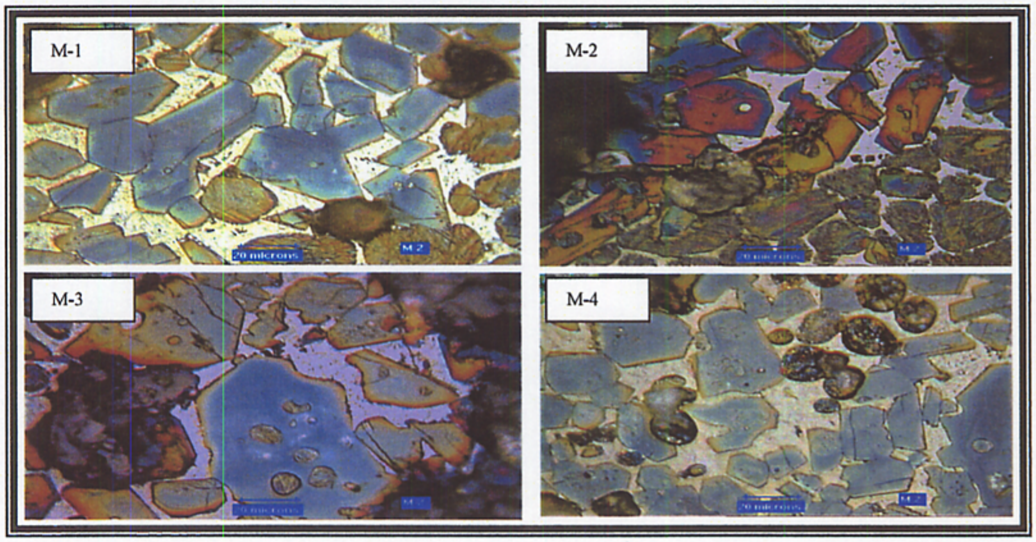
3.1.2 Cement Clinkers

In addition to cement compound composition and content an important parameter that affects cement reactivity and performance is the distribution and characteristics of cement phases. It has been found that clinkering temperatures and cooling rates at the end of the clinkering process not only affect the compound composition but also the reactivity of clinker compounds [6]. Petrographic examination of cement clinkers was therefore conducted to assess the effects of compound morphology on fresh and hardened concrete properties.

3.1.2.1 Clinker M:

Figure 3.8 shows several viewgraphs for M clinker. Alite (C_3S) crystals are very well developed with subhedral to euhedral structure. Typical alite crystal size is in the range of 20 to 40 microns with no obvious decomposition. Belite crystals (C_2S) are very well developed with very sharp edges. The average particle size for the belite crystals are about 10 to 30 microns. Although belites show very good distribution in the matrix, regions clustering is observed. The belite clusters may be largely originating from coarse silica rich particles in the raw feed. The tricalcium aluminate phase (C_3A), gray, is very fine and well intergrowed or interfingered with the ferrite matrix. The ferrite phase, tetracalcium aluminoferrite, is not attacked by the etching reagents; therefore, it is easily recognizable in the polished section as a white portion. Large and small pores are present as shadows in M-2 and M-1 respectively.

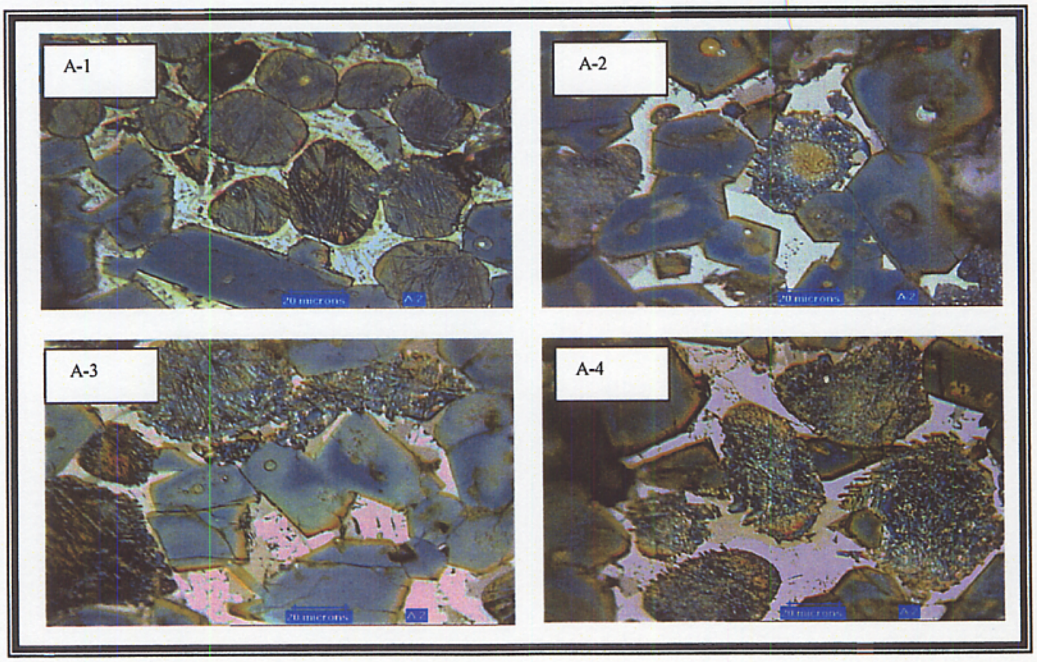
***Figure 3.8*: Microstructure of Clinker M**



3.1.2.2 Clinker A:

Alite (C_3S), blue, is very well developed and crystallized. Most of the alite crystals have subhedral to euhedral structure. The average alite crystal size is in the range of 30 to 50 microns. However, some crystals as large as 80 microns were observed. No obvious decomposition is observed. Most of the belite crystals (C_2S) developed well, but some of the belites show very severe ragged edge which is an indication of slow cooling process in some areas. Most of the belite crystals are about 20 to 40 microns. The aluminate phase (C_3A) appears to be coarse in the ferrite matrix. This is another indication of a slow cooling process. Slowly cooled aluminate phase is expected to have lower reactivity. Since C_3A is one of the main contributors towards early age strength in Portland cement, slowly cooled and large C_3A will affect early age strength development of cement, especially the strength before 3 days age. Later age strength development will not be significantly affected.

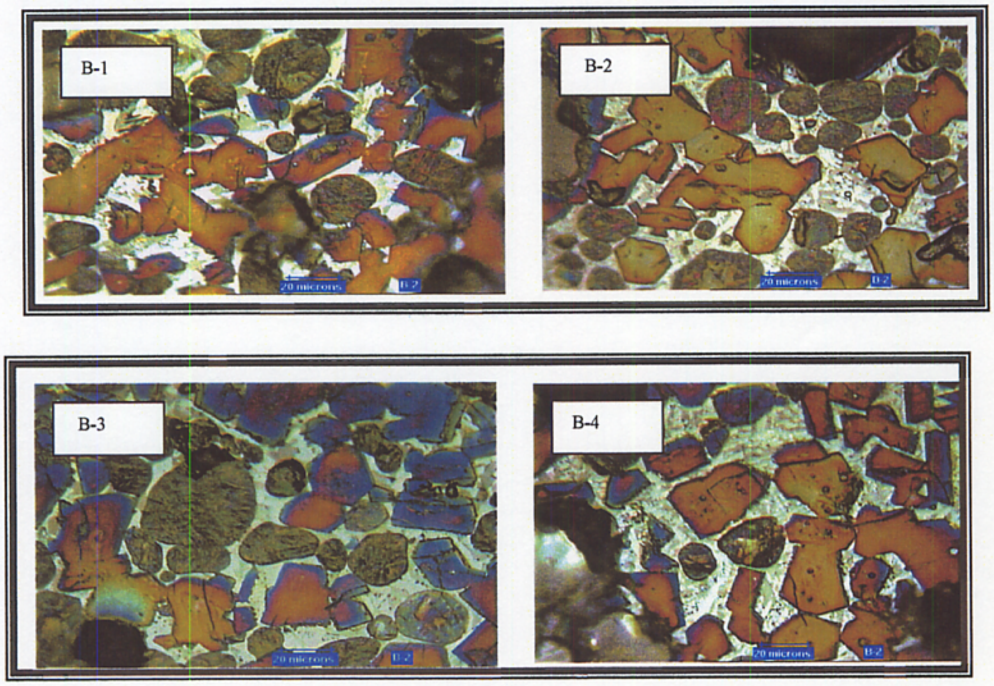
Figure 3.9 : **Microstructure of Clinker A**



3.1.2.3 Clinker B:

Alite (C_3S) particles , light green and purple, are very well developed and crystallized. Most of the alite crystals have subhedral to euhedral structure. The average alite crystal size is about 20 to 40 microns. No obvious decomposition is observed. Belite crystals (C_2S) are very well developed with very sharp edges. Belites show very good distribution in the matrix. Most of the belite crystals are about 10 to 30 microns. The tricalcium aluminate phase (C_3A) is small and well intergrown with the ferrite matrix. Based on the microstructure information from this clinker, both early age and later age strength development should be normal.

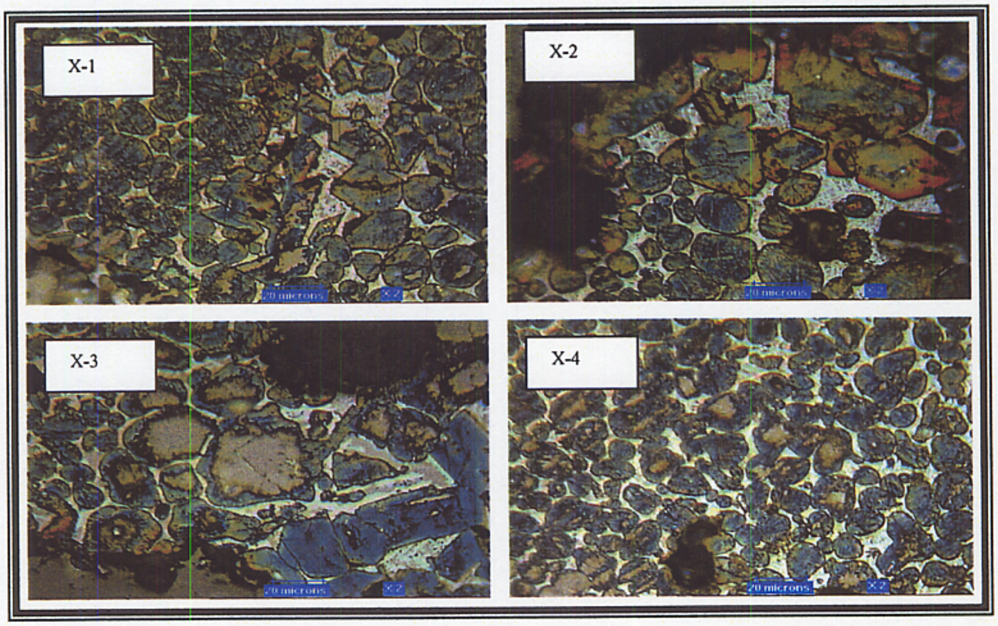
Figure 3.10 : **Microstructure of Clinker B**



3.1.2.4 Clinker X:

Most of the alite crystals(C_3S) are well developed and crystallized. But some nodules of alite show indication of decomposed edge. This may affect alite reactivity, especially at early ages. Majority of the alite crystal size is about 15 to 40 microns. Belite crystals (C_2S) are well developed with very sharp edges. Most of the belite crystals are about 5 to 20 microns. Concentrated alite and belite clusters are observed. Most of aluminate phase (C_3A) is small and intergrows very well with ferrite in the matrix. But in some nodules, aluminate phase is large. This also will affect early age strength development.

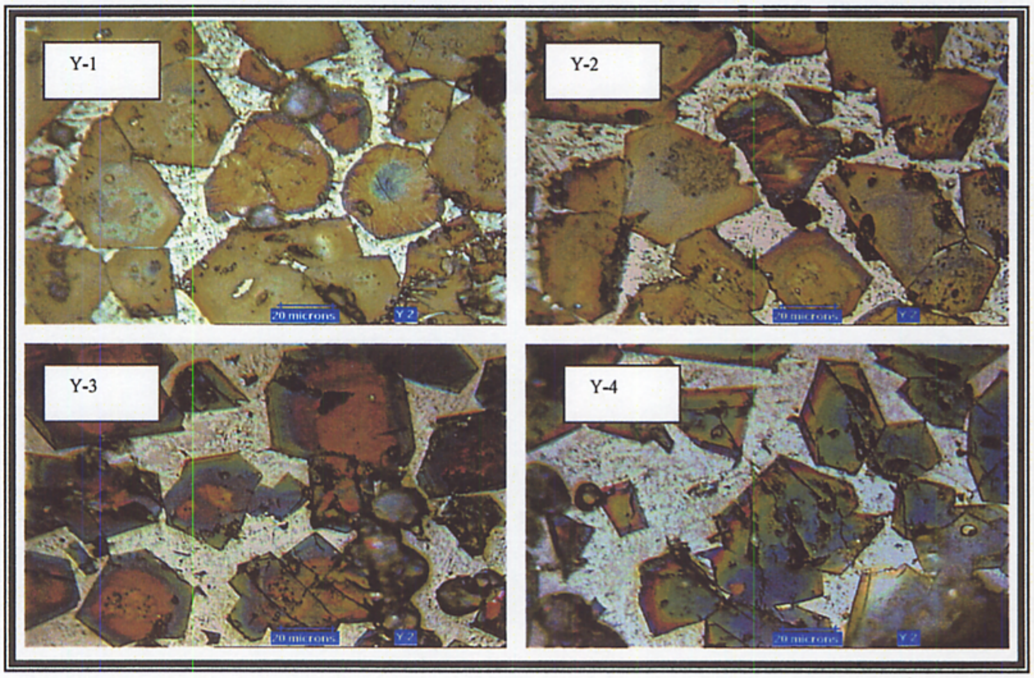
Figure 3.11 : **Microstructure of Clinker X**



3.1.2.5 Clinker Y:

Alite (C_3S) is very well developed and crystallized. Most of the alite crystals have subhedral to euhedral structure. Almost all the alite crystal size is larger that 20 microns. No significant smaller alite crystals are observed. If the clinker is not ground good enough to break down the alite crystals, strength development may be limited. No obvious alite decomposition is observed. Most of the belite crystala (C_2S) are developed well, but again majority of the belite crystals is larger than 20 microns. Large belite crystals will reduce its ability to contribute to ultimate strength. Aluminate phase (C_3A) is extremely small and intergrows very well with ferrite in the matrix. The C_3A in this clinker should be very reactive and will contribute to early strength development.

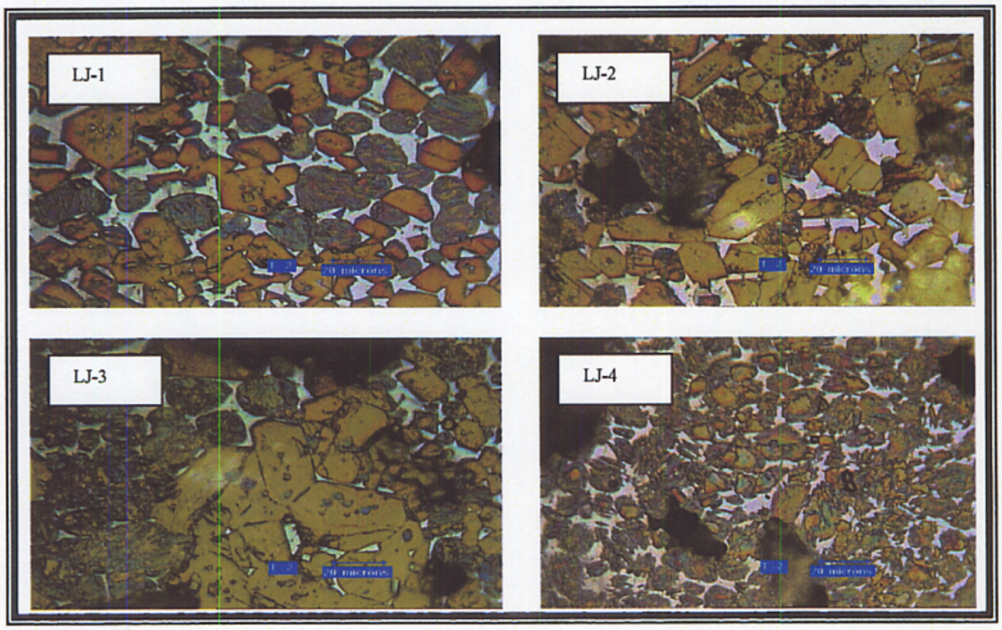
***Figure 3.12*: Microstructure of Clinker Y**



3.1.2.6 Clinker LJ:

Alite (C_3S) is very well developed and crystallized. Most of the alite crystals have subhedral to euhedral structure with an average crystal size of about 10 to 30 microns. No obvious decomposition is observed. Belite crystals (C_2S) are well developed with sharp edges. Most of the belite crystals are about 5 to 20 microns. There is a good belite distribution with some observed clustering. The aluminate phase (C_3A) is small and intergrown very well with ferrite matrix. It seems that the amount of C_3A is less compared with other clinkers. Less C_3A content in the clinker may have some effect on early age strength development. Later age strength development will not be significantly affected.

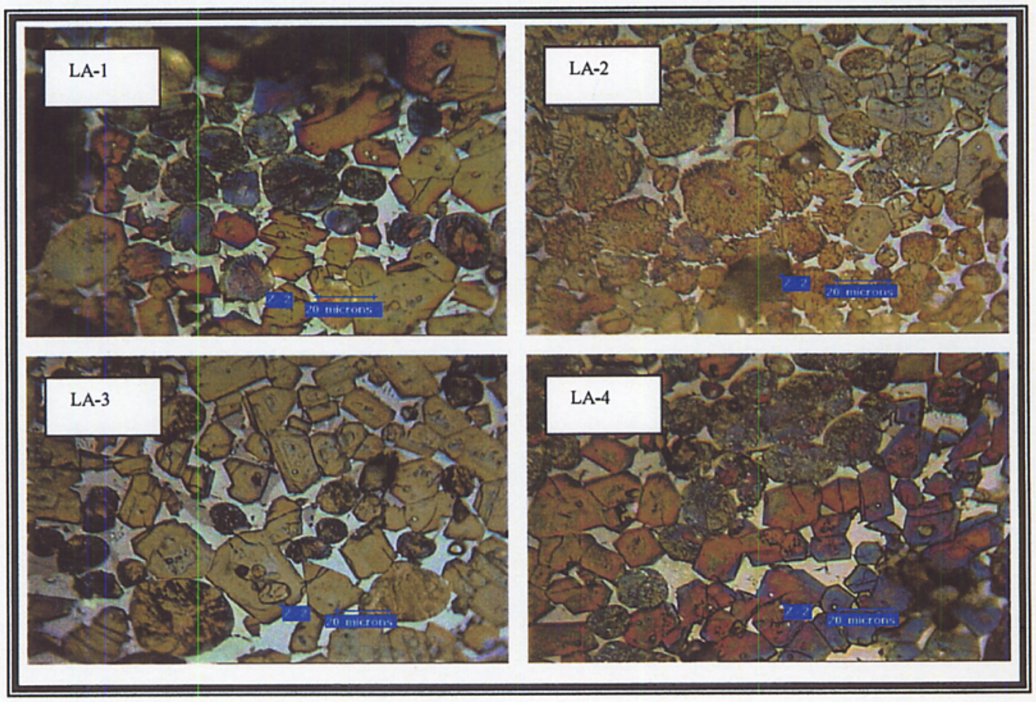
Figure 3.13 : **Microstructure of Clinker LJ**



3.1.2.7 Clinker LA:

Alite crystals have subhedral to euhedral structure. No obvious decomposition is observed. Large span of alite size is observed. Wide size distribution of alite size will help strength development at all ages. Belite crystals (C_2S) are well developed . It is also noticed the wide size distribution. Some of the belite shows mild ragged edge, which may be less reactive. In some of the nodules, the size of the aluminate phase (C_3A) is large. This may have some effect on sulfate durability.

Figure 3.14 : **Microstructure of Clinker LA**



3.2 Concrete Fresh Properties

3.2.1. Concrete Mix Design

In addressing the parameters that can be affected by changing the cement source, concrete mixes were prepared for all the as-received cements following FDOT 346 specifications for hot mixing of Class IV concrete. For all mixes, the same mix design was adopted including constant w/c of 0.41, cement content of 390 kg/m^3 and constant admixtures dosages. The temperature throughout the mixing procedures was maintained at 96° F +/- 1° F. In addition, fine and coarse aggregates were sorted by sieve analysis and then the aggregates weights were reconstructed using a uniform constant grading curve for all mixes as shown in Table 3.6 and 3.7. In order to conduct aggregate sorting, fine and coarse aggregates were oven dried to the oven dry condition prior to separating them into different aggregate sizes. Coarse aggregates weight was then reconstructed and the aggregates were allowed to reach the saturated surface dry condition prior to mixing. Three concrete mixes were prepared for each of the as-received cements except for cement M due to its limited supply. The total number of concrete mixes is 21. For each concrete property whether fresh or hardened property, each data point represent an average of three mixes. The concrete mix design adopted is presented in Table 3.8.

Table 3.6 : **Coarse Aggregate Grading**

Sieve Size	**WET MATERIAL**		**SSD**		**OVEN-DRIED**	
	Trial 1 (lbs)	Trial 2 (lbs)	Trial 1 (lbs)	Trial 2 (lbs)	Trial 1 (lbs)	Trial 2 (lbs)
#8	0.659	0.851	0.565	0.76	0.533	0.717
#4	1.597	1.687	1.541	1.629	1.458	1.544
# 3/8	1.446	1.868	1.396	1.827	1.338	1.752
# ½	1.796	2.287	1.773	2.251	1.71	2.164
# ¾	1.796	2.324	1.781	2.302	1.722	2.224

Table 3.7: **Fine Aggregate Grading**

Fine Aggregate (SSD Weights)					
	SSD	3 ft^3	Weight	% Ret. Corrected	1 ft^3
SIEVE	individual	(lbs.)	Corrected		(lbs)
4	0.003	0.35	0.10	0.001	0.03
8	0.011	1.57	1.00	0.007	0.33
16	0.096	13.21	14.50	0.105	4.83
30	0.282	38.86	39.46	0.286	13.15
50	0.315	43.45	43.55	0.316	14.52
100	0.260	35.86	38.50	0.279	12.83
200	0.029	3.97	0.70	0.005	0.23
Pan	0.004	0.61	0.08	0.001	0.03
Total	1.000	137.89	137.89	1.000	45.96

Table 3.8 : **Concrete Mix Design**

Constituent	1 cy. SSD	Volumes (ft^3)	BATCH WEIGHT	RATIOS
CEMENT	658 lbs	3.35	48.74 lbs	MORTAR
C.A.	1680 lbs	11.13	125.38 lbs	CAGG 60.0%
F.A.	1215 lbs	7.40	90.00 lbs	
WATER	32.4 gals	4.33	19.06 lbs	FAGG 40.0%
AEA	1.0 oz	0.81	2.19 ml	
WRDA	26.3 oz	0.00	57.65 ml	W/C 0.410
TOTAL	3823 lbs	27.01	TUW*	141.5 pft^3
* TUW = Theoretical Unit Weight				

Following Section 346 of the FDOT Standard Specifications for Road and Bridge Construction, for Class IV concrete, a target slump of three inches (3 in.) was used in designing the mixes. Cement M was used as a reference and the admixture dosage used in this cement was maintained constant for the other cement mixes. That is, mix design proportioning and admixture dosage were maintained constant in preparing all of the twenty concrete mixes. Slump variation as a function of time was monitored for all mixes over a period of 90 minutes following ASTM C143. Slump measurements were performed after the initial mixing and then every 30 minutes for a total of ninety minutes.

Fresh concrete properties that are measured in this study include: air content, unit weight, slump loss and setting time. The results of these measurements are presented in this chapter.

3.2.2 Air Content and Unit Weight

Air content and unit weight measurements for the concrete mixes are presented in Figures 3.15 and 3.16 respectively. As can be seen from Figure 3.15 for air measurements, air content variation was within 1% for all the cements studied here. Unit weight measurements were within approximately 1% variation. It can be therefore concluded that for the cements examined here, variation in the air content and unit weight were not significant.

Figure 3.15: Air Content of Fresh Concrete

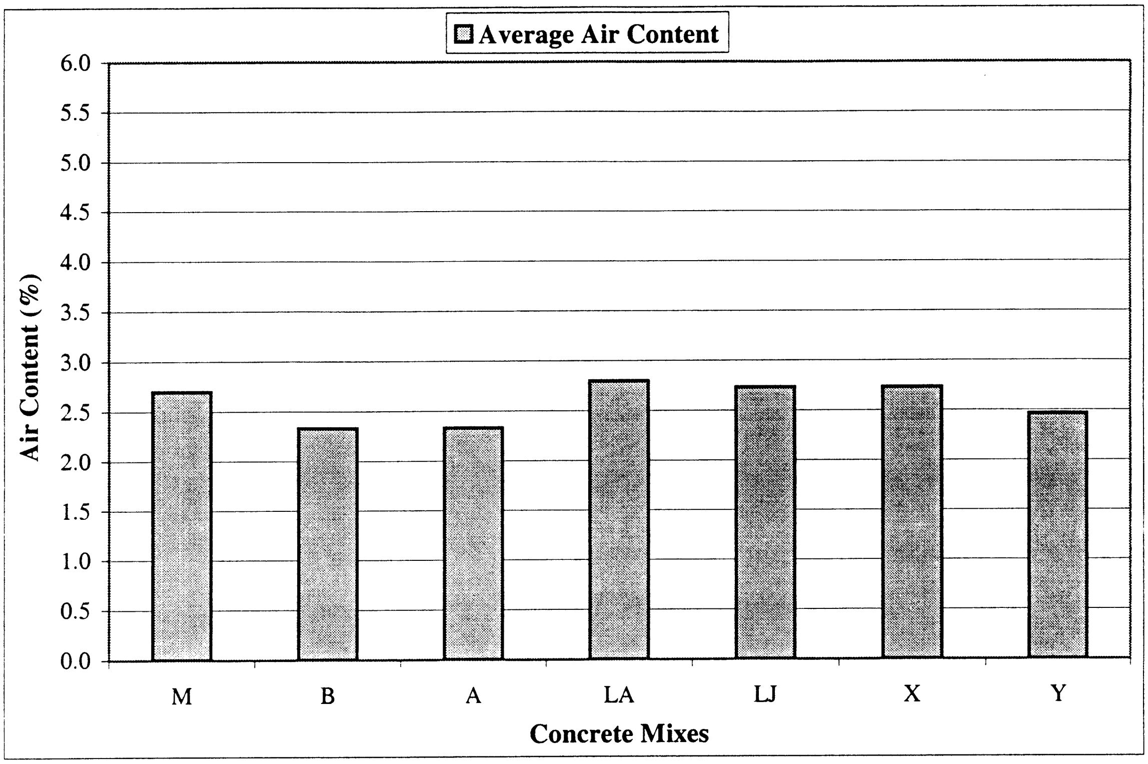
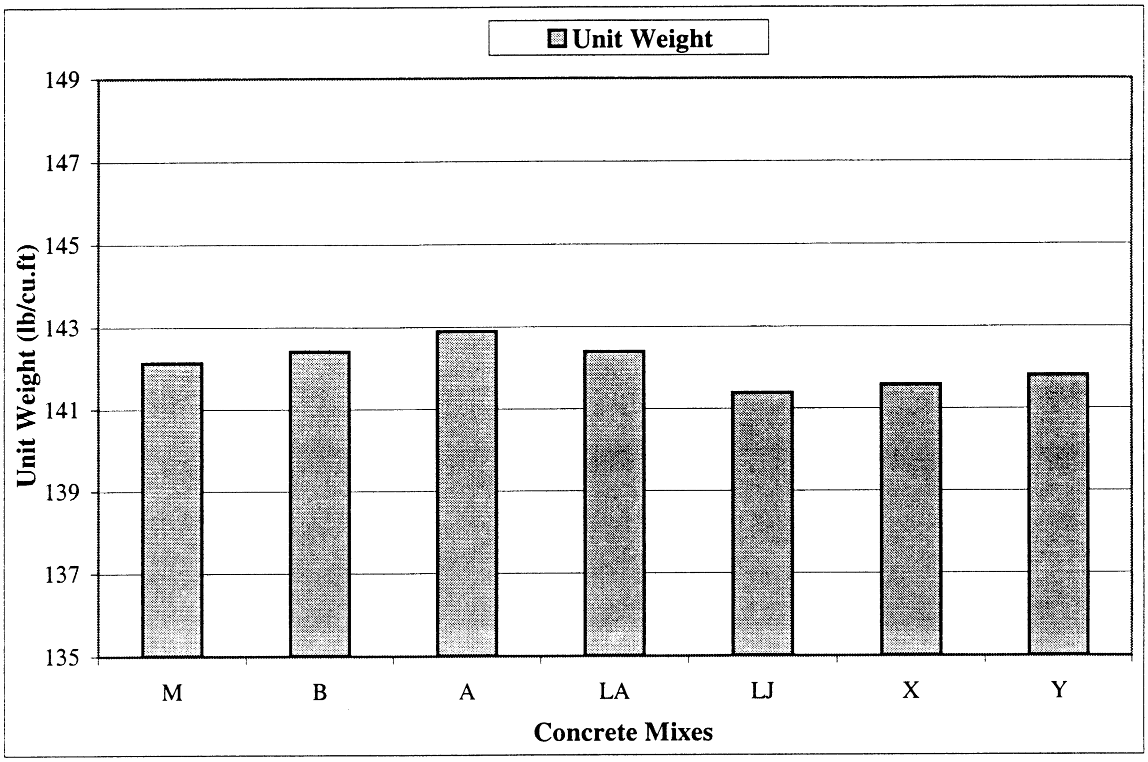


Figure 3.16: **Concrete Average Unit Weight**



3.2.2 Slump Loss

The variation in slump as a function of mixing time was monitored up to 90 minutes for the twenty mixes prepared in this study. The results for the variation in slump as a function of mixing time are depicted in Figure 3.17 .

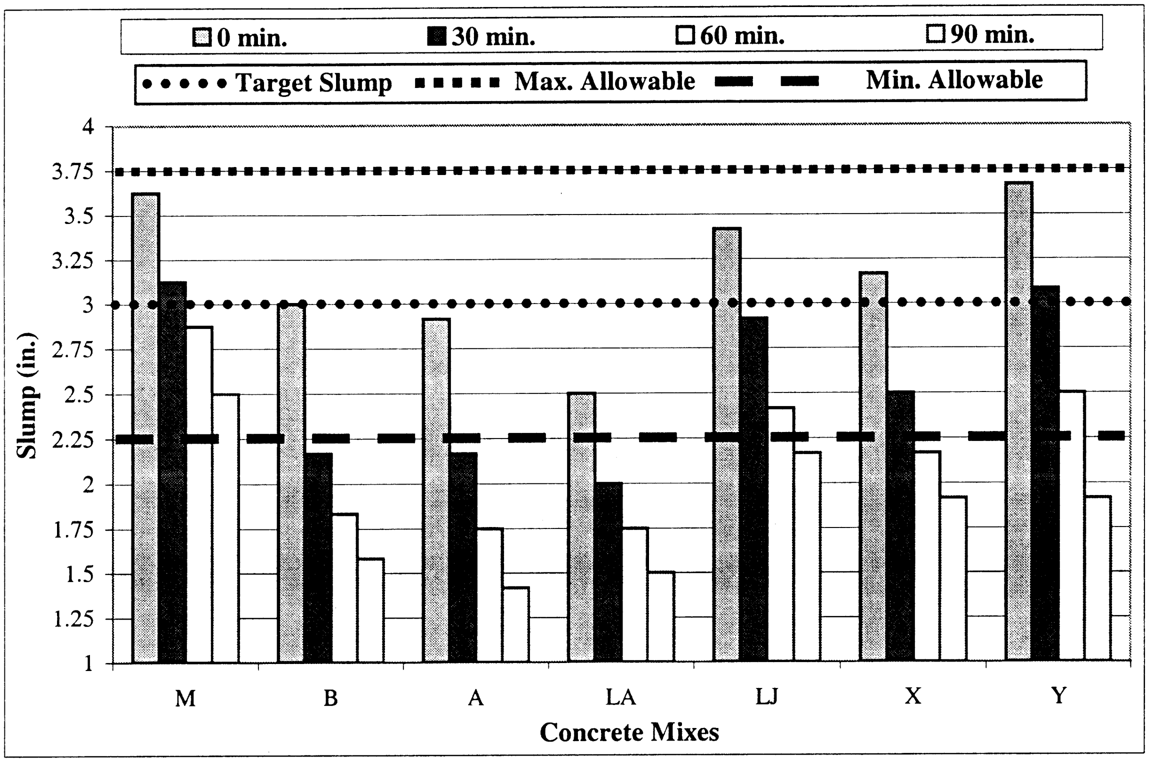
From Figure 3.17 it can be seen that the only cement mix that satisfied the FDOT specifications for slump under hot mixing conditions was the reference cement M mixes. This is not a surprising finding due to the fact that the cements chemical compound composition is different from the reference cement. In addition, there is variation in the calcium sulfate phases and content that is evident from the XRD results. Another important factor that needs to be considered is the water-reducing admixture that belongs to the lignosulfonic group of water reducers. Previous research has indicated that the SO_4 in the admixture compete and influence the solubility of the calcium sulfate phases. The nature of the interaction between SO_4 in the admixture and the cement calcium sulfate phases depends on the type of calcium sulfates; that is, gypsum, hemihydrate or anhydrite.

The general trend of the slump loss in the cements studied here is indicative of the decrease in the rate of slump loss with an increase in the total calcium sulfate content except for cement X. Though this cement had the highest C_3A content (8%), it also had the highest calcium sulfate content. However, 63% of the sulfate is in the anhydrite form, which is the least soluble. This may imply the adsorption of the admixture by the C_3A, thus leaving less of the admixture available in solution for water reduction or retardation.

Comparing Y cement with A and B cements, it can be seen that the three mixes share the same C_3A content of 6% (Bogue calculations), though mix Y had a higher slump loss than mixes B and A. XRD results for Y cement indicate a lower total calcium sulfate content of 3.6 as compared to mixes B and A which had calcium sulfate content of 4.5 and 4.4 % respectively.

Considering cement LJ and Y, both had similar C_3S content at 61 and 62% respectively; also their C_3A content are similar (5 and 6% respectively). LJ cement had a calcium sulfate content of 4.7 compared to 3.6% for cement Y. At 90 minutes, the slump loss for cement LJ is 42% less than Y.

Figure 3.17 : **Concrete Slump Loss During Extended Mixing Period and FDOT-346 Limits**



3.2.3 Setting Time

Setting times for concrete mixes is performed in accordance to ASTM C403 on wet sieved concrete through #4 sieve. Prior to running the penetration test, bleed water was sucked through appropriate pipets. Initial set is reported as the time corresponding to a penetration resistance corresponding to 500 psi while final set is reported as the time corresponding to a penetration resistance of 4000 psi.

On mixing cement with water, water becomes saturated with calcium hydroxide and sulfates during the first few minutes. The initial set of portland cement is generally attributed to the hydration of the calcium aluminate and tricalcium silicate. The rate of the reaction between the anhydrous cement compounds and water and the availability and the interaction of lime, alumina, silica and sulfates determine the speed of setting. The setting time of portland cement is generally controlled through the addition of gypsum to the cement clinker.

Figure 3.18 shows the initial and final setting times for different cement mixes. It can be seen that cement B had the longest setting time while cement X and Y had the shortest setting time, with a difference in setting time of 84 minutes. From the chemical oxide analysis and the calculated compound composition, cement B had the lowest tricalcium silicate among the cements studied here. Its C_3A is 6%, which falls towards the lower end among the cements studied here. In addition, the calcium sulfate content of this cement (Table 3.9) is in the mid range. However, a higher percentage of the calcium sulfate occurs in the form of gypsum. Cement X has a slightly higher tricalcium silicate content (54%) but its C3A content is the highest among the cements examined here (8%). Though calcium sulfate is highest for this cement, it occurs predominately in the least soluble form, that is, anhydrite. On the other hand, Y has a higher C3S content (62%) and the same C3A content as B. The calcium sulfate content for Y cement was reported earlier at 3.6% which is lower than that of cement B (4.5%) In addition, the calcium sulfate content is predominately hemihydrate as opposed to cement Y where there is approximate split in the calcium sulfate content between gypsum and hemihydrate. Different forms of calcium sulfate have different solubilities and mode of action. While increasing the gypsum content in portland cement increases the setting time, the increase in setting time with gypsum addition is not proportional to the amount of gypsum added. The relationship of hemihydrate content to the setting time is different. Hemihydrate or Plaster of Paris retards the setting of portland cement more than gypsum due to its higher solubility and higher sulfur trioxide concentration. However the addition of large quantities of hemihydrate above a certain limit, promotes an opposite effect; that is, quick setting.

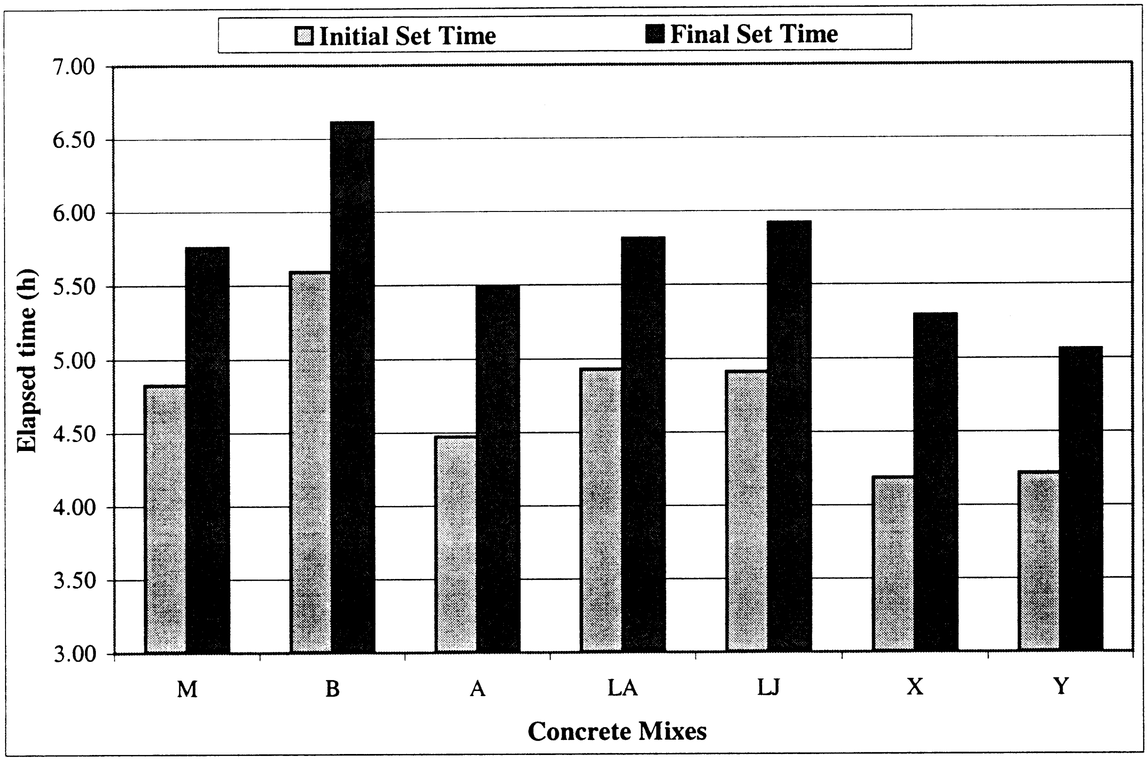
In addition to the impact of cement compound composition on the setting time of cements, an additional effect that is as important is the interaction of the water reducer/retarder admixture with different cement compounds and different forms of calcium sulfate phases. These interactions would result in different setting times for each cement as can be seen from the results presented here. An admixture dosage that is appropriate for one cement might be inappropriate for another.

From the fresh properties studied here, it can be seen that changing cement source had an impact on slump and slump loss in addition to the setting time. This is attributed to variation in the cement compound composition and phases reactivity. On the other hand, for the cements studied here, the air content and unit weight measurements did not show significant variation.

Table 3.9 : **Cement Compound Composition and Calcium Sulfate Content**

Cement	C3S (%)	C2S (%)	C3A (%)	C4AF (%)	Gypsum (% By XRD)	Hemihydrate (% By XRD)	Anhydrite (% By XRD)	Total Calcium Sulfate (% By XRD)
M	60	14	7	10	0.8	3.9	0.0	4.7
B	50	26	6	10	2.5	2.0	0.0	4.5
A	53	22	6	10	0.2	4.2	0.0	4.2
LA	66	8	7	11	0.1	2.7	1.9	4.7
LJ	61	11	5	14	1.1	3.6	0.0	4.7
X	54	19	8	10	0.6	1.3	3.2	5.1
Y	62	12	6	11	0.5	3.1	0.0	3.6

Figure 3.18: **Average Setting Times of Concrete Mixes**



3.3 HARDENED PROPERTIES

3.3.1 Concrete Compressive Strength

Concrete cylinders were prepared and cast in accordance to the following specifications: ASTM C192 , ASTM C39 and FDOT 346 for hot mixing. Batching for the seven as-received cements was done using the same mix design and maintaining hot mixing conditions. Figure 3.19shows the results for the strength gain as a function of curing time for the seven cements for a period of 28 days. From the results depicted in Figure 3.19, it can be seen that all mixes pass FDOT-346 Class IV strength criterion of 5500 psi. However, if the overdesign requirement is adopted (minimum compressive strength of 6900 psi) then, mixes cements Y and LA do not pass the FDOT-346 strength requirement for the 28 days compressive strength of 6900 psi.

The data indicate that for early hydration times (up to seven days) strength gain was primarily a function of fineness and tricalcium silicate content, in agreement with the literature [20 - 24]. This can be clearly seen from Figures 3.20 and 3.21 for 1, 3 and 7 days of hydration. At an age of 1 day, mixes containing cements LA and M had the highest compressive strength. These two cements have highest tricalcium silicate content and fineness. Cement A had the coarsest particle size distribution in addition to lower tricalcium silicate content which resulted in lower early strength. Though cements B and X have tricalcium silicate content similar to cement A, their compressive strength at 1 day was higher due to their higher fineness.

For longer hydration times, Figure 3.22, strength gain seems to be dependent not only on the dicalcium silicate [20-24, 26] content but also on the clinker phase morphology [11, 32]. Study of the clinker microstructure by optical microscopy revealed that the size and reactivity of the belite phases affects the strength development of concrete. Considering cement X and cement B, cement X has a dicalcium silicate content of 19 % compared to 26% for B. The compressive strength gain for these two cements between 14 and 28 days of hydration was 620 psi and 450 psi respectively. If the strength gain is controlled solely by the dicalcium silicate content, then the strength gain for cement B should be higher than that for X. In addition, both cements have similar fineness. However, the belite particles for cement B are coarser than that obserevd for cement X as can be seen from Figures 3.23 and 3.24.

Another example is the case of cement LJ and cement Y. Both cements LJ and Y has similar fineness (3920 and 3850 cm^2/gr, respectively) and similar dicalcium silicate content (11 and 12% respectively). The strength gain attained by cement LJ was 550 psi between 14 and 28 days as opposed to 270 psi for Y. However, if the morphology of the belite particles is considered, it can be seen that the belite particles in LJ exhibited excellent reactivity and particle size between 10 to 25 microns. However, for the Y cement, the belite particles are coarse and roundish with an average particle size between 20 to 40 microns which is indicative of lower reactivity.

***Figure 3.19* : Concrete Compressive Strength**

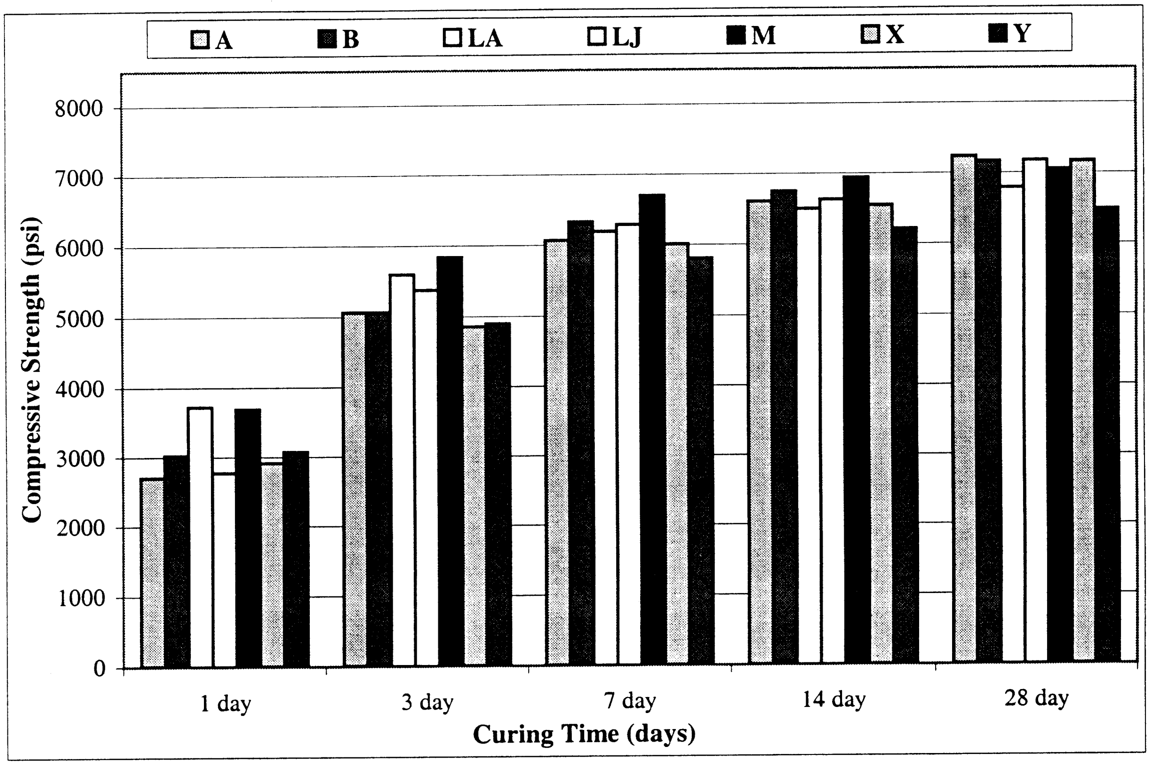


Figure 3.20 : **Compressive Strength of Concrete vs. Blaine Fineness**

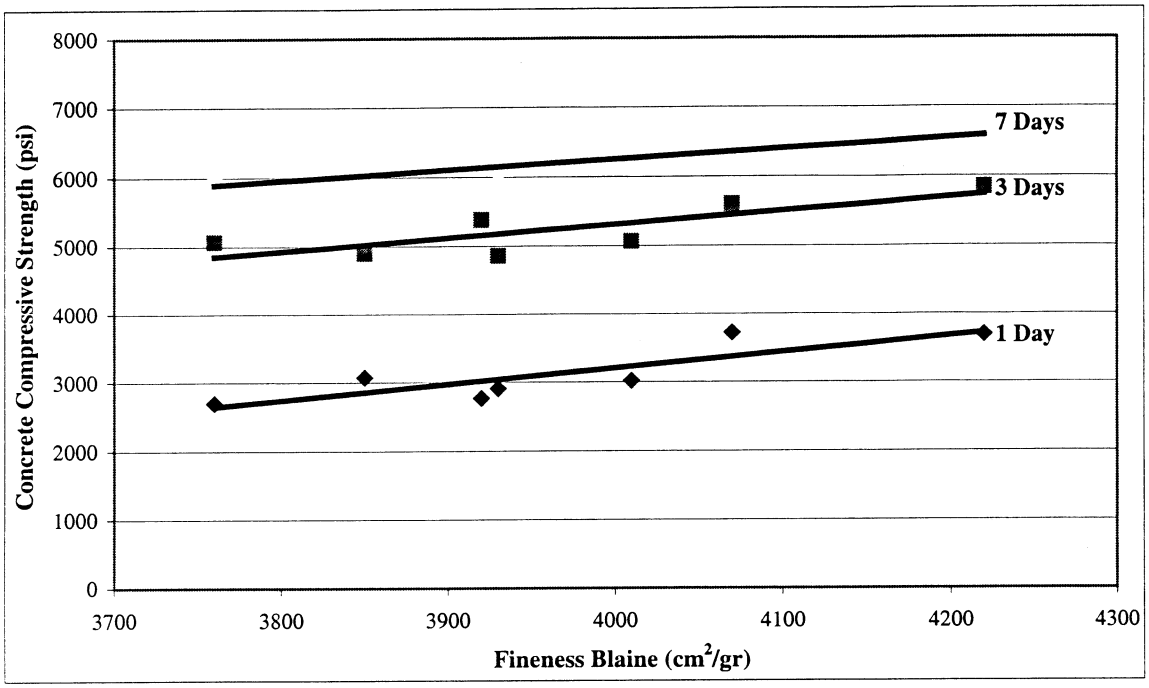


Figure 3.21 : **Concrete Compressive Strength vs. C_3S Content**

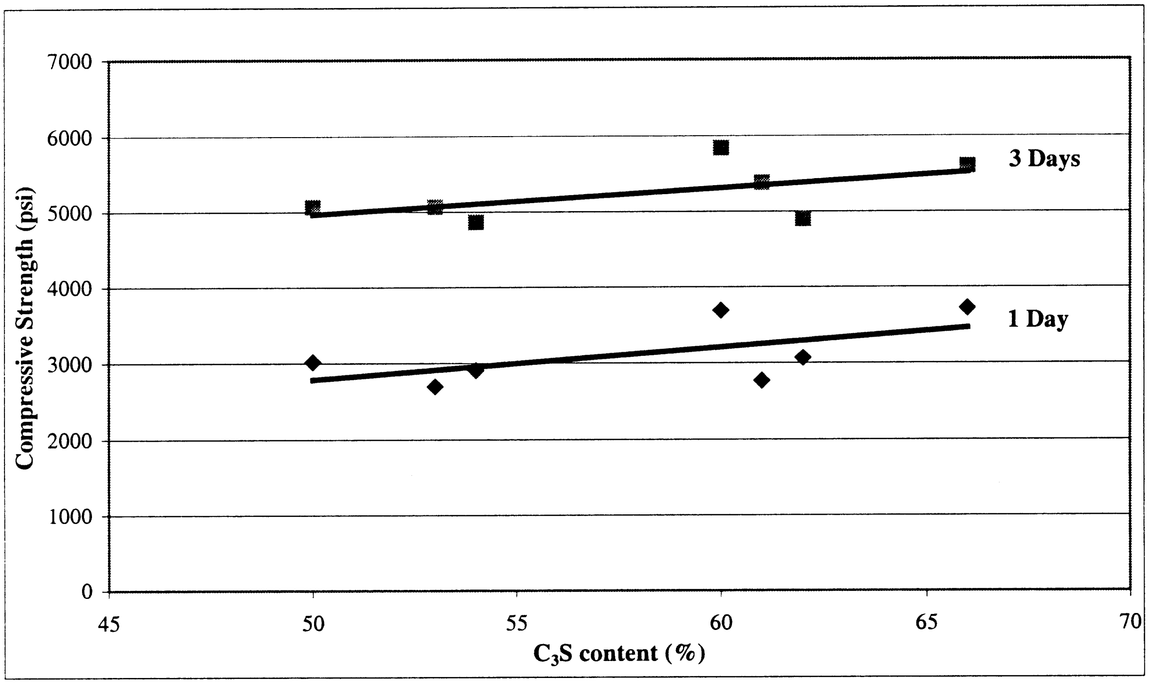
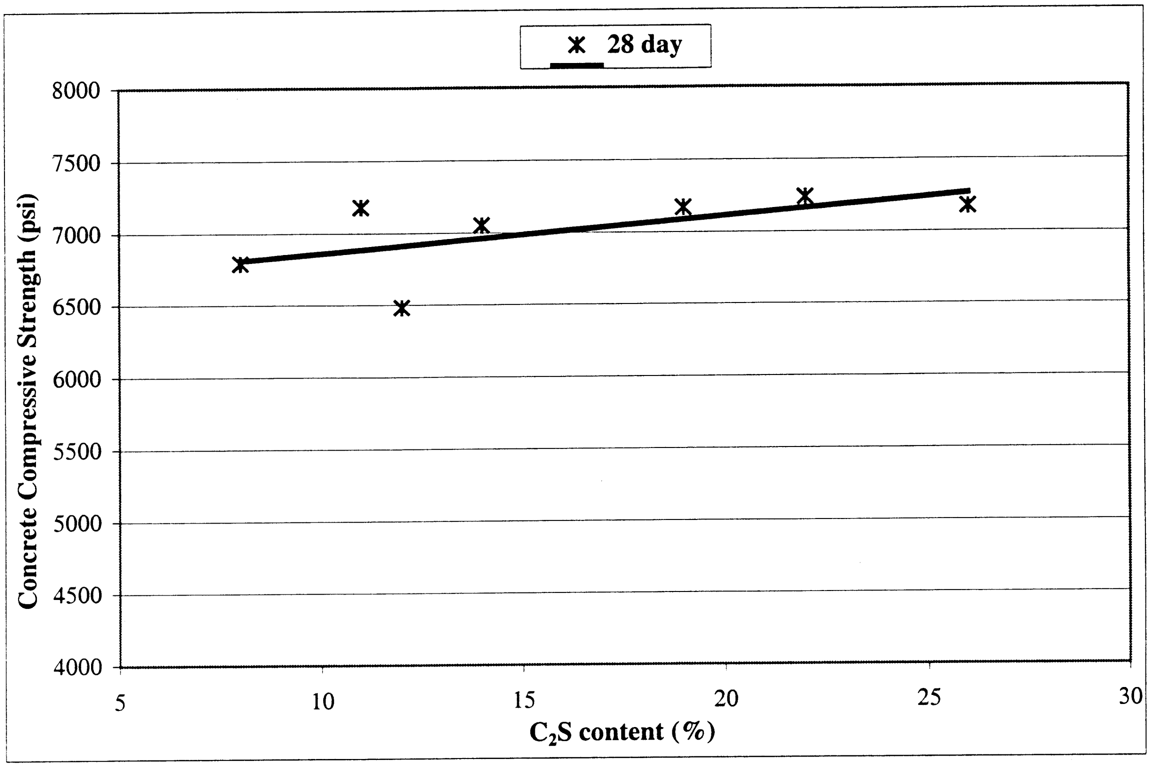


Figure 3.22: **Concrete Compressive Strength vs. C_2S Content**



In conclusion, it seems that the chemical compound composition of the as-received cements is not the only contributing factor to the strength behavior of the concrete examined in this study. Both, cement fineness and phase morphology are also critical parameters that affect the strength behavior of concrete mixes.

Figure 3.23 (a): **Clinker LJ and Y Belite Particles**

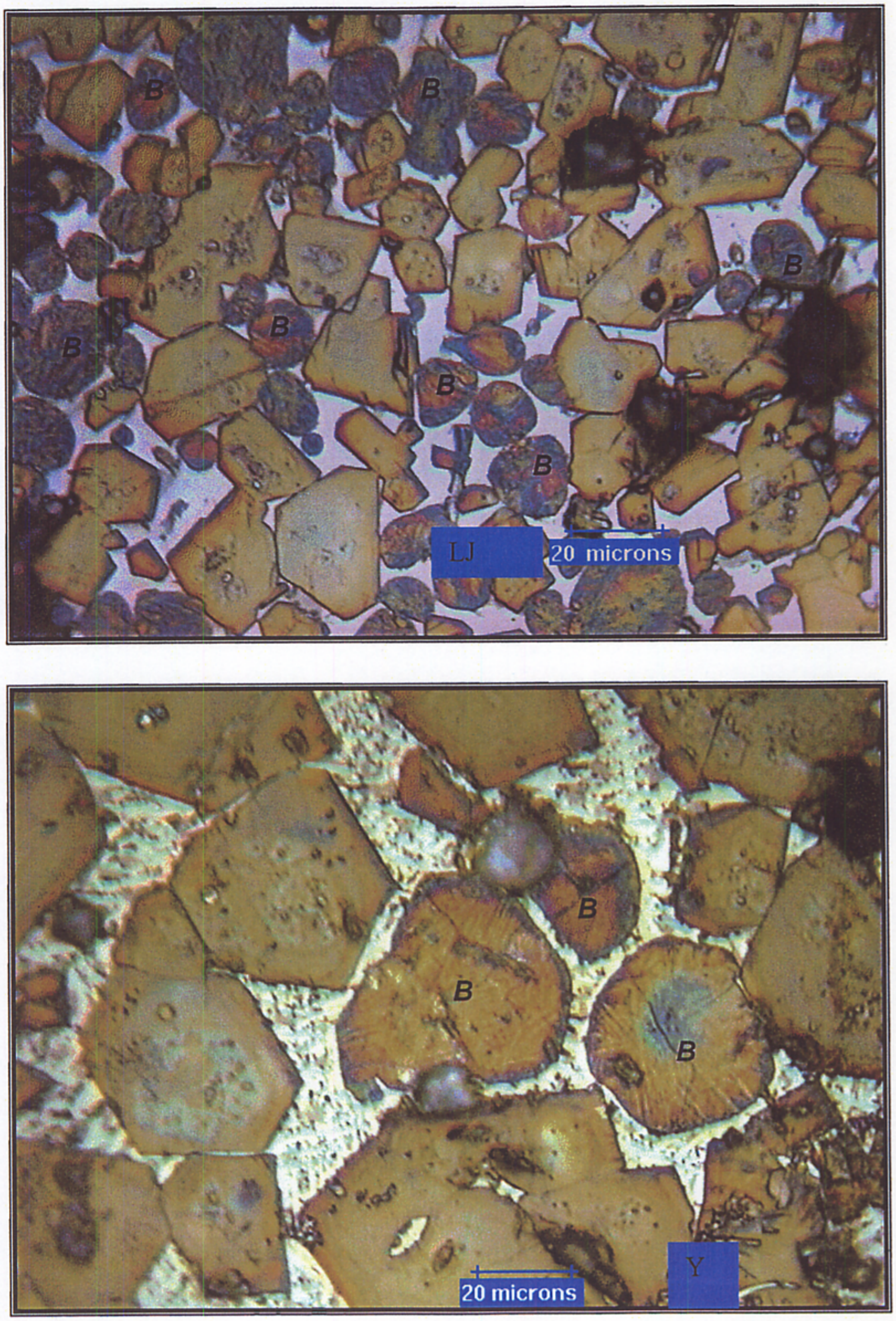


Figure 3.23 (b): **Clinker LJ and Y Belite Particles**

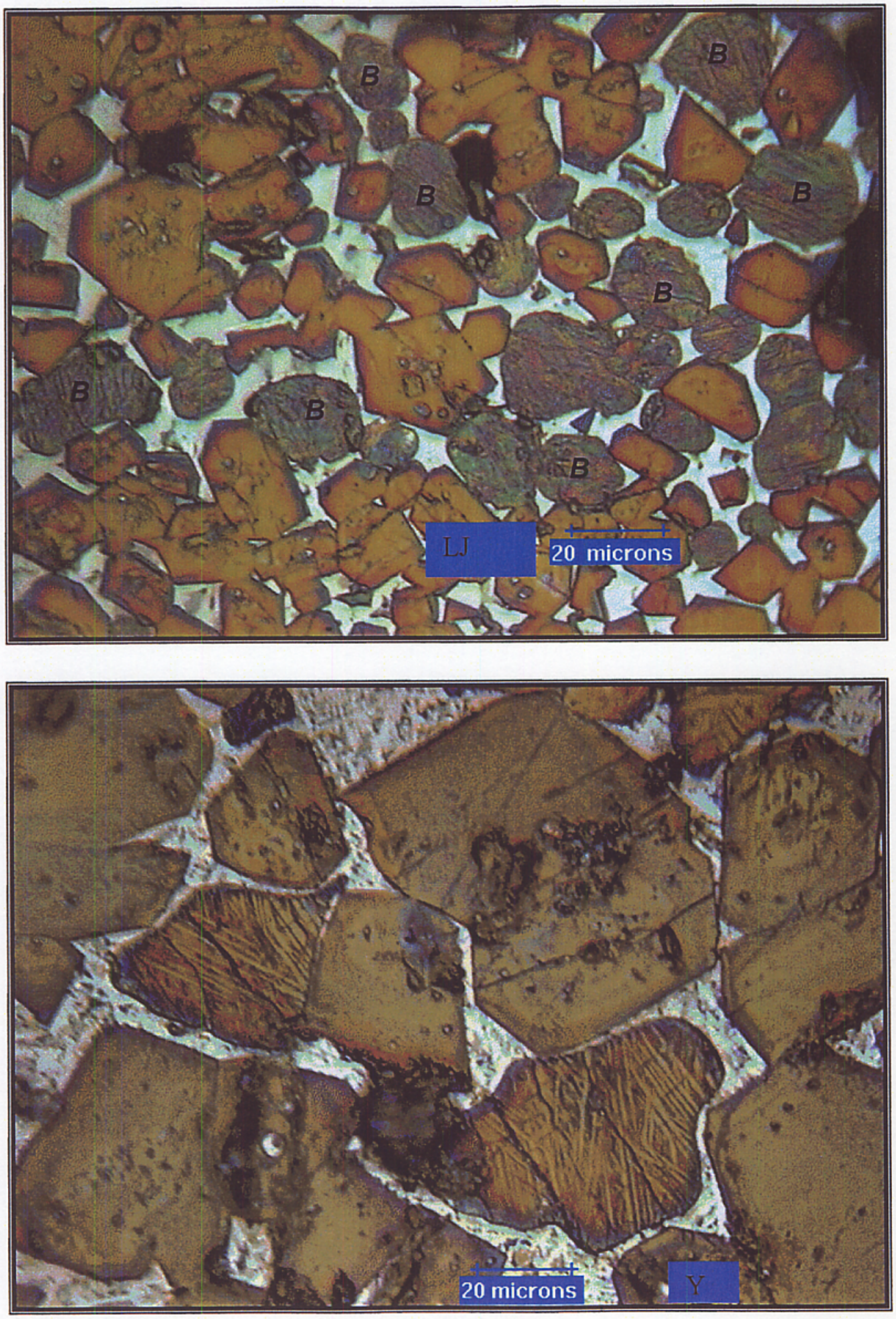


Figure 3.24(a): **Clinker B and X Belite Particles**

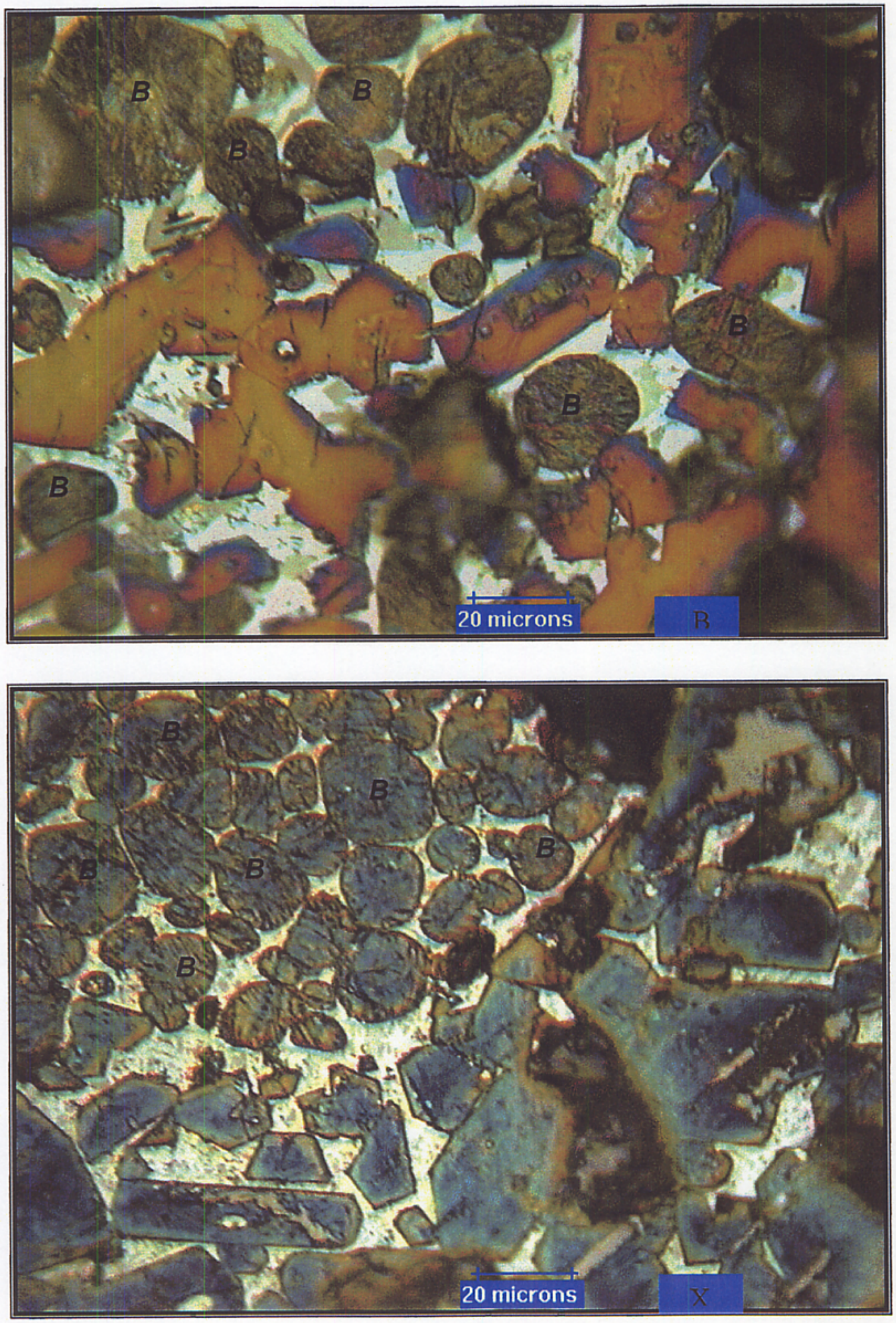
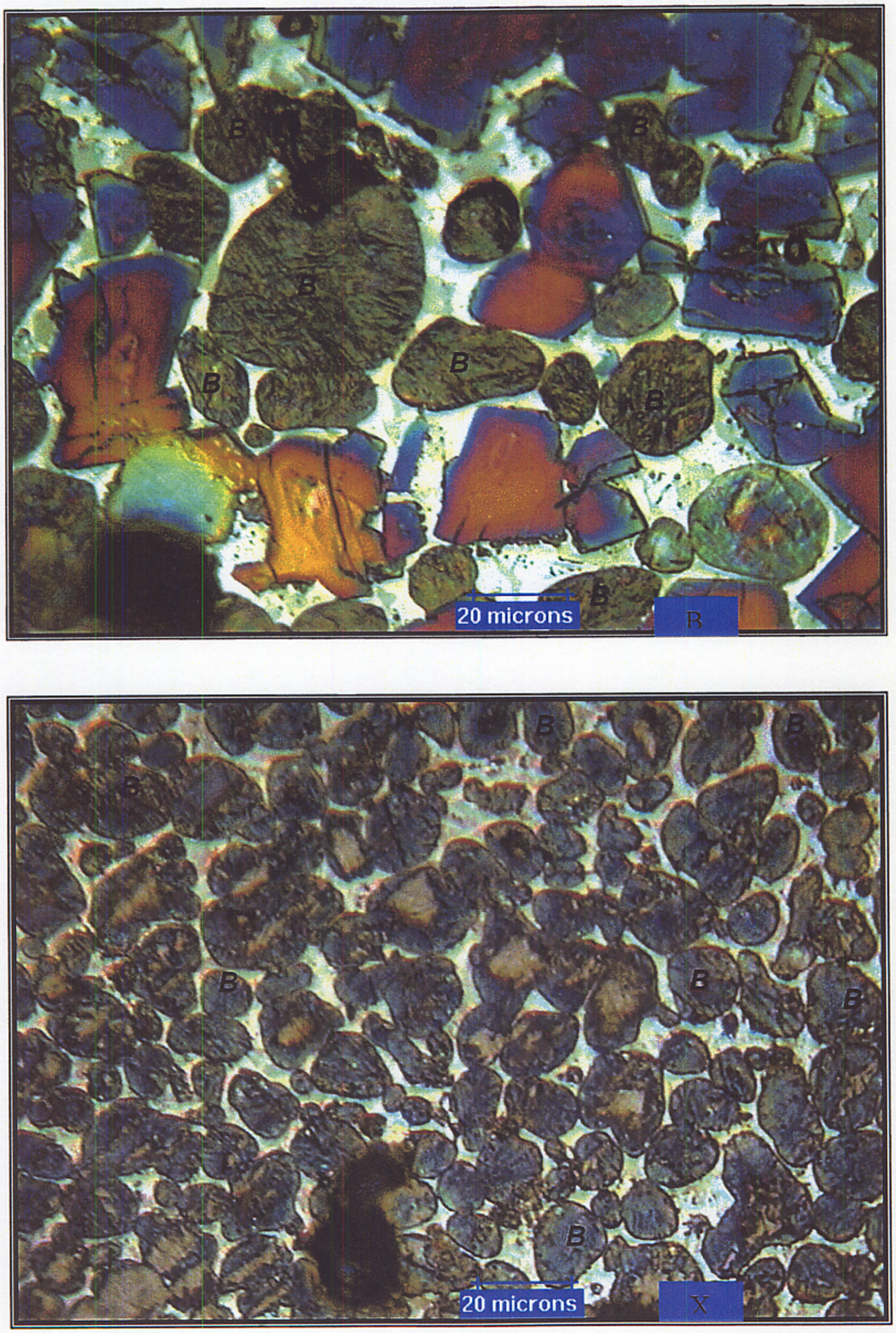


Figure 3.24 (b): **Clinker B and X Belite Particles**



3.3.2 Mortar Linear Expansion

Length changes experienced by mortar bars exposed to a sodium sulfate solution [5 %] were conducted over a period of 360 days. For each cement, 6 mortar bars were prepared in accordance with ASTM C 1012. The results for the expansion behavior are depicted in Figure 3.25 where it can be seen that Cement LA had the highest expansion [0.45%] while the lowest expansion was that experienced by Cement A [0.075] for the reported exposure period of 360 days. Comparing ASSHTO cements; that is Cements B, A and X, it can be noticed that variation in the expansion behavior was more than 3 folds. Comparing ASTM Type II cements, the variation in percentage expansion between the lowest and the highest expanding cements resulted in twice the percent expansion. In addition, one of the ASSHTO Type II cements [B cement] expanded more than ASTM Type II cement [LJ].

The mechanism of concrete deterioration due to sulfate presence is dependent on the sulfate type. While calcium sulfates reacts with calcium aluminate hydrate to produce expansive ettringite, sodium sulfates react on calcium hydroxide and forms expansive gypsum. In the presence of aluminates, expansive gypsum might transform to ettringite. The extent to which this reaction would proceed depends on the removal of sodium hydroxide from the solution. It has been reported that with 5% sodium sulfate in solution only one third of sulfur trioxide content will be deposited as gypsum when equilibrium is reached. The following is the series of reactions to be considered:

$$Ca(OH)_2 + Na_2SO_4 \,.\, 10H_2O = CaSO_4.2H_2O + 2NaOH + 8H_2O \qquad [1]$$

$$4CaO.Al_2O_3.19H_2O + 3(CaSO_4.2H_2O) + 16H_2O$$

$$= 3CaO.\,Al_2O_3.\,3CaSO_4.31H_2O + Ca(OH)_2 \qquad [2]$$

From the previous presentation and equations, it can be therefore concluded that the sodium sulfate attack will be influenced primarily by the calcium hydroxide content and the tricalcium aluminate content of the cement. The amount of calcium hydroxide liberated by cements is primarily released from tricalcium silicate hydration and also the dicalium silicate. It is therefore to be expected that the ratio of the tri/di calcium silicates should be indicative of the rate of calcium hydroxide production. In addition since the fineness of cement influences its reactivity, through making more surfaces available for interaction with the water of hydration, it will therefore be expected that higher fineness should affect the expansion behavior through its effect on cement reactivity. Increasing the tricalcium aluminates will also make available more calcium aluminate hydrates for interaction with the formed gypsum.

Table 3.10 shows the ratio of the silicate phases and the tricalcium aluminate content together with fineness for the seven cements studied here. Though mortar permeability/porosity is appreciated for its impact on durability, its effect is considered secondary in this analysis due to the fact that all of the mortar bars were prepared with a constant w/c. The data in Table 3.10 and Figure 3.25 indicate that expansion is predominately affected by the tri/di calcium silicate ratio and secondarily by tricalcium aluminate content and cement fineness. This can be seen through comparing Y and A cements. Both of these cements have the same tricalcium aluminate content of 6% and similar fineness [3850 for Y and 3760 for A]. The silicates' phases ratio in Y cement is double that of A cement. At 365 days of exposure to sodium sulfate environment, cement A has experienced less expansion than Cement Y, 0.075% as opposed to 0.4% respectively. Also, if the fineness effect is to be considered, at the same tricalcium aluminate content, cement B expansion behavior needs to be considered. Cement B has similar silicates ratio to Cement A; however, its fineness is higher. Cement B has experienced 0.25% expansion at 365 days which is higher than that experienced by cement A [0.075%] but lower than that of cement Y [0.45%]. Cement Y has lower fineness but higher tri/di calcium silicate ratio than Cement B.

In conclusion, among the AASHTO cements, cement B has the highest expansion for the period of exposure reported in this study; among ASTM Type II cements, cement LA showed the highest expansion. There was an overlap in the expansion behavior for the

AASHTO and ASTM cements examined here. An AASHTO Type II cement with the lowest silicates ratio showed similar expansion behavior to an ASTM Type II cement with the lowest tricalcium aluminate content (5%). From the expansion results presented here, it is clear that durability assessement from expansion data indicates the significance of C_3S/C_2S ratio, C_3A content and cement fineness on the expansion behavior of cements obtained from different sources. An observation that was also made in this study is the existence of different forms of calcium sulfates in the as-received cements. Most of the calcium sulfates existed in the hemihydrate form except for two cements X and B. for these two cements calcium sulfate was predominately in the form of gypsum for B and anhydrite in the case of X. As the solubility of these forms of calcium sulfates are different, they are expected to influence the initial calcium aluminate hydrates formation. It is suggested that the forms of calcium sulfates and their impact on concrete durability be addressed in a separate study.

Figure 3.25 : Expansion of Mortar Bars Cured in 5 %Sodium Sulfate Solution

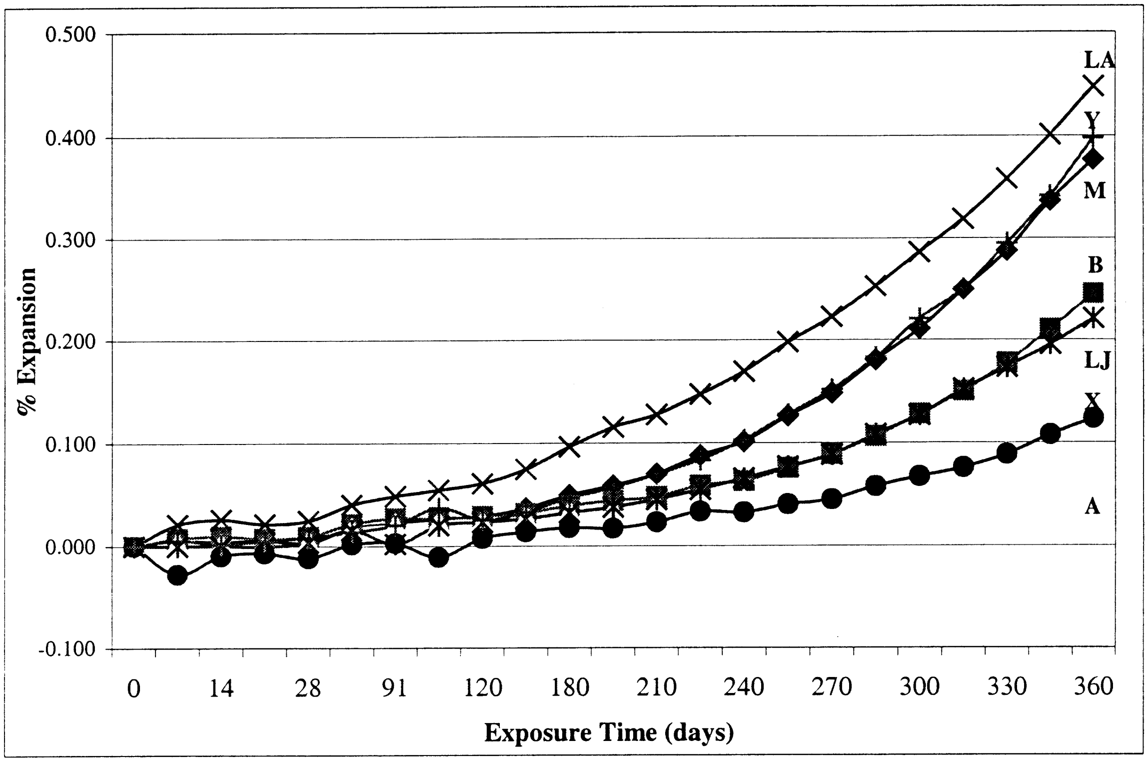


Table 3.10: Phases in As-Received Cements

CEMENT	C_3S/C_2S	C_3A	FINENESS(cm^2/gr)
LA	8.3	7	4070
Y	5.2	6	3850
M	4.3	7	4220
B	1.9	6	4010
LJ	5.6	5	3920
X	2.8	8	3930
A	2.4	6	3760

3.3.3 Rapid Chloride Permeability

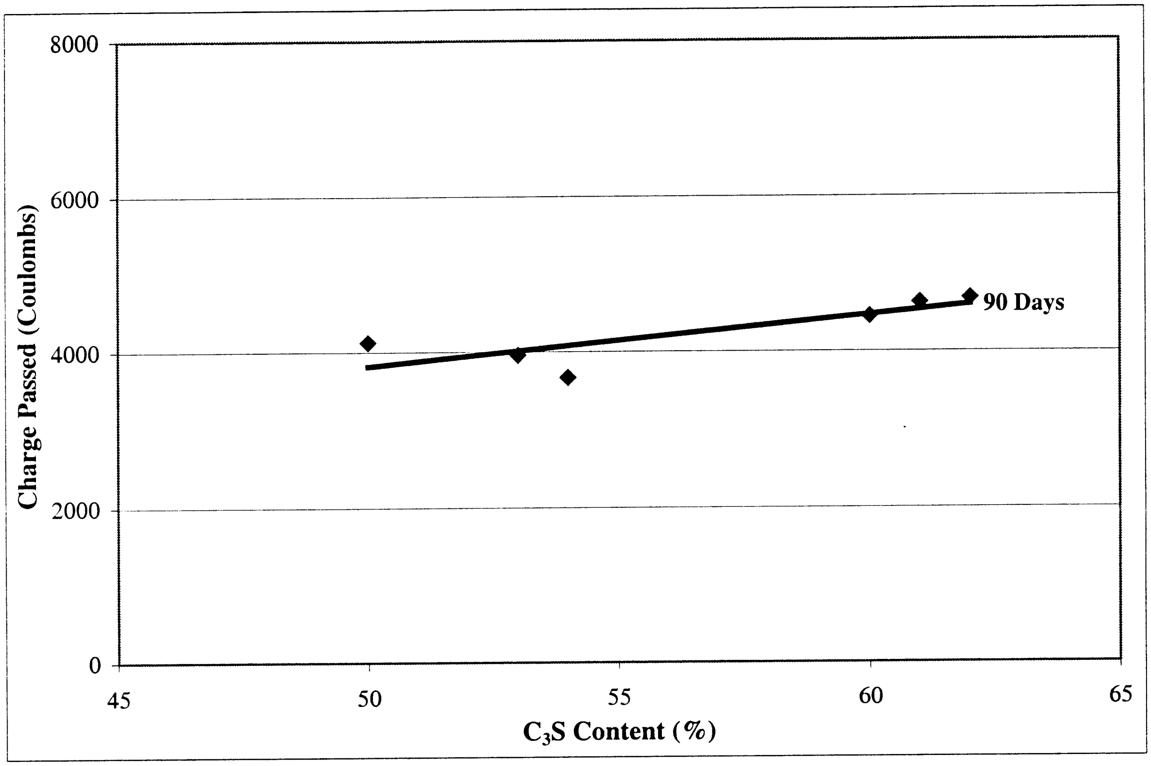
Concrete cylinders were cast in accordance with ASTM C192 and cured in a 5% sodium sulfate solution. For each concrete mix, three cylinders were cast for each testing age with a total of 21 cylinders for all of the as-received cements. The test cylinders were prepared using constant w/c and admixture dosage. The mixing conditions are the same as those used in assessing fresh concrete properties. The exact mix proportion is given in Table 3.8. Rapid chloride permeability tests were conducted by the Gainesville Materials Research Office of the Florida Department of Transportation in accordance with ASTM C1202. The results are given in Table 3.11 for all cement mixes for ages 28, 60 and 90 days.

Table 3.11 **: RCP Test Results for Specimens Cured in 5% Sodium Sulfate Solution.**

Cement	Charge Passed at 28 days of Curing (Coulombs)	Charge Passed at 60 days of Curing (Coulombs)	Charge Passed at 90 days of Curing (Coulombs)
M	5020	4743	4446
B	5473	4629	4122
A	5202	4055	3955
LA	3559	3618	3556
LJ	5741	4655	4621
X	4558	3970	3664
Y	5780	4714	4682

Due to the fact that concrete cylinders were cure in sodium sulfate solution to the specified testing ages, it should be anticipated, when analyzing the data, that the sulfate resistance of each cement will impact the permeability test results. The expansion data, presented in the previous section indicate the significance of tricalcium silicates and cement fineness on the sulfate attack. Whether expansive reactions are due to gypsum and/or ettringite formation, the effective result remains to be the same; that is, more opened microstructure that is prone to the ingression of aggressive ions. Considering the permeability data at 90 days, Figure 3.26, with the exception of LA cement, it is observed that in general ASHTOO cements [A, X and B] had lower permeability than ASTM cements [M, LJ and Y]. All of the ASTM cement permeability values are in the high range while for the ASSHTO cements the permeability values were in the moderate range with the exception of Cement B which has a fineness value of 4010 cm^2/g.

Figure 3.26 : **Chloride Permeability as a function of Tricalcium Silicate Content (Cured in 5 % Sodium Sulfate Solution)**



CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The following is a summary of the findings of the current investigation on the substitution of a cement source within a mix design:

1. Cements of the same type but from different sources exhibit wide variation in compound content, Blaine fineness, particle size distribution, and compound morphology. In addition, calcium sulfate was found to exist in different forms; that is, gypsum, hemihydrate and dihydrate.
2. Substitution of a cement source within a mix design, with the same cement type of a different source, results in different concrete setting behavior; that is, a difference in the initial setting time of up to 84 minutes.
3. In addition to differences in the setting behavior, maintaining the same mix design proportioning while varying the cement source, resulted in variation in the initial slump values by more than one inch. For an extended mixing period of 90 minutes some cements experienced a slump loss of 2 inches while others experienced a 1 inch slump loss.
4. Fresh properties that seem not to be affected with varying the cement source within a mix, for the cements examined here, is the air content. Variation in air content was less than 1%.
5. Concrete compressive strength varied by approximately 700 psi at 28 days with varying cement source.
6. Durability of concrete, assessed through mortar expansion, showed a wide variation in the deterioration behavior attributed to the variation of the cement source. Reported expansion at 480 days was above 1% for some of the Type II cements examined here and as low as 0.14% for others.
7. Concrete durability, assessed through rapid chloride permeability, yielded durability classification from moderate to high permeability for the

different cement sources examined in this study. RCP values were higher for higher C_3S content.

The following are suggested recommendations based on the findings of this study:

1. Substitution of a cement source within a mix design should not be allowed without appropriate testing and justification that includes not only fresh concrete properties but also sulfate and chloride permeability when the original mix design requires such properties.

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