Investigation of Calcite Fineness on the Physico-Mechanical Properties of Ordinary Portland Cement

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ABSTRACT

Investigation of Calcite Fineness on the physico-Mechanical Properties of Portland Cement.

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Addis Ababa University, 2013

The use of limestone as a partial replacement of Ordinary Portland Cement (OPC) has several advantages like Technical, Economical and Environmental.

The present study aimed at investigating the physico-mechanical properties of fresh and hardened cement pastes of Portland limestone cement (PLC) made by blending clinker, gypsum and fined calcite. Where the percentages of limestone are 0%, 5%, 10%, 15%, 20% and 25% by mass and the particle sizes are 6 μm, 12 μm, 18 μm and 24 μm used to replace a part of Ordinary Portland cement. The resulting specimens were compared for, standard consistency, setting time, soundness, and compressive strength. Generally, the results show that as the Calcite fineness increase, the compressive strengths of PLC also increases for some amount whereas, when the amount of fined calcite increases in PLC the compressive Strength of the mortars decreases. However, the specimens have competitive strength for the replacement value of Calcite powder up to 20% by mass of clinker with particle size 6 μm, These represents a significant reduction of energy, raw material consumption, costs and environmental advantages by reducing CO_2 emission over ordinary Portland cements. Setting time, both initial and final setting times, result were decreased with an increase Calcite in PLC. Furthermore, at the same level replacement, the cement pastes of $6\mu m$ and $12\mu m$ of limestone show lower setting time than those using, $18\mu m$ and $24\mu m$, respectively.

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GLOSSARY OF TERMS AND ABBREVIATIONS

C: CaO; S: SiO_2; A: Al_2O_3; F: Fe_2O_3; S: SO_3

AFt:	Aluminate-Ferrite-Trisubstituted or Ettringite
AFm:	Aluminate-Ferrite-Monosubstituted, Monosulphoaluminate, or Monosulphate
A5-F6:	Amount of filler Percentage 5% by mass with Fineness 6 μm
ASTM:	American Society for Testing and Materials
C_3A:	Tricalcium Aluminate
C_4AF:	Tetracalcium Aluminoferrite (ferrite phase)
CPC:	Controlled Portland Cement
C_3S:	Tricalcium Silicate (alite)
C_2S:	Dicalcium Silicate (belite)
LF:	Limestone Fine (Powder)
MCE:	Mugher Cement Enterprise
OPC:	Ordinary Portland Cement
PLC:	Portland Limestone Cement
PSD:	Particle Size Distribution
W/C:	Water/Cement ratio
XRF:	X-RayFluorescence

CHAPTER ONE

1.1. INTRODUCTION

1.1.1. Background to Research

Cement production and consumption are considered important indicators of economic growth. Considering the amount of produced cement, concrete is clearly the most used construction material.

Portland cement was developed from natural cements made in Britain in the early part of the nineteenth century, and its name is derived from its similarity to Portland stone, a type of building stone that was quarried on the Isle of Portland in Dorset, England[1].

The majority of the cementitious binder used in concrete is based on Portland cement clinker, which is an energy-intensive process. In addition, it produces a large amount of greenhouse gas emissions, mostly CO_2, resulted of releasing CO_2 from limestone in the pyro-processing of clinker. On the other hand, the concrete industry is one of the major consumers of natural resources. In order to reduce energy consumption, cost, CO_2 emission and increase production, cement plants produce blended cements are comprised of supplementary cementitious materials such as slag, natural pozzolan, fly ash and limestone.

Nowadays limestone has been widely used to add or replace a part of Portland cement to produce Portland limestone cement and Portland composite cement.

The Limestone is calcareous sedimentary rock mainly consisting of calcium carbonate ($CaCO_3$), commonly called calcite. Limestone is used in cement and concrete for

various purposes, namely, as a raw material for clinker production and as coarse or fine aggregate. Limestone powder is produced by finely grinding limestone in quarrying operations and has been suggested for use as an additive in portland cement.

The use of Portland cement containing limestone is a common practice in European countries. The recent European Standard EN 197 identifies two types of Portland limestone cements (PLC): Type II/A-L containing 6–20% and Type II/B-L containing 21–35%. In addition, the inclusion of 5% of filler material that can be calcareous is accepted in all cements. During the 1990s, Latin American countries also moved in this direction and the use of limestone filler in Portland cements (PCs) was standardized. After many years of discussion, in 2004 the ASTM C150 standard specification for Portland cement was modified to allow the incorporation of up to a 5% mass fraction of limestone in ordinary Portland cements [2].

An extensive survey of the literature conducted by the Portland Cement Association [3] concluded that "in general, the use of up to 5% limestone does not affect the performance of Portland cement. This type of cement is formulated to achieve certain goals in technical, economic, and ecological fields. Among the technical benefits, there are the increase of early strength, the control of bleeding in concrete with low cement content, and the low sensibility to the lack of curing [4]. The economic benefits are related to development similar to that of Portland cement at low production and investment costs per ton [5]. The ecological advantages are the possibility to obtain cement with a significant reduction of CO_2 and NO_2 emissions per ton of cement manufactured the conservation of fossil fuels and mineral resources.

Moreover, in response to economic development aiming at using natural resources, countries like Ethiopia have been pursuing policies that aimed at optimizing the use of local materials. Ethiopia for example- is boasting an ambitious program for the Greatest Renascence Dam (Abay Dam), and infrastructure facilities. The program includes the construction of High way roads, Residential house, and other basic infrastructure such as schools, universities and hospitals. This program has raised challenges to the construction industry among which is the availability of good quality construction materials, especially those for concrete production. In Ethiopia, crushed limestone are surplus, so it is inevitable to do further study to use optimal amount of crushed calcite (limestone) as the main source of aggregates used in concrete.

1.1.2. Ethiopian's Cement Industry

The cement industry in Ethiopia has grown steadily over time. At the time of freedom in 1991G.C, there were only 3 cement factories, Dire Dawa was established in 1938E.C Addis Ababa Cement Plant in 1957 E.C and Mugher Cement Enterprise first line in 1976 E.C and second line in 1982 E.C [6].

Cement is mainly produced in two forms: Ordinary Portland Cement (OPC) and Portland Pozzolana Cement (PPC). In Ethiopia, approximately 18 percent of the total production was historically OPC, while 82 percent was PPC. The grades of the two cement types produced in Ethiopia are OPC-type CEM II; grade 42.5 and PPC-type CEM II; grade 32.5. Due to increased infrastructure construction the demand for OPC is growing fast and is now taking a share of up to 25- 30% of the total supply [7].

Currently, there are 18 cement factories, which produce 12.46 million tonnes of cement annually. The National Cement new project, CH Clinker, Ture, Dire Dawa

and Ethio-Cement factories are expected to fully launch production this Ethiopian budget year (2012). Following the new policy of the government's five-year Growth and Transformation Plan, the high cement demand as compared to supply not balanced. Over the past four years, cement consumption has risen by an average of 35% each year, well above the growth rates seen during this period for both overall GDP growth (11%) and the construction sector (10%). This annual growth rate is expected to remain almost the same for the next five years.

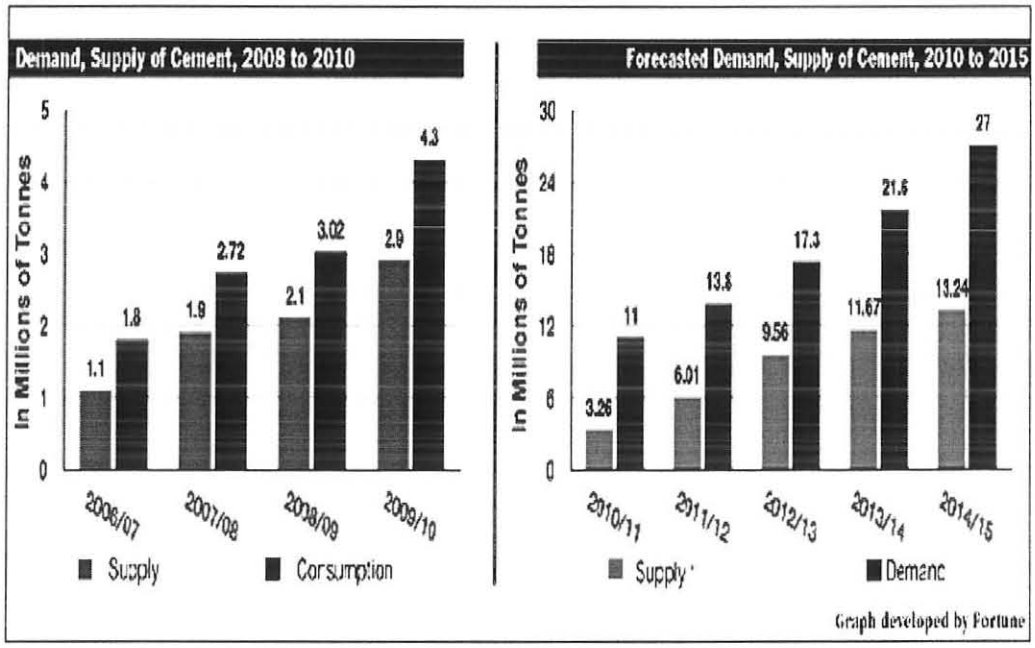


Figure: 1.1. Cement Consumption [8].

The government of Ethiopia is endeavoring to attain the five-year cement production target, which envisions raising the national cement production capacity to 27 million tonnes per year.

In view of high demand during the period of free economic policy, a number of new plants are in progress to set up and many others introduced great extensions to increase their existing output [8].

The past data of Ethiopian's cement production from 2000-20011 is given in Table. 1.1

Table: 1.1. Ethiopian's cement plant production capacity from 2000-20011G.C.

Plant	Annual production capacity of cement (tons)
Derba MIDROC Cement Plc	2,300,000
Mugher Cement Enterprise	2,200,000
Mossobo Cement factories	2,200,000
East Cement	750,000
Capital Cement	450,000
Enchini Medrock Cement factories	300,000
Abissinia	108000
CGC Cement	150000

Due to lack of research and development activities in the cement manufacturing industry of Ethiopia in one hand and shortage of qualified material scientists on the other hand, very little research has been carried out on the use of indigenous materials as cement substitutes. This research will help in filling this gap at National level.

1.1.3. Scope of the Study

The scope of this research involves preparation of Portland limestone cement (PLC) samples by grinding clinkers, gypsum, and limestone with different amount and fineness level using distinct raw mix-design. Finally, by adding distilled water on the prepared sample the following Cement Tests will be cover:

Chemical composition, Standard consistency, Setting time, Expansion (Soundness), Compressive and Flexural strength of the specimens.

1.1.4. Outline of the Thesis

This paper has six chapters and addresses various aspects of Portland cement as follows.

Chapter one explains background information of cement and literature review of the research. This chapter provides a good understanding of manufacturing process of cement, physical and chemical properties of Calcite, Portland cement, Portland limestone Cement (PLC) and hydration of cement.

Chapter two describes the general and specific part of objectives. These determine what to analyze, develop, investigate, and explore to address the point of research.

Chapter three introduces methodology of the Research. This is done under two headings: (i) Experimental materials, for example, Clinker, Gypsum, Sand, Calcite, and Water. (ii) Experimental program, which addresses Variation in physical and chemical properties and compound composition of cement. Detailed description of the methods adopted in preparing the test samples comprising selecting raw material and Clinker, grinding, raw-mix designing, casting, curing and testing of samples are also described in this chapter.

Chapter four give further details about experimental Results and Discussions. These describe the effect of fined calcite in ordinary Portland cement on physico-mechanical properties.

Chapter five gives economical and environmental analysis on the experimental results

Chapter six draws the main conclusions from this research work and gives recommendations for future research.

1.2. LITERATURE REVIEW

Concrete is made from a properly proportioned mixture of hydraulic cement, water, fine and coarse aggregates, and often, chemical or mineral admixtures. The most common hydraulic cement used in construction today is Portland cement.

The successful use of concrete in construction depends not only on knowing the right proportions of materials to use for a particular job, but also, knowing how to select the right materials. This requires a knowledge of the properties of each of the materials and understanding the tests used to measure those properties.

There are several varieties of hydraulic Portland cement, as recognized by the American Society for Testing and Materials (ASTM C 150), which vary in their properties. Hydraulic cement is defined as cement that sets and hardens by chemical reaction with water and is capable of doing so underwater [9].

Portland cement is a finely ground gray powder chemically formed by combining raw materials containing calcium oxide (CaO), silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3), heating this mixture to a high temperature, and then grinding the resulting material, called clinker. In the following sections, we will review the production, composition and properties of the various Portland cements.

1.2.1. Cement manufacturing process

Historically, the development of the cement manufacturing processes are categorized in four process routes namely dry, wet, semi wet and semi dry processes [10]. Apart of these techniques, dry process is the most economical and advanced technique. Therefore, the following review covers only the dry process.

In principle, the manufacture of Portland cement is simple. It is made from abundant raw materials. Intimately blended raw materials, usually limestone and clay, are heated in a kiln from 1400 to 1600 ^{0}C (2550 to 2900 ^{0}F), the temperature at which these materials chemically interact to form the cementitious compounds in Portland cement. Considerable attention is paid to the various stages of processing to maintain good quality control. This processing requires 60 to 80 separate and continuous operations, the use of a great deal of heavy machinery and equipment, and the consumption of large amounts of fuel and electrical energy. Typical steps in the manufacture of Portland cement are illustrated in Fig. 1.2.

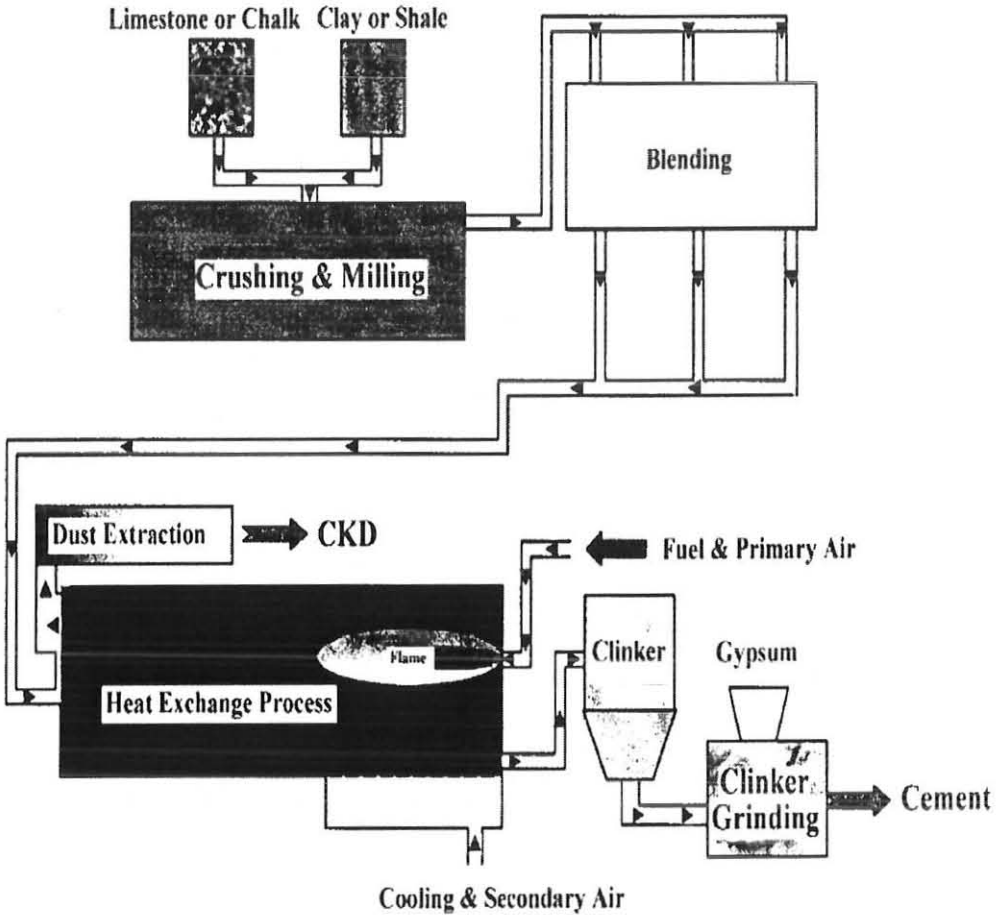


Figure: 1.2. Cement manufacturing process [11]

Raw material preparation

The manufacture of Portland cement requires blending raw materials to obtain appropriate proportions of lime (CaO), silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). High-quality cements require raw materials of proper chemical composition and proportioned to precise quantities. Limestone, which consists primarily of calcium carbonate, is the most common source of lime, although other raw materials such as dolomite, chalk, shell deposits, and calcareous muds are used for this purpose. The location of cement plants is most often determined by the occurrence of suitable calcareous (lime-rich) deposits, and proximity to the market area. Clays or silts are preferred since they are already in a finely divided state; but shales, schist, and other argillaceous rocks are also used.

A nearby quarry is the source of the basic material. The raw material is transported to the primary crusher by truck or rail. Upon leaving the primary crusher, the material is then conveyed to a secondary crusher system where it is reduced to maximum size of usually less than 25 mm. The crushed material is then stored in a raw material storage facility.

The ground material is then transported by pneumatic means through a pipeline to storage and blending silos. The material is constantly blended and checked for uniform chemical composition. A finely ground mixture typically consisting of approximately 75% calcium carbonate, 15% silicon dioxide, 3% aluminum oxide, and 2% iron oxide provides the major components in the raw materials. The raw materials also contain a certain amount of volatiles (less than 5% by mass). Some of these volatiles are alkalis (potassium oxide and sodium oxide), sulfur, and chloride [12]. In addition to the major elements, which make up cement, smaller concentrations of

almost every other element will be present in the raw materials. Magnesium, titanium, manganese, and phosphorous are common but they are minimized to prevent potentially deleterious effects on cement burning and quality. Minor trace metals can also be present in the raw materials but are also kept at low levels to avoid adverse effects [13]. A uniform mixture also ensures that the kiln temperature can be kept fairly constant, near the optimum burning temperature.

Pyroprocessing

Once the raw feed has been satisfactorily ground and blended, it is ready to enter the kiln where pyroprocessing (burning) occurs. The rotary kiln is a long steel cylinder inclined a few degrees from the horizontal, and rotated at 60 to 200 rpm about its axis. Modern kilns are up to 6 m (20 ft) in diameter and over 180 m (600 ft) long, with a production capacity exceeding 5000 tons/day. The raw feed enters at the high end and the combination of rotation and inclination slowly moves the material the length of the kiln.

Burning fuel, consisting of powdered coal, fuel oil, or gas, is forced into the lower end of the kiln, producing temperatures of 1400 to 1600 ^{0}C (2550 to 2900 F) in the hottest part of the kiln. As the raw feed moves through the kiln, water and carbon dioxides are driven off from the constituents in the form of gases (calcination). The residual oxides recombine in the hottest part of the kiln, the clinkering zone, to form new chemical compounds. Heating to these high temperatures consumes large quantities of energy, much of which is lost with the exiting gases. Often the heated exhaust gases are used to raise the temperature of the incoming feed in special heat exchangers called preheaters.

Final processing

Material exiting the kiln is known as clinker; dark-gray, porous nodules (13 to 50 mm) in diameter that are still hot. The four major compounds of clinker that constitute approximately 95% of the clinker, by mass are: tricalcium silicate (C_3S) (35 – 65%), dicalcium silicate (C_2S) (10 – 40%), tricalcium aluminate (C_3A) (0 – 15%), and tetracalcium aluminoferrite (C_4AF) (5 – 15%) [12]. C_3S and C_2S are commonly referred to as alite (impure C_3S) and belite (impure C_2S), respectively. Alite typically contains 3 – 4% of substituent oxides, the most significant of which are Fe_2O_3, MgO, and Al_2O_3. Belite may contain 4 – 6% of substituent oxides of which Al_2O_3 and Fe_2O_3 are most common. Alite and belite constitute about 65 – 75% of PC and the combined total content of the four principal clinker compounds in PC is approximately 85%.

The clinker is cooled by forced air, then conveyed to storage or immediately to ball mills where it is ground to the fine gray powder. A small amount of gypsum is interground with the clinker in order to control setting behavior, strength development, and volume stability. The ball mills used for finish grinding are similar to the mills used to grind the raw materials. They are equipped with air separators that remove the fine particles and return the coarse material to the mills for further grinding. The final cement is so fine that 90% or more passes through a sieve having 60 openings per square millimeter. The cement is stored in large silos until ready for distribution. Cement is typically shipped in bulk by truck, train, or barge, although most plants also have equipment for bagging cement into bags [12].

1.2.2. Types of Portland cement

There are different standards for classification of Portland cement. The two major standards are the ASTM C150 standard, used primarily in the U.S., and European EN-197-1 standard.

American Standard

Five principal types of Portland cement are listed in ASTM C 150. The typical compound composition of these cements is given in Table 1.2. It can be seen that the sum of C_3S + C_2S is approximately 75% by mass for each of the five types, so Portland cements could be called calcium silicate-based cements.

Table: 1.2. Typical compound composition of Portland cement [14]

Cement Type	ASTM C 150	C_3S	C_2S	C_3A	C_4AF	Fineness (m^2/Kg)
I	General purpose	55	19	10	7	370
II	Moderate sulfate resistance(and moderate heat of hydration as option	51	24	6	11	370
III	High early strength	56	19	10	7	540
IV	Low heat of hydration	28	49	4	12	380
V	Sulfate-resistant	38	43	4	9	380

European standard

EN 197-1 defines 5 classes of common cement that comprise Portland cement as a main constituent. These classes differ from the ASTM classes [15].

I. **Portland cement**: comprising Portland cement and up to 5% of minor additional constituents.

II. **Portland composite cement**: Portland cement and up to 35% of other single constituents.

III. **Blast furnace cement**: Portland cement and higher percentages of blast furnace slag.

IV. **Pozzolanic cement**: Portland cement and up to 55% of pozzolanic constituents.

V. **Composite cement**: Portland cement, blast furnace slag and pozzolana or fly ash.

Constituents that are permitted in Portland composite cements are blast furnace slag, silica fume, natural and industrial pozzolans, siliceous and calcareous fly ash, burnt shale and limestone [15].

1.2.3. Physical and Chemical Properties of Portland Cement

1.2.3.1. Physical Properties of Portland Cement

ASTM C 150 has notified certain requirements regarding physical properties for each type of cement. These properties comprise: (i) fineness (ii) specific gravity (iii) soundness, (iv) standard consistence, (v) setting time, (vi) compressive strength, (vii) heat of hydration and (viii) loss of ignition. All of these properties have an effect on the functioning of cement in concrete. Out of these properties only those which are important are discussed in the following section [2].

Fineness

Fineness of cement is the total surface area of cement grains available for hydration. It determines the level of grinding of cement clinker in grinding mill of plant and affects the rate of hydration. Greater the fineness more is the surface available for hydration, resulting greater early strength and more rapid release of heat (the fineness of Type III is greater than that of Type I cement) [16]. The Wagner Turbidimeter and the Blaine's air permeability test for determining cement fineness are both required by the American Society for Testing Materials (ASTM) and the American Association for State Highway Transportation Officials (AASHTO). Average value of fineness of modern cement ranges from 3,000 to 5,000 cm^2/g [17].

Consistency

Consistency indicates the degree of density or stiffness of cement. Therefore, it is necessary to determine the amount of water content for a given cement to get a mixture of required consistency. Consistency of cement is measured by vicat apparatus. The paste is said to be of standard consistency, when the penetration of plunger, attached to Vicat apparatus, is 33-35 mm.

The moisture content of the standard paste is written as a percentage by weight of the powdered cement. The normal range is between 26-33%. This test precedes the test of cement for soundness, setting time, tensile strength or for compressive strength [18].

Setting Time

The setting characteristics of portland cement paste are defined by initial set and final set. Initial set indicates the approximate time at which the paste begins to stiffen

considerably, while final set roughly indicates the time at which the paste has hardened and can support some load. These times of set are tested according to standardized procedures and have no special relationship to concrete setting behavior. Generally, initial set occurs within 1 to 4 h, and final set in 3 to 6 h. Setting times are affected by minor constituents in the cement such as alkalis and sulfates, by fineness, water-cement ratio, ambient temperature, and inclusion of mineral and chemical admixtures. Concretes generally set more slowly than cement paste because of the higher water-cement ratios. There are two types of abnormal setting behavior that should be mentioned:

(i) *False set*: This refers to the rapid setting that occurs without the liberation of much heat. Plasticity can be regained by further mixing without the need to add more water, and thus is not a problem where concrete is mixed for long periods (ready-mixed concrete). Increasing mixing time when possible will help to reduce a false set problem.

(ii) *Flash set (or quick set)*: This behavior is accompanied by the liberation of considerable heat. The plasticity of the mixture cannot be regained with additional mixing or water [19].

Soundness

Soundness refers to the capability of the cement paste to maintain its volume after setting, and is associated with the existence of extreme amounts of free lime or magnesia in the cement or supplementary cementitious material. A cement paste should not undergo a large change in volume once it has been set. However, some expansion may occur due to gradual hydration or due to some other reactions of some

compounds there in the hardened cement, namely free lime, magnesia and calcium sulfate. Free lime absorbs moisture and expands many times to its original volume and develops considerable heat and thus causes disintegration of concrete in which this cement is used. Expansion in OPC is limited to 10 mm or 0.5%.

It is essential that cement concrete does not undergo large changes in volume after setting. This change in volume is known as unsoundness and may cause cracks, distortion and disintegration of concrete. Bektas et al. [20] investigated the effect of Portland cement fineness on the results of ASTM C1260 tests. He concluded that mortar-bar expansion was promoted with increased cement fineness regardless of clinker alkali, aggregate reactivity or soak solution normality.

Compressive Strength

The compressive strength of concrete is one of the most important mechanical properties. In most structural applications, concrete is employed primarily to resist the compressive forces. In those cases where other stresses (for e.g. tensile) are of primary importance, the compressive strength is still frequently used as a measure of the resistance because this strength is the most convenient to measure. For the same reason, the compressive strength is generally used as a measure of the overall quality of the concrete.

As shown in Fig. 1.3, the rate of early strength development depends on cement composition. Other factors that affect strength gain are cement fineness, use of supplementary cementitious materials, curing temperature, chemical or mineral admixtures, water-cement ratio, and curing conditions.

The rate of early strength gain is directly correlated with the rate of hydration. The ultimate strength reached does depend to some extent on the initial rate of strength gain [20]. The faster the early strength gain, the lower the ultimate strength, as can be seen in Fig. 1.2.

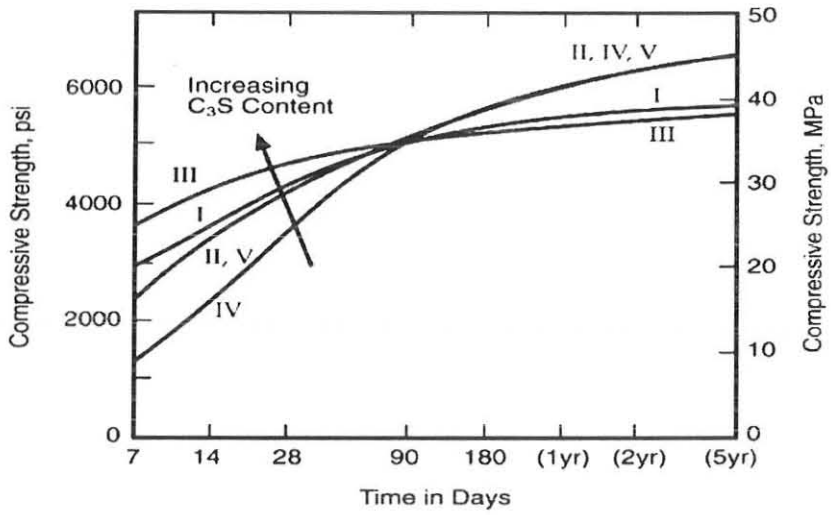


Figure: 1.3. Rates of strength development for concrete made with different cement types [21].

1.2.3.2. Chemical Properties of Portland Cement

All cements are classified based on their chemical composition and most its Physical properties are determined using their chemical properties. Therefore, a basic understanding of Portland cement chemistry can help one understand how and why it behaves as it does.

ASTM C 150 imposes the standard chemical needs for each type. ASTM defines the following phase compositions in Portland cement: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF) [22]. The actual compounds are mostly multifaceted chemical crystalline and

amorphous compositions, named by cement chemists as "elite" (C_3S), "belite" (C_2S), and different forms of aluminates. The performance of each type of cement depends on the concentration of these components. Role of these compounds, their hydration behaviour, and their effect on the behaviour of cements are given in full detail in literature. Some of the most comprehensive references regarding the chemistry of cement consists of those written by [23,24] Various analytical methods such as X-ray diffraction and analytical electron microscopy are used by scientists in order to explain in detail the reaction of cement with water (hydration process) and to enhance its properties.

1.2.4. Portland Cements Hydration

Anhydrous Portland cement cannot bind sand and rock; it acquires the adhesive property only when mixed with water. This is because the chemical reaction of cement with water commonly referred to as the hydration of cement, yields products that process setting and hardening characteristics.

1.2.4.1. Mechanism of Hydration

The hydration of Portland cement (PC) involves the reaction between clinker minerals, calcium sulphate and water. Although extensive research has been conducted on the hydration of PC, the hydration mechanism is still not fully understood. The hydration process has been comprehensively reviewed by Tayler [12]. It is believed that the general principle of hydration is the dissolution of anhydrous phases to the precipitation of much less soluble products, typically colloidal and microcrystalline hydrates that form the hardened paste [25].

The reaction between PC and water is mostly an exothermic reaction that takes place in a sequence of stages. Traditionally, isothermal conduction calorimetry has been used to follow the progression of hydration by monitoring the rate of heat liberation of the cement paste. Most researchers have identified five stages of PC hydration. A typical isothermal conduction calorimetric curve for a Type I PC is shown in Figure 1.3 with the stages of hydration indicated as: (1) initial reaction (pre-induction), (2) induction, (3) acceleration, (4) deceleration, and (5) slow continued reaction [11].

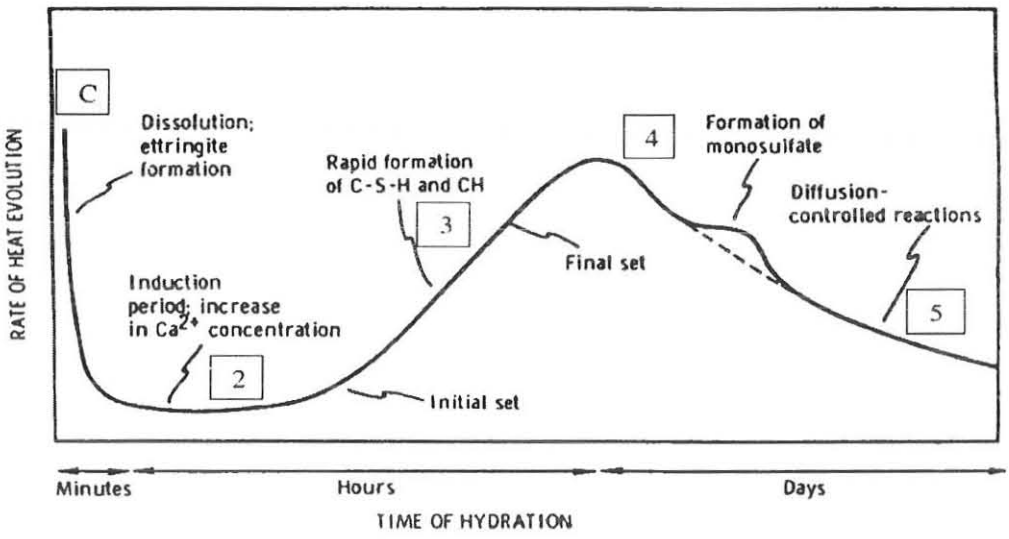


Figure: 1.4. Heat evolution of PC paste during hydration stages: (1) initial reaction, (2) induction, (3) acceleration, (4) deceleration, and (5) slow continued reaction [26].

The hydration products primarily affecting the strength are calcium silicate hydrates (C-S-H phases). Further hydration products are calcium hydroxide, sulfatic hydrates (AFm and AFt phases), and related compounds, hydrogarnet, and gehlenite hydrate. Calcium silicates or silicate constituents make up over 70 % by mass of silicate-based cements. The hydration of these compounds and the properties of the calcium silicate hydrates produced are therefore particularly important. Calcium silicate hydrates

contain less CaO than the calcium silicates in cement clinker, so calcium hydroxide is formed during the hydration of Portland cement. This is available for reaction with supplementary cementitious materials such as ground granulated blast furnace slag and pozzolana. The simplified reaction of alite with water may be expressed as:

$$2Ca_3OSiO_4 + 6H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$$

This is a relatively fast reaction, causing setting and strength development in the first few weeks.

The reaction of belite is

$$2Ca_2SiO_4 + 4H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2$$

This reaction is relatively slow, and is mainly responsible for strength growth after one week.

It is widely accepted that gypsum is added to PC to control the reaction of C_3A. Most researchers believe that this allows the setting and hardening to be controlled by the C_3S and water reaction [26]. Gypsum and alkali sulfates provide readily soluble sulfate and it reacts with tricalcium aluminate ('C_3A') to form various aluminate and sulfoaluminate phases, collectively referred to as Ettringite phases [27, 28]. Some examples are:

$$3CaO.Al_2O_3(s) + 3CaSO_4(s) + 32H_2O(l) \longrightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O(s)$$

$$3CaO.Al_2O_3(s) + 3CaSO_4(s) + 12H_2O(l) \longrightarrow 3CaO.Al_2O_3.3CaSO_4.12H_2O(s)$$

The AFt continues to form if sufficient sulfate ions are present in the solution. Once the sulfate is depleted, the remaining C_3A reacts with the AFt to form monosulphates (AFm).

$$3CaO.Al_2O_3.3CaSO_4.32H_2O(s) + 3CaO.Al_2O_3(s) + 4H_2O \longrightarrow 3Ca_4(AlO_3)_2(SO_4).12H_2O$$

The calcium aluminoferrite C_4AF reacts slowly due to precipitation of hydrated iron oxide.

$$2Ca_2AlFeO_5 + CaSO_4 + 16H_2O \longrightarrow Ca_4(AlO_3)_2(SO_4).12H_2O + Ca(OH)_2 + 2Fe(OH)_3$$

The pH-value of the pore solution reaches comparably high values and is of importance for most of the hydration reactions [29].

A representation of the relative volumes of the major compounds in the microstructure of hydrating PC pastes as a function of time is shown in Figure: 1.5.

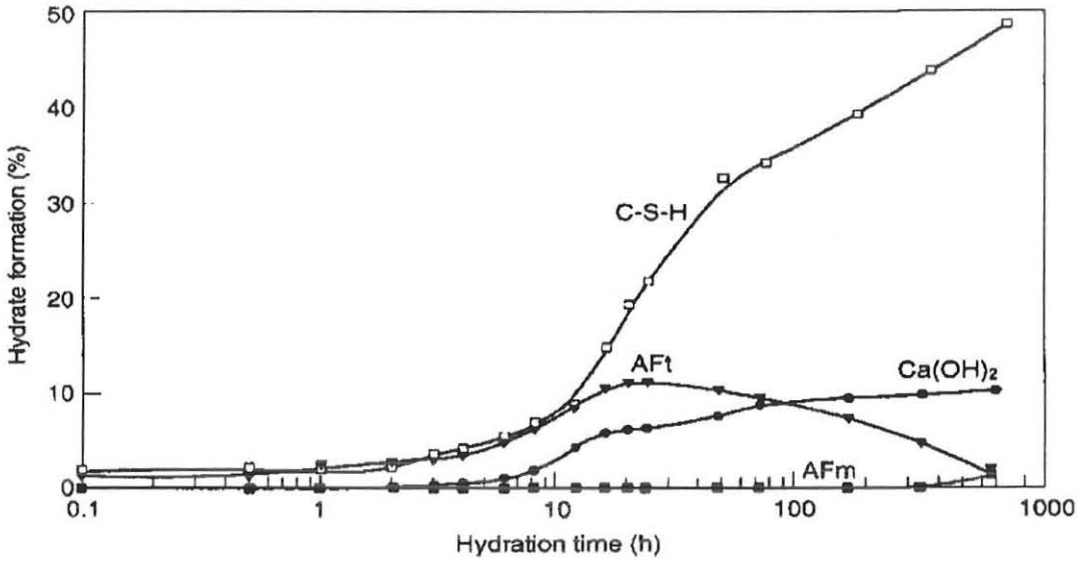


Figure: 1.5. Relative volumes of the major compounds in the microstructure of hydrating PC pastes as a function of time [28].

Initial Hydrolysis (Pre-induction Period)

The first stage of PC hydration is initial hydrolysis. As soon as PC contacts water, an initial heat peak occurs that mainly involves C_3A, C_4AF, alkali sulfates, free lime, and Calcium sulfates. The C_3A and C_4AF first react very rapidly and exothermally, which results in the contribution of calcium and aluminate ions into solution. Iron is not typically soluble. The aluminate concentration then reduces within seconds due to the precipitation of AFt, which forms a layer over the cement particles. Alkali sulfates, hemihydrates, and gypsum provide the readily soluble sulfates which contribute to AFt formation at this stage. Free lime usually dissolves rapidly and exothermally but the amount varies widely depending upon its reactivity. Reactive free lime in sufficient amounts can lead to portlandite supersaturation [26].

The dissolution of alkali sulfates is very rapid and endothermic. The alkalis enter into solution and reach constant concentration within one minute of hydration. In order to balance the cations and anions in solution as SO_3 begins to combine with other elements to form AFt, the alkali sulfates are replaced by alkali hydroxides which rapidly increase the pH of the solution.

At normal temperatures, hemihydrate is the most soluble form of calcium sulfate, dihydrate is less soluble, and anhydrite is the least soluble. PCs that contain high levels of metastable sulfates – such as hemihydrate and calcium langbeinite – often react to form the precipitate phases gypsum and/or syngenite. These phases can lead to observable changes in workability [26].

Induction

The second stage of PC hydration is a period of reduced heat evolution after the initial reaction. The lack of heat evolution, however, does not mean there is nothing occurring. The slow formation of early C-S-H and AFt leads to an increase in viscosity [12].

According to Odler [28] there is a reaction which begins to slows significantly, $d\alpha/dt = 0.01\ day^{-1}$. The causes of the induction period and its termination have been the subject of many studies. The exact reason for this induction period is not known. Several theories have been proposed that involve some sort of mixture saturation from the intense burst of hydration in the pre-induction period. One theory states that the 'C-S-H' layer quickly covers the surface of dissolving 'C_3S', slowing the reaction. As time passes, the 'C-S-H' becomes more permeable and the reaction accelerates. Another theory states that the solution may become supersaturated with $Ca(OH)_2$ because the surfaces of $Ca(OH)_2$ crystal nuclei are poisoned by silicate ions. The high concentration of aqueous $Ca(OH)_2$ limits the rate of dissolution of the silicate species to negligible rates. Eventually the level of aqueous $Ca(OH)_2$ becomes too high and calcium hydroxide crystallizes, allowing the hydration reactions to continue. Another theory speculates that two types of 'C-S-H' are formed. The rate of "first-stage" 'CSH' is dependent on the concentration of aqueous $Ca(OH)_2$. As the concentration of aqueous $Ca(OH)_2$ decreases, the production of "first-stage" 'C-S-H' stops, causing induction. Hydration resumes later when the thermodynamic barrier for the nucleation of "second-stage" 'C-S-H' is overcome [28]. Taylor [12] stated that the rate of reaction in the induction phase is controlled by nucleation and growth of the C-S-H formed in the main reaction; the induction period ends when C-S-H growth begins.

The termination of the induction period coincides with crystallization of calcium hydroxide, referred to as *Portlandite*. The length of the induction period seems to depend upon how quickly the calcium concentration rises to reach the maximum calcium hydroxide supersaturation. This supports the idea that a certain minimum calcium hydroxide concentration is required for the onset of the acceleration stage [26]. Setting does not occur during the induction phase unless abnormal setting occurs. Flash set is a common form of abnormal setting and occurs when there is an inadequate supply of calcium and sulfate ions to react with the C_3A, which results in the early formation of monosulfoaluminate (AFm) phases. False set, another common form of abnormal setting, most commonly occurs when there is an excess of sulfate in the liquid phase leading to secondary gypsum formation. A false set paste can be re-mixed to regain its plastic form, while a flash set paste cannot.

Acceleration

Following induction, the reaction rate accelerates to approximately $d\alpha/dt = 1\ day^{-1}$. At this point, the hydration processes are limited by the nucleation and growth of the hydration products. This acceleration stage is characterized by rapid hydration of 'C_3S', followed slowly by the hydration of 'C_2S' [28].

The acceleration phase of PC typically represents the change from a plastic to rigid consistency (initial and final set) and early strength development. Setting is the formation of a network of partially hydrated cement particles connected by PC hydration products [30].

It is generally accepted that initial setting is controlled by the hydration of C_3S. Under normal conditions, initial set and the transition from the induction phase to the

acceleration phase are reported to be correlated. The termination of induction will typically not correlate with pastes that undergo abnormal setting (false or flash) since very little heat is evolved during false set. It is important to note that the termination of induction and the beginning of the acceleration are not always well-defined [26]. Final setting, as defined in ASTM C150, normally occurs near the mid-point of the acceleration phase.

There is a high rate of heat evolution during this phase. The acceleration phase of C_3S hydration performs very similarly to the acceleration phase of PC. In both instances, the main reaction is the formation of C-S-H and portlandite. It is generally accepted that the rate of hydration in the acceleratory period is controlled by the nucleation and growth of C-S-H. The rapid formation of hydrates leads to solidification and a decrease in porosity. Sulfates, and possibly other ions, are significantly adsorbed and/or entrapped by C-S-H [26]. The major heat peak of the PC hydration curve occurs at the end of acceleration [12].

Deceleration

The rate of C-S-H formation and portlandite decreases during the deceleration phase. This results in reduced rate of heat evolution. There is general agreement that the main reaction (C_3S hydration) makes a transition from chemical control to diffusion control sometime prior to the acceleration peak and continues in the deceleration phase. This is likely due to the precipitation of hydrates surrounding the C_3S particles, although the form of the diffusion barrier is not clear [26].

The sulfate in the liquid solution begins to decline due to continued formation of AFt as well as uptake by the C-S-H. The sulfate depletion typically occurs between 12 and

36 hours and is indicated by a small peak during deceleration. At the time of sulfate depletion there is a conversion of AFt formation to AFm formation. If there is an excess amount of sulfate in the liquid phase and depletion does not occur, AFt will continue to form until C_3A is depleted [26].

Slow Continued Reaction

The continuous strength gain and reduction in porosity of paste, mortar, and concrete occurs during the slow continued reaction phase, but at a continually decreasing rate.

Beyond one day, the only ions in solution above concentrations of a few mmol/l are potassium, sodium, and hydroxyl ions. The concentrations of these ions tend to rise slightly approaching a limit after about 28 to 90 days, primarily due to consumption of the fluid phase (from ongoing hydration) [12]. Although the strength and porosity development are important to the long term performance and durability of concrete, hydration studies during this phase are limited [31].

1.2.5. Limestone (Calcite)

The Limestone is calcareous sedimentary rock mainly consisting of calcium carbonate ($CaCO_3$), commonly called calcite. Limestone is used in cement and concrete for various purposes, namely, as a raw material for clinker production and as coarse or fine aggregate. Limestone powder is produced by finely grinding limestone in quarrying operations and has been suggested for use as an additive in portland cement. [32, 33].

1.2.5.1. Geological Formation of Calcite

Calcitic limestone of dimension-stone quality is predominantly found within the Jurassic Antalo limestone (central part of the country) and the Hamanlei Series (east-central part). The best exposures and the most interesting deposits of the Antalo Limestone are found in the central part of the Abay Valley, and side valleys such as the Jema, Wonchit and Muger valleys.

The *Jema* and *Wonchit* limestone deposits occur in the bottoms of the valleys of the same names. The lower part of the limestone unit is by far the most interesting, since this is the part where the bed thickness reaches more than one metre [34]. The limestone is essentially a calcareaous, fossilifereous sandstone with poorly developed structure; colour varies from brown to off-white. At the present time, these limestone deposits are not being exploited, due to difficult access (the access road is of poor quality) and locally closely spaced joints.

Large limestone deposits are also found in the eastern part of Ethiopia, in the *Harar-Hakimgara* areas. The Hakimgara limestone has beds varying from some tens of centimetres to several metres in thickness [35].

Generally, extraction of commercial-sized blocks is possible in the thicker beds, exceeding one metre in thickness, where the spacing of vertical joints is wide. The limestone is partly fossiliferous, and contains abundant stylolites. The colour varies between yellowish-brown and dark grey, the latter occurring in irregularly distributed reduction patterns. Quarrying operations are carried out by both the National Mining

Company and the Ethiopian Marble Industry in the vicinity of Harar. The limestone forms hills and the area is considered to have a large potential for easily accessible deposits [36].

1.2.5.2. Chemical and Physical Properties of Calcite

Chemical Properties of Calcite

Limestone is a naturally existing mineral that consists principally of calcium carbonate ($CaCO_3$). The chemical composition of limestone varies widely depending on the route by which they were formed, the sedimentary environment and the changes brought about by diagnosis.

Limestone is made up of varying proportion of chemicals such as calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), silica (SiO_2), alumina (Al_2O_3), iron oxide (FeO_3), sulphate (SO_3), and phosphors(P_2O_5) The main impurities in raw limestone (for cement) which can affect the properties of finished cement are magnesia, phosphate, leads, zinc, alkalis and sulfides [37].

Standard EN 197-1 requires that, in Portland limestone cement, the limestone contains at least 75% $CaCO_3$ by weight, with less than 1.2% clay and less than 0.2% organic material. One of the major impurities in limestone is magnesium carbonate ($MgCO_3$), which is deleterious for concrete. Consequently, the content of $MgCO_3$ is required being less than 4% [38].

Physical Properties of Calcite

Physical properties of all EN 197-1 cements (whether containing limestone or not) fall into three basic classes, 32.5, 42.5, and 52.5, which refer to the lower end of a 28-d

Strength Class	Compressive Strength (MPa)				Initial setting time, (min)	Soundness (expansion) (mm)
	Early Strength (N/mm^2)		Later Strength(N/mm^2)			
	At 2 day	At 7 day	At 28 day			
32.5N	-	≥ 16	≥ 32.5	≤ 52.5	≥ 75	≤ 10
32.5R	≥ 10	-				
42.5N	≥ 10	-	≥ 42.5	≤ 62.5	≥ 60	
42.5R	≥ 20	-				
52.5N	≥ 20	-	≥ 52.5	-	≥ 45	
52.5R	≥ 30	-				

strength range requirement [15]. Basic requirements are shown in Table 1.3.

Table: 1.3. Basic Physical Requirements of European Cements.
Due to significant differences between test methods, these values cannot be directly compared with ASTM or CSA requirements [15]

Consistency

Generally, as the amount of limestone increases, the water of consistency decreases slightly that up to 15%. The finely ground limestone (F5 and F10) have a positive effect on the consistency, they play the role of plasticizer. Beyond this percentage these fines have a thickening effect. The coarse particles (F15 and F29) have a weak effect with means on consistency [39].

Guemmadi et al [40] found that the consistency of low w/c cement pastes (w/c 0.24 - 0.26) varied with both the fineness and replacement level of limestone, but no clear trend was observed.

Setting Time

Based on the information provided in the literature, it appears that cements with limestone may have a slight effect on setting time; however this does not appear to be a concern for the addition rates of interest (i.e., up to 15%). In general, it has been reported that the influence of limestone on setting time was strongly related to the fineness of the limestone. As the limestone was ground finer, the setting time decreased [41].

El-Didamony et al. [42] reported that low levels of limestone addition (up to 5%) showed an increase in the set time of cement pastes; however, as the limestone content increased, the set time began to decrease, resulting in a similar final set between 10% and 15% addition rates as compared to the same cement without limestone. The times of set continued to decrease at higher rates of addition (20%). Moir and Kelham [43] also reported that higher replacement levels (about 20%) led to a shorter setting time, relative to a control without limestone.

Hooton [44] reported results from a study in which commercial cements were produced from the same clinker to manufacture ordinary portland cements and cements with up to 5% limestone. No consistent effect of the limestone on the heat of hydration or in setting times was observed.

Heikal et al. [45] reported on results where limestone was used as a filler (from 0% to 20% by mass). Heikal reported that all of these materials had a surface area of

approximately 310 m^2/g. They reported a decrease in setting time due to a particle packing effect as well as the carboaluminate reactions that occur in these materials; however, the results showed that the final set time was increased with limestone replacement.

Mounanga et al. [46] reported that limestone filler could be used to reduce the setting time for concrete systems containing fly ash and blast-furnace slag. They suggested synergistic benefits of using other supplementary cementitious materials in systems where a portion of the cement has been replaced with limestone.

Soundness

The effect of calcareous addition on the autoclave expansion of OPC has not been studied extensively. The recent findings show that the addition of calcareous material (limestone) up to the range of 5-7% in cement mortar has small influence on shrinkage as compared to siliceous additives. From the results of autoclave and Le-Chatelier expansion as observed by investigators there is no remarkable effect on the soundness of OPC paste with up to 10% replacement by additives [47].

Compressive Strength

Like other properties, the strength of concrete produced with portland-limestone cement (PLC) is influenced by the quality and quantity of the limestone, the clinker and other cement ingredients, and the particle size distribution of the finished cement.

Limestone contents up to 15% may actually increase early-age strength as a combined result of improving particle packing [48], increasing the rate of cement hydration [49; 50], and production of calcium carboaluminate [51]. Schmidt [52] reported

similar strengths for limestone levels up to 10%. However, Hawkins et al. [53] showed that finer grinding is required in some cases even at lower levels of limestone (up to 8%).

1.2.5.3. Hydration of Portland Cement Blended with Calcite

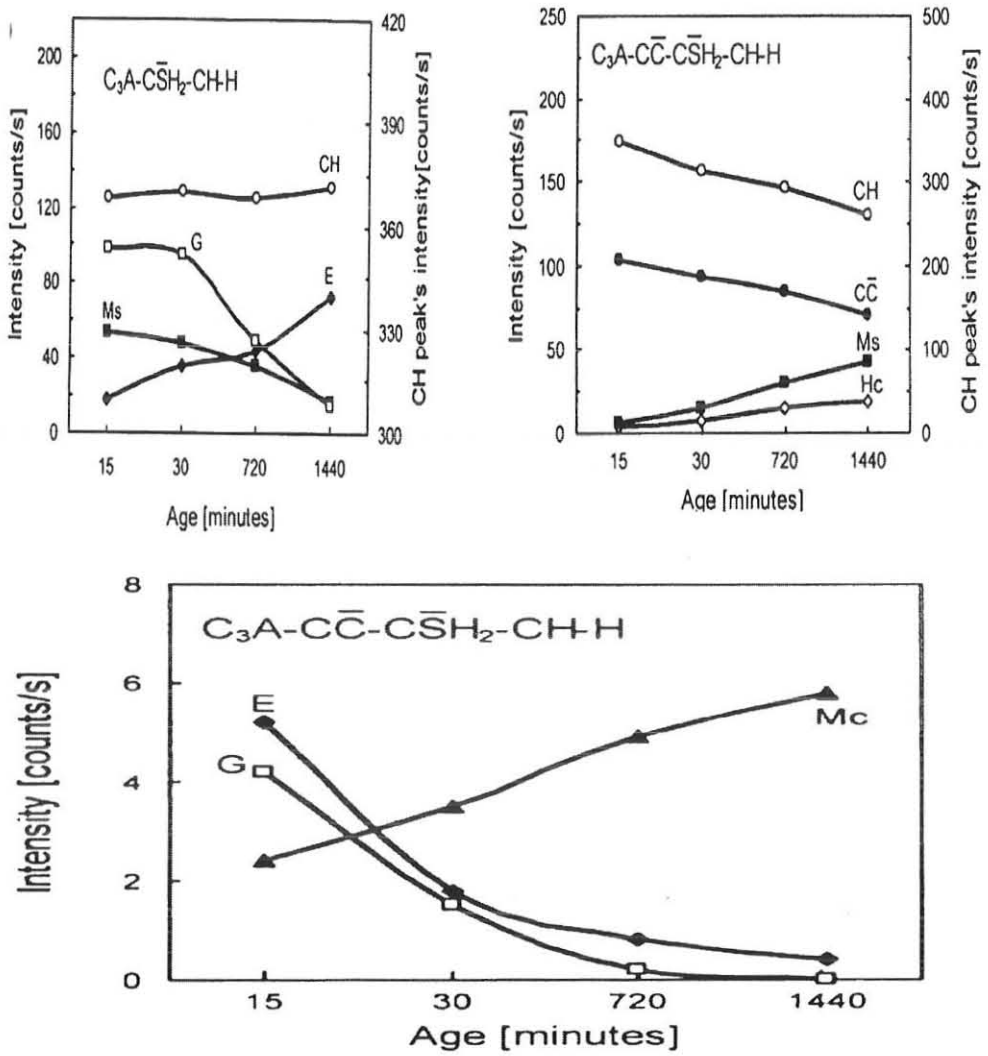
In order to get a better understanding of the hydration of PC blended with limestone powder, the effect of $CaCO_3$ on the hydration of clinkers is discussed first.

The effect on C_3A hydration

During normal PC hydration, C_3A and calcium sulfate react to form AFt. Sulfate depletion typically occurs before the C_3A consumption is complete, resulting in the conversion of AFt to AFm. The presence of calcium carbonate, however, alters these reactions. First, AFt formation is accelerated in the presence of calcium carbonate [54]. Second, the conversion of AFt to AFm is delayed or prevented due to the reaction between C_3A and calcium carbonate to form calcium carboaluminates. The formation of calcium carboaluminates occurs as some of the sulfate ions are replaced by carbonate ions during C_3A hydration [55].

More recently, Kakali et al. [56] found that $CaCO_3$ suppresses the conversion of AFt to AFm and reacts with C_3A to produce monocarbonate hydrate from the beginning in the $C_3A + CaCO_3$ system. According to Bonavetti et al. [57], in the $C_3A + CaCO_3 + CH + H_2O$ system, the phases of calcium monocarboaluminate and calcium hemicarboaluminate are observed, but no calcium tricarboaluminate is formed. In the $C_3A + CaCO_3 + CaSO_4 \cdot 2H_2O + CH + H_2O$ system, AFt, AFm, calcium monocarboaluminate and calcium hemicarbonate hydroxide are the hydration products. Compared with the $C_3A + CaSO_4 \cdot 2H_2O + CH + H_2O$ system, both the

formation of AFt and the conversion of AFt to AFm are accelerated. After 15 minutes AFt decreases and AFm increases 1.5 times up to 24 hours in the



$C_3A + CaCO_3 + CaSO_4 \cdot 2H_2O + CH + H_2O$ system as shown in Figure 1.6.

Figure: 1.6. Evolution of compounds in the $C_3A+CaCO_3+CaSO_4 \cdot 2H_2O+CH+H_2O$ system and the $C_3A+CaSO_4 \cdot 2H_2O+CH+H_2O$ system [57].

Ms = monosulfoaluminate E=ettringite, G=gypsum, CC = calcium carbonate

Mc = mono-carboaluminate, Hc = hemicarboaluminate, and CH = calcium hydroxide.

The effect on C_3S hydration

Calcium carbonate additions also influence the hydration of C_3S. Taylor [12] stated that the accelerating effect of carbonates in suitable concentrations appears to be confined to the initial stage of reaction. The accelerating effect occurs with pure C_3S as well as with PC and is, therefore, associated with the behaviour of that phase. Limestone enhances the rate of formation of C-S-H and CH, probably because it offers nucleation sites for growth. Ramachandran [58], however, reported that calcium carbonate also forms a complex with the hydrated products of C_3S.

More recently, Kakali et al. [56] reported that the addition of $CaCO_3$ accelerates the hydration of C_3S and results in the formation of calcium carbosilicate hydrate. The XRD study shows that the formation of calcium carbosilicate hydrate starts from 60 days. The above observations indicate that $CaCO_3$ not only modifies the hydration of C_3S, but also reacts with it to form calcium carbosilicate hydrate.

According to Andrej Ipavec et al. [59] in the early age of hydration of calcite containing Portland cement, hemicarboaluminate forms that converts into monocarboaluminate with the progress of hydration time. In their system, hemicarboaluminate formed within the first day and the content of hemicarboaluminate increased up to the third day of hydration. After 3 days of hydration, a conversion into monocarboaluminate began and the intensities of hemicarboaluminate reflections diminished gradually. They were still present in a 28 day hydrated sample, while none could be detected in a 100 day hydrated sample. Monocarboaluminate strongest reflection first appeared in a 3-day hydrated sample and from then on the intensities of monocarboaluminate reflections increased steadily

up to 100 days of hydration. Monocarboaluminate content of 6.871.1 wt % (for a 100 day hydrated sample) indicates that monocarbonate represents one of the major crystalline phases in hydrated calcite-containing Portland cement.

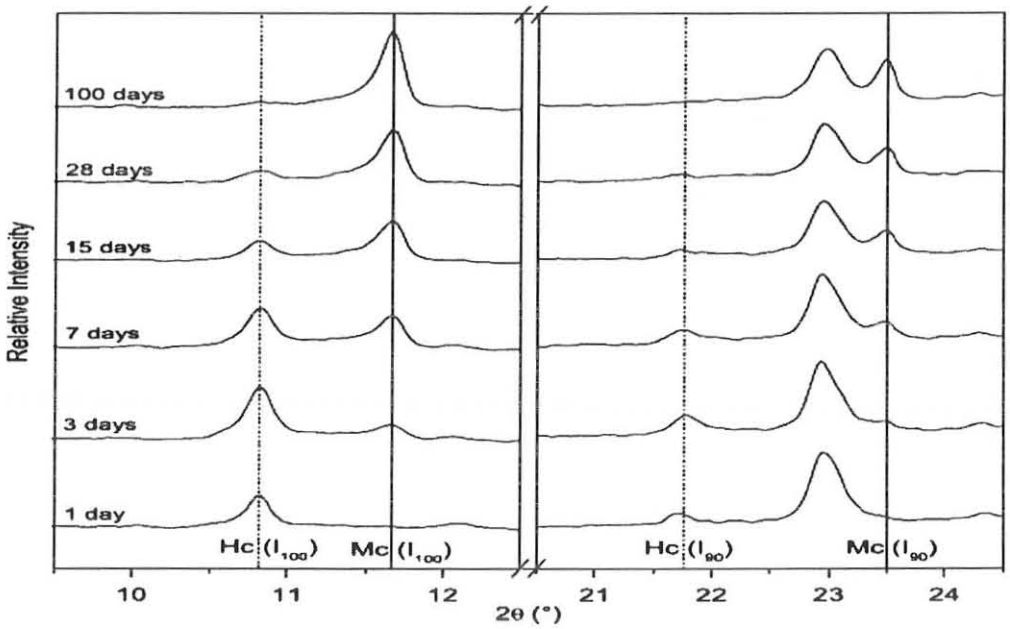


Figure: 1.7. The comparison of X-ray diffraction patterns of carboaluminate phases in hydrated calcite-containing cement at different stages of hydration [59].

CHAPTER TWO

2. Objectives of the Research

2.1. General Objectives

The aim of this study is to investigate the effect of different level of calcite fineness and quantity as filler of Portland cement on physico-mechanical properties of the cement paste with respect to technical, economical, and ecological fields and to produce a mortar that will satisfy the performance requirements under particular conditions of use.

2.2. Specific Objectives

1. Analyze the chemical & mineralogical compositions of limestone, gypsum and clinker.
2. Investigate the compressive strength of mortar as a function of fined limestone (calcite) adds percentage.
3. Investigate the effect of fineness on the hydration reactions process, standard consistency, soundness (expansion), and setting time.

CHAPTER THREE

3. Materials and Methods

3.1. Materials

This chapter presents a study on different materials with respect to their chemical and physical properties, which are the main components in the raw mix design. Some of the physical investigations were carried out in Construction Design Share Company (CDSE, Addis Ababa, Ethiopia) laboratory. The remaining investigation were undertaken in Mugher cement Enterprise quality control assurance department.

Clinker was taken from Mugher cement Enterprise. First, the size of clinker was reduced with the help of ball milling to the surface area of 3500 cm^2/g Blain value. Then using X-ray fluorescence the chemical and Mineralogical composition of clinker sample was calculated as shown in Table 3.1.

Sand, which was used in the mix design- CEN-NORMSAND EN 196-1, Germany, was obtained from Mugher cement enterprise for quality control of cement production.

Calcite of high limestone ($CaCO_3 > 90\%$) was collected from Mugher cement Enterprise Quarry. The raw calcite was first crushed, milled, homogenized and dried in the laboratory before use. Its chemical composition was examined using X-ray fluorescence, and is shown in Table: 3.1.

Table: 3.1. Chemical composition of clinker and limestone

Clinker		**Calcite**	
Chemical components	%	Chemical components	%
Calcium oxide (CaO)	64.50	Calcium oxide (CaO)	52.95
Ferric oxide (Fe_2O_3)	2.76	Ferric oxide (Fe_2O_3)	0.39
Aluminium oxide (Al_2O_3)	3.68	Aluminium oxide (Al_2O_3)	0.68
Silicon dioxide (SiO_2)	21.50	Silicon dioxide (SiO_2)	1.76
Magnesium oxide (MgO)	0.98	Magnesium oxide (MgO)	0.88
Sulphate oxide (SO_3)	1.82	Sulphate oxide (SO_3)	0.02
Sodium oxide (Na_2O)	0.12	Sodium oxide (Na_2O)	0.26
Potassium oxide (K_2O)	0.95	Potassium oxide (K_2O)	0.29
Chlorine (Cl)	0.10	Chlorine (Cl)	0.01
LOI	1.35	LOI	0.60
F-CaO(free calcium)	0.70		
Mineralogical composition	%	Chemical characteristics	%
C_3S	56.20	$CaCO_3$	94.54
C_2S	19.70	TOC	< 0.20
C_3A	5.10		
C_4AF	8.40		

By XRF

Distilled water was used throughout the experiment to reduce the effect of mineral water in the physical and chemical properties of the test.

Gypsum was also taken from the source of MCE. Before it was blend with clinker and limestone, it was first crushed, dried and milled to the size of 3500cm^2/g. The chemical composition of gypsum calculated with the help of X-ray fluorescence are presented in Table: 3.2.

Table: 3.2. Chemical composition of Gypsum

Chemical components	**%**
Calcium oxide (CaO)	37.06
Ferric oxide (Fe_2O_3)	0.17
Aluminium oxide (Al_2O_3)	0.34
Silicon dioxide (SiO_2)	2.09
Magnesium oxide (MgO)	0.22
Sulphate oxide (SO_3)	39.06
Sodium oxide (Na_2O)	0.30
Potassium oxide (K_2O)	0.01
Chlorine (Cl)	0.07
Calcium carbonate($CaCO_3$)	66.18
LOI	8.00

3.2. Methods

In this chapter detail descriptions of experimental procedures used in the investigations are presented.

3.2.1. Preparation of Test Samples

The interest of this research is to investigate the effect of fined calcite on the physical properties of Portland cement. Therefore, in order to get the desired physical properties clinker and limestone were selected based on the chemical and mineralogical properties as we mentioned in the above.

The first target was to prepare Portland limestone cement (PLC) samples with different values of calcite fineness but the limestone has uniform in chemical composition and other parameters. It was planned to manufacture PLC samples of four-selected batch with different fineness values in the laboratory.

The following steps were taken in this regard:

1. More than 50 kg of cement clinker of the same chemical composition was collected from MCE while the plant was running smoothly. The clinker was crushed into semi-powdered by passing through a Jaw crusher of larger size in the laboratory and the crushed clinker was further turned into powdered form using an industrial ball mill to the surface area of 3500cm^2/g Blain value. The clinker was then stored temporarily in Aluminum container.
2. Grinding of limestone at different level of fineness is one of the basic preparation of this research. Therefore, Limestone was collected from MCE Quarry and grinded with different round and retention time (milling time) and the result (the fineness of limestone) was checked by Blaine's air permeability apparatus and grinding stopped at different desired levels in MCE. And also (again) measured the particle size of the powdered limestone (Calcite) using hydrometer analysis in Construction Design Share Company (CDSC), Addis Ababa, Ethiopia, based on AASHTO T88 and ASTM Standard D 422-63, "Standard Test Method for Particle-Size Analysis of Soils," procedure. Both results and there correlation listed as follows in Table: 3.3.

Table: 3.3. Particle size diameter and Blaine value of limestone

Sample code	Particle diameter (μm)	Blaine Value (cm^2/g)
F6	6	5400
F12	12	4840
F18	18	4200
F24	24	3571

In addition to the above point chemical result of the sample must satisfy the following three points ($CaCO_3$>75%, Clay<1.20g/100g, TOC ≤0.20% (so called -LL) or TOC≤0.5% (so called -L)).Thus the used limestone satisfied this entire requirement.

3. Gypsum was also crushed into semi-powdered and again milled into powder form by passing through the same small sized jaw crusher.

4. The resulting clinker from step (1) with Gypsum from step (4) and calcite at different amount and fineness levels step (2) was mixed and homogenized with a spatula for 4 min in MCE laboratory. The Prepared raw-mix (the so-called PLC) in this way was then sealed in small Aluminum container and listed in different batches as shown in Table: 3.4, 3.5, 3.6, and 3.7.

Table: 3.4. Raw mix-design Batch-1 for PLC.

Mixed Code	Preparation of mixes (amount) 450g		
	Clinker (%)	Limestone (%)	Gypsum (%)
A_0 - F_0	95	-	5
A_5 –F_6	90	5	5
A_{10}-F_6	85	10	5
A_{15}-F_6	80	15	5
A_{20}-F_6	75	20	5
A_{25}-F_6	70	25	5

Table: 3.5. Raw mix-design Batch-2 for PLC.

Mixed Code	Preparation of mixes (amount) 450g		
	Clinker (%)	Limestone (%)	Gypsum (%)
A_0 - F_0	95	-	5
A_5 –F_{12}	90	5	5
A_{10}-F_{12}	85	10	5
A_{15}-F_{12}	80	15	5
A_{20}-F_{12}	75	20	5
A_{25}-F_{12}	70	25	5

Table: 3.6. Raw mix-design Batch-3 for PLC.

Mixed Code	Preparation of mixes (amount) 450g		
	Clinker (%)	Limestone (%)	Gypsum (%)
A_0 - F_0	95	-	5
A_5 - F_{18}	90	5	5
A_{10}-F_{18}	85	10	5
A_{15}-F_{18}	80	15	5
A_{20}-F_{18}	75	20	5
A_{25}-F_{18}	70	25	5

Table: 3.7. Raw mix-design Batch-4 for PLC.

Mixed Code	Preparation of mixes (amount) 450g		
	Clinker (%)	Limestone (%)	Gypsum (%)
A_0 - F_0	95	-	5
A_5 - F_{24}	90	5	5
A_{10}-F_{24}	85	10	5
A_{15}-F_{24}	80	15	5
A_{20}-F_{24}	75	20	5
A_{25}- F_{24}	70	25	5

The second target was to investigate the physical effect of the above-prepared PLC, using the mix-design batches. The test specimens for strength tests were then cast in steel mold with 40 x 40 x 160 mm^3 prism in compliance with the EN 196-1:1994 and compacted on jolting apparatus with 60 jolts for the first layer. All specimens were

prepared with one part cement to three parts of standard sand proportioned by weight with sufficient water (1:3:0.44).

After casting, primarily all mortar blocks were placed in a shelf with relative humidity of above 65% and room temperature of between 20-22^{0}c to enable the mortars achieve enough strength for water curing by ensuring that moisture is retained and not lost rapidly. Then all the mortar blocks were immersed in a water-curing pond until testing period. Each of the blocks were marked using permanent ink marker in each case to clearly show the code, date and time of production and testing.

3.2.2. Testing for Chemical Composition of Cement

XRF is a systematic method to find out the chemical composition of all kinds of materials. The material can be solid, liquid, powder, filtered or other form. The method is fast, exact and non-destructive, and usually requires only a minimum of specimen preparation. Chemical composition of all samples was determined by XRF Cement Spectrometer in MCE labratory.

3.2.3. Testing for Physical Properties of PLC

Consistency

The standard consistency of fresh cement paste was determined in accordance with BS 4550 PART 3 using the Vicat apparatus. The procedure used is described below.

i. 125 gram of water was added to 500 g of cement (PLC) in a mixing bowl, while taking care to avoid leakage of water or cement.
ii. Mixing was started without delay and the time was noted to the nearest minute as 'zero time'.

iii. The mixer was stopped after 90 seconds for 30 seconds during which the paste sticking to the wall and bottom part of the bowl was separated by means of a suitable rubber or plastics scraper and was put in the middle of the bowl.

iv. The mixer was then restarted and was run for a further 90 seconds. In this way, the mixing was done for a total duration of 3 minutes.

v. The plunger of the Vicat apparatus was lowered to rest on the base-plate and the pointer was fixed for the scale to read zero. Then the plunger was raised to the uphold position.

vi. The mould of the apparatus was packed with the paste. Just after levelling the cement paste, the mould and the base-plate were shifted to the Vicat apparatus and positioned centrally under the plunger.

vii. The plunger was lowered smoothly until it was in contact with the paste.

viii. In that position it was kept for between 1 second and 2 seconds in order to keep away from initial velocity or forced acceleration of the moving parts.

ix. The plunger was then allowed to pierce vertically into the centre of the paste.

x. The scale was read at least 5 second after penetration had slowed down or 30 second after the release of the plunger, whichever was earlier.

xi. The scale reading was noted, which indicates the space between the bottom face of the plunger and the base-plate, together with the water content of the paste expressed as a percentage by mass of the cement.

xii. The test was repeated with cement pastes of different water contents until one was found to produce a distance between plunger and base-plate of 6 (±2) mm. The water content of that paste was noted to the nearest 0.5% as the water content for standard consistency.

Setting time

The setting times of fresh cement paste were recorded complying BS EN 196-3:2005 using the Vicat apparatus. The procedure adopted is described below.

Initial setting times

1. The quantity of water required for standard consistence was added to 500 g of cement and this was placed in the bowl of the mixer.
2. Steps (ii) to (iv) described in the previous section were repeated.
3. For initial setting time, needle of the Vicat apparatus was lowered to touch the base plate and the pointer was fixed on the scale to read zero. Then the needle was raised to the uphold position.
4. The mould of the Vicat apparatus was packed with the cement paste. After leveling the cement paste, the mould and the base-plate were shifted to the Vicat apparatus and positioned under the needle.
5. The needle was lowered slowly until it touched the paste.
6. Steps (viii) and (ix) explained in the previous section were repeated.
7. The scale was read when penetration had nearly stopped, or 30 seconds after the release of the needle whichever was earlier.
8. The scale reading was recorded, which indicates the space between the end of the needle and the base-plate, together with the time from zero.
9. The penetration was repeated on the same specimen at conveniently spaced positions, not less than 8 mm from the rim of the mould or 5 mm from each other and at least 10 mm from the last penetration position, at conveniently spaced intervals of time, e.g. at 10 minutes intervals.

10. The time beyond 'zero time' and the time at which the distance between the needle and the base-plate was 6 (±3) mm, recorded to the nearest minute, was the initial setting time.
11. The specimen was reserved for the determination of the final setting times.

Final setting times

1. Steps (1) and (2) for the determination of initial setting times were repeated.
2. The needle with attachment for final setting was lowered to touch the base-plate and the pointer was adjusted for the scale to read zero. Then the needle was raised to the uphold position.
3. The mould of the Vicat apparatus was filled with the paste. After leveling the cement paste, the mould and the base-plate were shifted to the Vicat apparatus and positioned under the needle.
4. The time at which the needle first penetrates only 0.5 mm into the specimen was noted as the final setting time. This time was that at which the ring attachment first failed to mark the specimens.

Soundness

Soundness/Expansion of the samples was carried out as per BS 4550 PART 3. The 'Le Chatelier Apparatus' consisting of a small brass cylinder split along its generatix was used. In this apparatus, two indicators with pointed ends are attached to the cylinder on either side of the split. In this manner, the widening of the split, caused by the expansion of cement is greatly magnified and can be easily measured. A neat cement paste of standard consistency was prepared and filled in the cylinder placed on glass plate. The cylinder was covered after filling by another glass plate. The whole assembly was then immersed in water at 20 (+1) °C for 24 hours. After 24 hours, the

distance between indicators was measured. The mould was then immersed in water again and brought to boiling in 25 to 30 minutes. After boiling for one hour the assembly was taken out. After cooling, the distance between the indicators was again measured. The increase in this distance represented the expansion of cement i.e. soundness.

Compressive and Flexural Strength

The compressive and Flexural strength test were conducted in accordance with EN 196-1 on mortar with the help of a compression-testing machine. Just before the test, the mortar was taken out of the water tank and the surface was dried using a dry cloth. This was to make certain that the sample was tested at a Saturated Surface Dry (SSD) state. The specimen was first placed under flexural strength test and the two broken half parts were tested for compressive strength, Reported values are the average, satisfying that the standard deviation is less than 5% of the average value.

Figure: 3.2. Specimens soaked in water tank.

CHAPTER 4

4. Experimental Results and Discussions

In this chapter, the results are discussed under two sections, viz. variation of physical properties of cement (PLC) due to different amount as well as fineness of the filler and the effect of these variations on mechanical properties of mortar.

4.1. Consistency

Consistency indicates the degree of density or stiffness of cement. It is the amount of water content required for a given quantity of cement to get a cement paste of standard consistency.

The results of Standard consistency test for various amount of fined calcite filled cement were conducted and plotted in Fig: 4.1. using Table: (4.1), (4.2), (4.3), and (4.4).

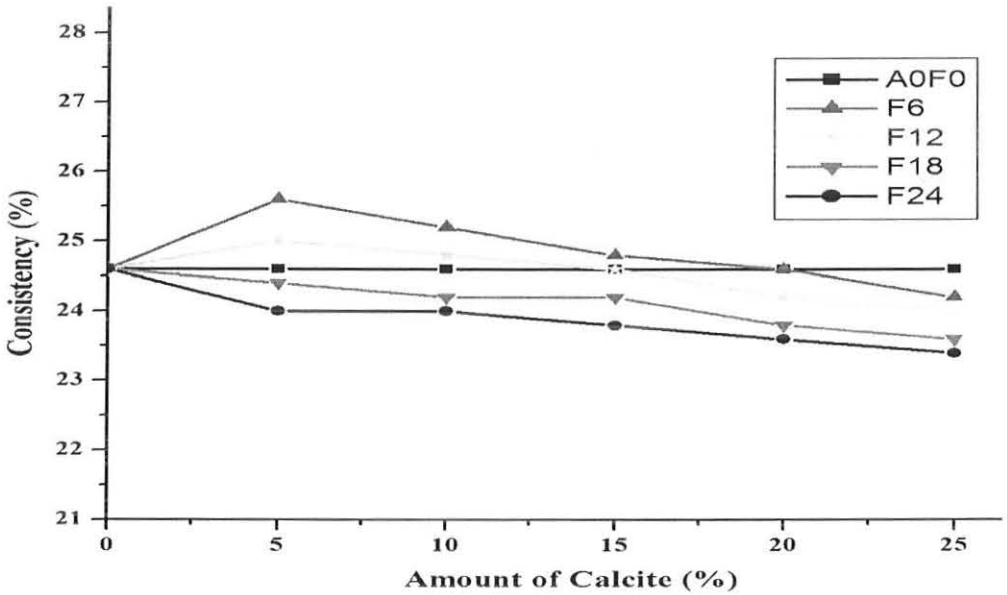


Figure: 4.01. Consistency of the PLC paste.

The graph (4.1) shows as the amount of limestone increases, the water of consistency decreases slightly. However, with the increase of fineness (F6 and F12) more surface area is available for hydration from the same weight of cement. Thus, more water will be required to produce the cement paste of the standard consistency.

Table: 4.1. Consistency and setting time

Batch no.	Sample Code	Standard Consistency (%)	Setting Time (min)	
			Initial	Final
1	A_0 - F_0	24.6	96	150
	A_5 –F_6	25.6	90	145
	A_{10}-F_6	25.2	95	150
	A_{15}-F_6	24.8	89	144
	A_{20}-F_6	24.6	86	139
	A_{25}-F_6	24.2	85	135

Table: 4.2. Consistency and setting time

Batch no.	Sample Code	Standard Consistency (%)	Setting Time (min)	
			Initial	Final
2	A_0 - F_0	24.6	96	150
	A_5 –F_{12}	25	94	148
	A_{10}-F_{12}	24.8	98	154
	A_{15}-F_{12}	24.6	93	146
	A_{20}-F_{12}	24.2	90	141
	A_{25}-F_{12}	24	87	137

Table: 4.3. Consistency and setting time

Batch no.	Sample Code	Standard Consistency (%)	Setting Time (min)	
			Initial	Final
3	A_0 - F_0	24.6	96	150
	A_5 –F_{18}	24.4	95	150
	A_{10}-F_{18}	24.2	99	155
	A_{15}-F_{18}	24.2	93	149
	A_{20}-F_{18}	23.8	92	145
	A_{25}-F_{18}	23.6	89	140

Table: 4.4. Consistency and setting time

Batch no.	Sample Code	Standard Consistency (%)	Setting Time (min)	
			Initial	Final
4	A_0 - F_0	24.6	96	150
	A_5 –F_{24}	24	98	154
	A_{10}-F_{24}	24	102	156
	A_{15}-F_{24}	23.8	96	151
	A_{20}-F_{24}	23.6	96	146
	A_{25}-F_{24}	23.4	92	144

4.2. Setting Time

The general consensus is that the fineness of limestone (calcium carbonate) is a factor influencing setting time of cement pastes. However, the magnitude of this effect differs among various studies [60].

In this paper, the effect of powdered Calcite on setting time of cement was carefully investigated .The result of initial and final setting time of cement paste are tabulated in Table (4.1), (4.2), (4.3), and (4.4) and plotted in Fig. (4.2) and (4.3), respectively.

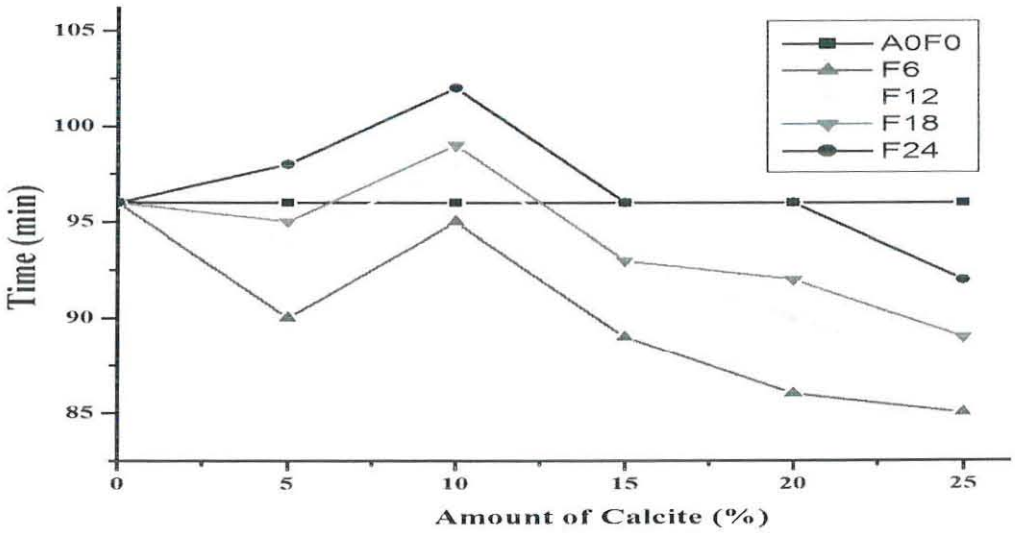


Figure: 4.02. Initial setting time

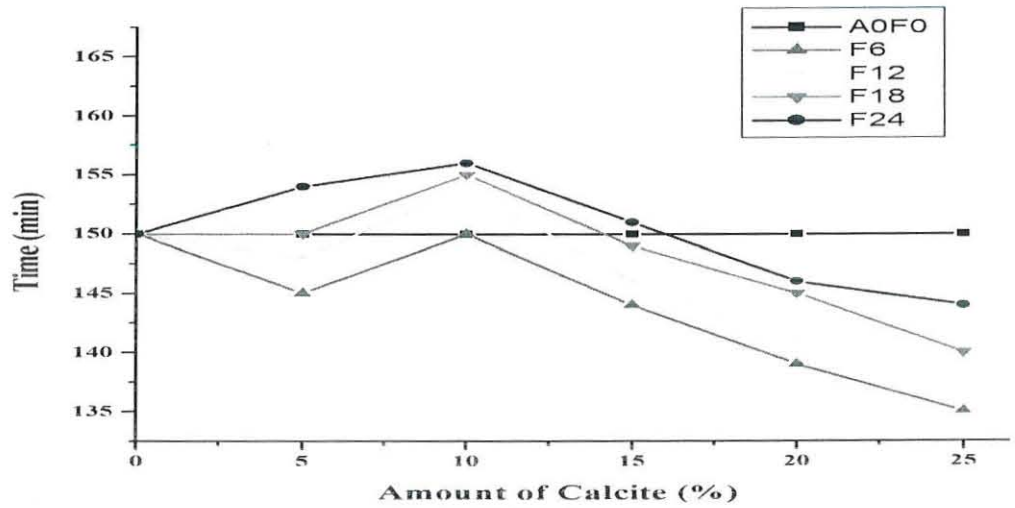


Figure: 4.03. Final setting time

Vuk et al [61] investigated cement pastes of different fineness and C_3S contents at some percent of limestone replacements. Initial and final set times were found to decrease as fineness increased. The decrease was more pronounced in cements with low C_3S. Tsivilis et al [62] found that limestone affected both initial and final set to a minor degree generally decreasing as fineness increased. Guemmadi et al [63] found that the setting time of pastes varied with the fineness, but no clear trend was observed.

In this research, Figure (4.2) and (4.3) show the initial and final setting time of PLC pastes at different amount and fineness level of Calcite. The result indicates that both initial and final setting time of the PLC paste at the same level of calcite more reduced for more fined limestone.

EN 197-1:2000 limits the initial setting time for composite Portland cement not to be less than 45 minutes. ASTM C 150 limits setting time to be between 45 to 375 minutes [64].

4.3. Soundness

Soundness is the ability of hardened cement paste to retain its volume after setting. Soundness issues generally result from the delayed or slow hydration of magnesium oxide (MgO) and/or calcium oxide (CaO free lime). It is essential that cement paste, once it has set, does not undergo a large change in volume; in particular there must be no appreciable expansion. According to the Ethiopian standard, the expansion of Portland cement shall not exceed 10 mm [65].

Table: 4.5. Soundness (expansion) of PLC paste.

Sample Code	Expansion
A_0 - F_0	1mm
A_5 - F_6	1mm
A_{10}-F_6	1mm
A_{15}-F_6	1mm
A_{20}-F_6	1mm
A_{25}-F_6	1mm

Sample Code	Expansion
A_0 - F_0	1mm
A_5 - F_{12}	1mm
A_{10}-F_{12}	1mm
A_{15}-F_{12}	1mm
A_{20}-F_{12}	1mm
A_{25}-F_{12}	1mm

Sample Code	Expansion
A_0 - F_0	1mm
A_5 - F_{18}	1mm
A_{10}-F_{18}	1mm
A_{15}-F_{18}	1mm
A_{20}-F_{18}	1mm
A_{25}-F_{18}	1mm

Sample Code	Expansion
A_0 - F_0	1mm
A_5 - F_{24}	1mm
A_{10}-F_{24}	1mm
A_{15}-F_{24}	1mm
A_{20}-F_{24}	1mm
A_{25}-F_{24}	1mm

Due to the above mentioned specification, the results of this study shown in Table 4.5 indicate that there is no noticeable difference between the controlled PC and blended PLC. In addition, all test results are well below 10mm. Therefore, all Calcite filled and controlled specimens are acceptable in terms of soundness/expansion from the viewpoint of Ethiopian standard.

4.4. Compressive Strength

Compressive strength is the most important criterion for assessing Cement quality. Virtually all cements testing specification stipulates minimum strength requirements at certain ages. The strength development of a cementitious system is influenced by the PLC type or, more specifically, the mineralogical and physical properties of the PLC.

ASTM C465 states that mortar compressive strengths (ASTM C109) of blends with partial replacement of PC shall not be less than 95% of the control PC at all ages. Therefore, 95% of PC compressive strength at the same age is considered an adequate level to assess performance of the Calcite-PC blends.

In this research the compressive strength of all mortars were determined at 2, 7, and 28days in accordance with EN 196-1. The compressive strength of all batches was determined using an average of 126 specimen's measurements at a constant w/b ratio of 0.44.

The average compressive strengths for each coded mortar control and blended are presented in Figure (4.4), (4.5), (4.6) and (4.7) and tabulated in Table (4.6),(4.7),(4.8), and (4.9).

Table: 4.6. Compressive Strength of PLC-Mortar Batch no.1.

Batch No.	Sample Code	Compressive Strength		
		2-Day Strength (MPa)	7-Day Strength (MPa)	28-Day Strength (MPa)
1	A_0-F_0	**26.20**	**37.15**	**47.07**
	A_5-F_6	**29.44**	**41.64**	**51.59**
	A_{10}-F_6	**28.41**	**40.17**	**48.78**
	A_{15}-F_6	**27.28**	**39.18**	**47.72**
	A_{20}-F_6	**26.56**	**38.27**	**46.99**
	A_{25}-F_6	**25.28**	**36.38**	**44.05**

Table: 4.7. Compressive Strength of PLC-Mortar Batch no.2.

Batch No.	Sample Code	Compressive Strength		
		2-Day Strength (MPa)	7-Day Strength (MPa)	28-Day Strength (MPa)
2	A_0-F_0	**26.20**	**37.15**	**47.07**
	A_5-F_{12}	**28.52**	**40.20**	**49.59**
	A_{10}-F_{12}	**27.77**	**38.78**	**47.58**
	A_{15}-F_{12}	**26.52**	**37.60**	**46.23**
	A_{20}-F_{12}	**25.83**	**36.61**	**44.19**
	A_{25}-F_{12}	**24.51**	**34.14**	**43.06**

Table: 4.8. Compressive Strength of PLC- Mortar Batch no.3.

Batch No.	Sample Code	Compressive Strength		
		2-Day Strength (MPa)	7-Day Strength (MPa)	28-Day Strength (MPa)
3	A_0-F_0	**26.20**	**37.15**	**47.07**
	A_5-F_{18}	**27.96**	**39.97**	**48.27**
	A_{10}-F_{18}	**27.18**	**37.89**	**47.02**
	A_{15}-F_{18}	**26.34**	**36.90**	**44.48**
	A_{20}-F_{18}	**25.71**	**35.52**	**43.01**
	A_{25}-F_{18}	**23.88**	**32.67**	**41.13**

Table: 4.9. Compressive Strength of PLC- Mortar Batch no.4.

Batch No.	Sample Code	Compressive Strength		
		2-Day Strength (MPa)	7-Day Strength (MPa)	28-Day Strength (MPa)
4	A_0-F_0	**26.20**	**37.15**	**47.07**
	A_5-F_{24}	**27.14**	**38.35**	**47.40**
	A_{10}-F_{24}	**26.67**	**36.78**	**46.72**
	A_{15}-F_{24}	**25.46**	**35.12**	**43.29**
	A_{20}-F_{24}	**24.67**	**33.56**	**42.05**
	A_{25}-F_{24}	**22.79**	**31.96**	**40.00**

The following graphs want show that the effect of fineness and amount of calcite on cement (OPC) in relation to mechanical properties, so called compressive strength, of mortar at 2 day, 7 day, and 28 days.

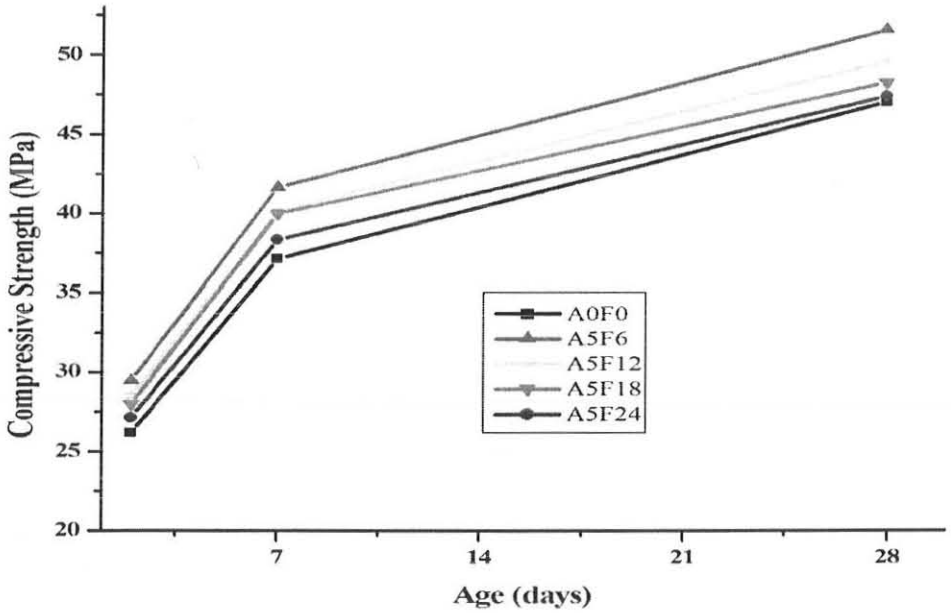


Figure: 4.04. Compressive strength development of Mortars produced PLC with 5% Calcite.

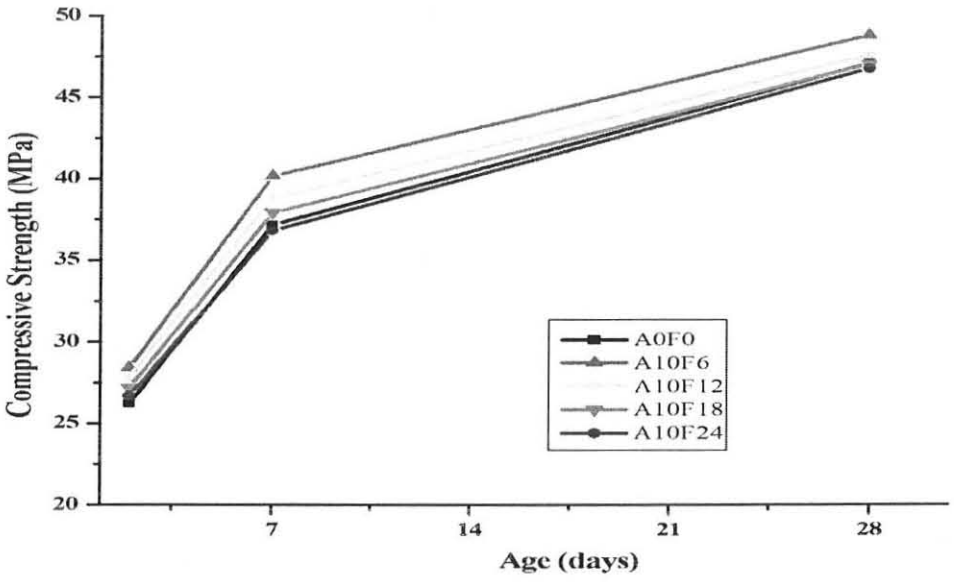


Figure: 4.05. Compressive strength development of Mortars produced PLC with 10% Calcite.

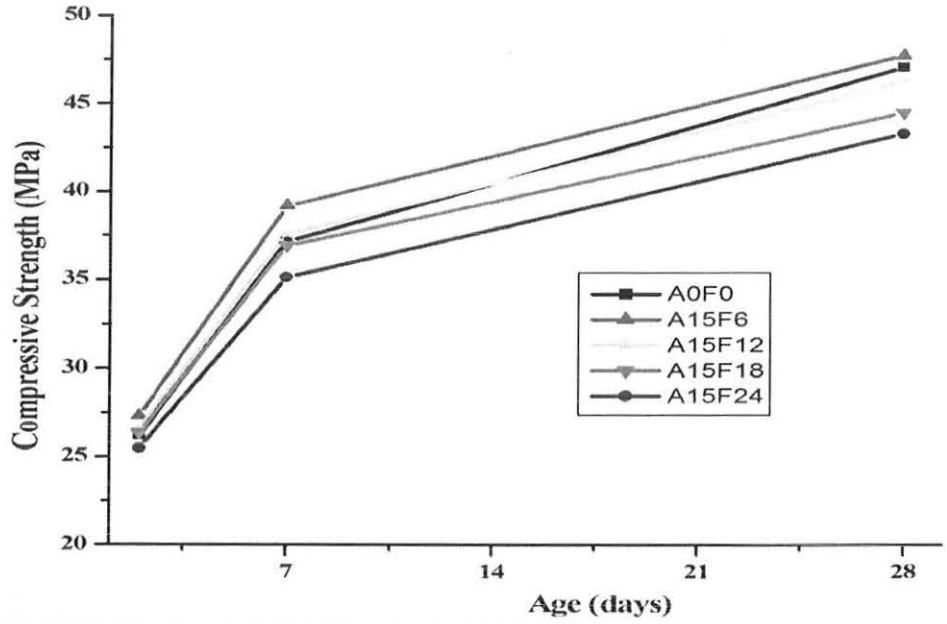


Figure: 4.06. Compressive strength development of Mortars produced OPC with 15% Calcite.

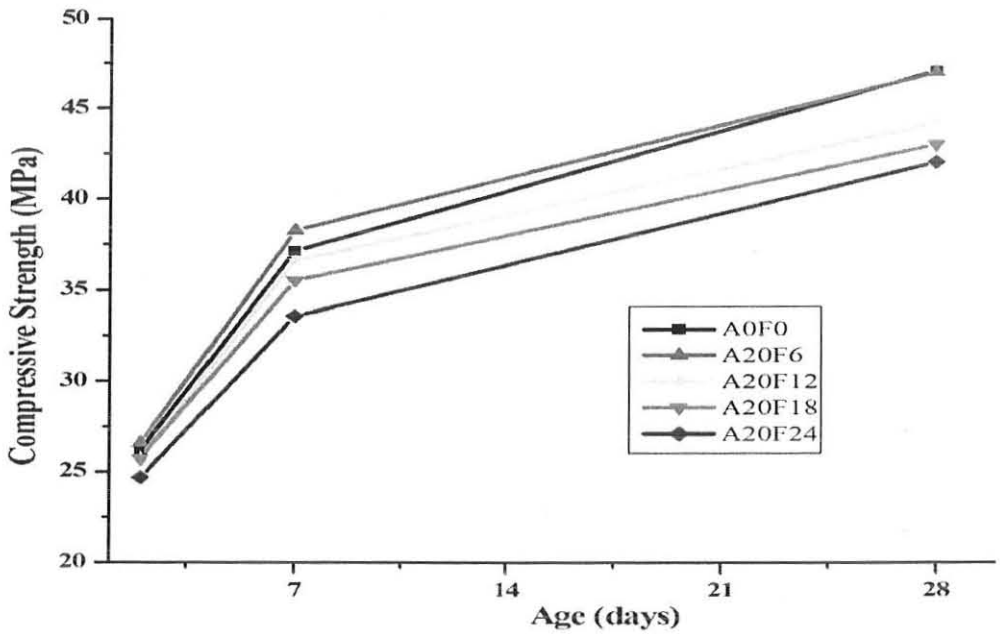


Figure: 4.07. Compressive strength development of Mortars produced PLC with 20% Calcite.

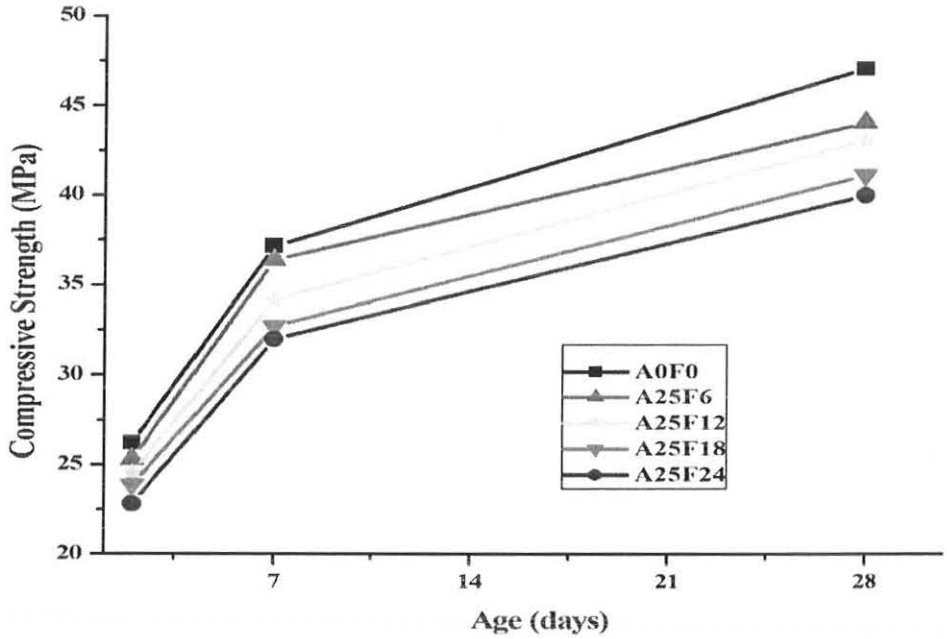


Figure: 4.08. Compressive strength development of Mortars produced PLC with 25% Calcite.

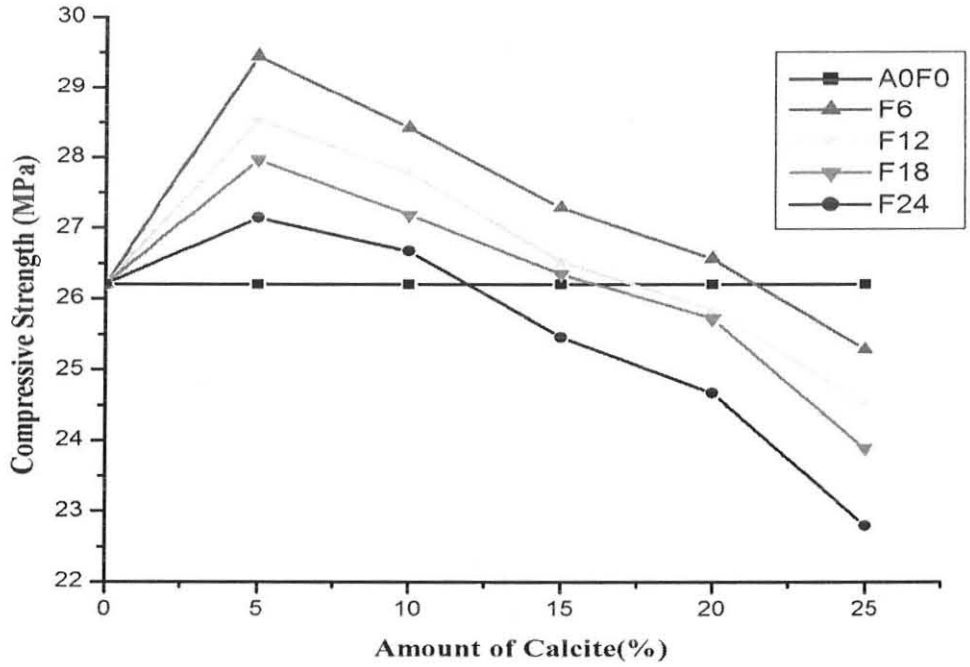


Figure: 4.09. 2 days Compressive strength of PLC Mortars with different amount of Calcite.

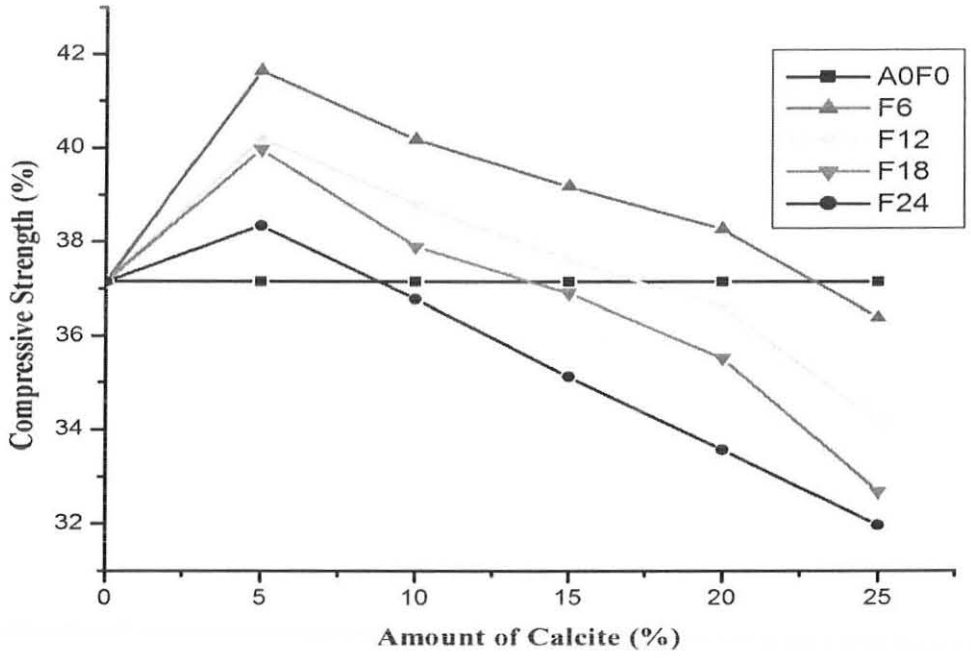


Figure: 4.10. 7 days Compressive strength of Mortars produced PLC with different amount of Calcite.

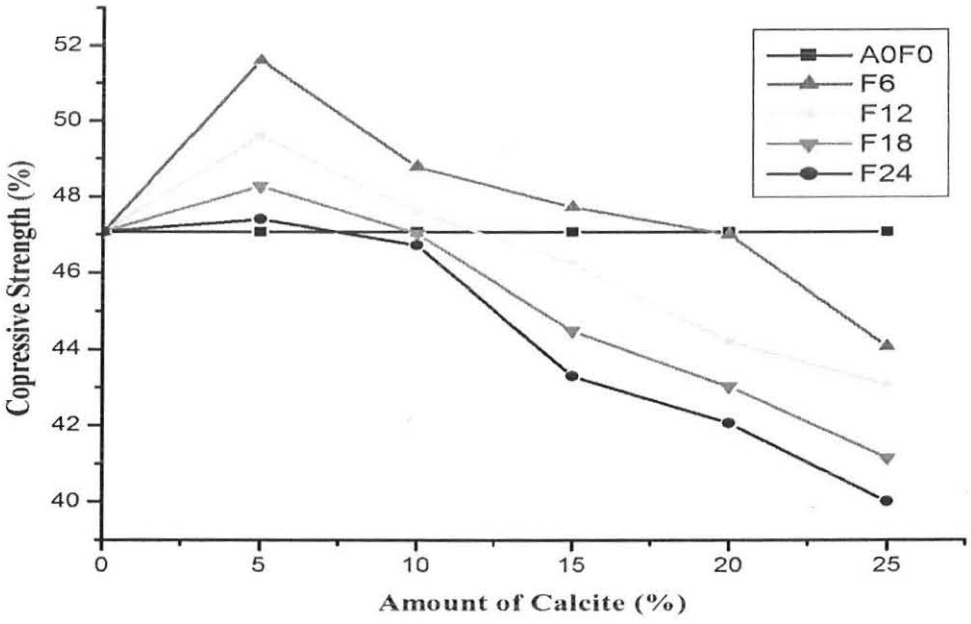


Figure: 4.11. 28days Compressive strength of Mortars produced PLC with different amount of Calcite.

Figures (4.4), (4.5), (4.6), (4.7), and (4.8) represents the comparison curves of compressive strength of mortar versus 5%, 10%, 15%, 20%, and 25% of fined Calcite at fineness level of F6, F12, F18, and F24 , respectively, for different specimens at the same curing age of 2, 7 and 28 days.

A 5%, of calcite replaced PC, the so-called PLC, in Fig (4.4) shows that the compressive strength of PLC mortar is dependent on the particle size of the filler (calcite) in PLC. Moreover the calcite at a smaller particle size of 6 μm (larger surface area) showed a better performance in compressive strength than the others particle size of 12 μm, 18 μm, and 24 μm, respectively. However, from the result of graph (4.4) at age 2, 7, and 28days, 5% of calcite replaced PLC mortar at a level of fineness 6 μm 12 μm, 18 μm, and 24 μm has better performance than the controlled PC mortar compressive strength.

As shown in the Fig.4.5, a 10% calcite filled PLC with a particle size of 6 μm, 12 μm, and 18 μm provide more strength than the control OPC compressive strength. In addition, calcite with 24 μm particle size PLC has similar compressive strength as that of the controlled OPC.

A 15% addition of limestone, as shown in the Fig.4.6, with fineness 6 μm, and 12 μm on OPC offered competitive strength with that of the control OPC compressive strength. However, calcite filled PLC with particle size of 18 μm and 24 μm resulted in a compressive strength reduction than the control OPC mortar.

Fig. 4.7 shows the compressive strength of 20% calcite filled PLC at 2, 7, and 28days of curing. It was found that the compressive strength of PLC using 6 μm was higher than those using calcite 12 μm, 18 μm, and 24 μm, respectively. As the result showed

by the graph, 20% with fineness 6 μm calcite filled PLC has competitive strength with the control OPC.

A 25% Calcite filled PLC with fineness 6 μm, 12 μm, 18 μm, and 24 μm as shown in the Fig.4.8 that there is a compressive strength reduction as compared to the control OPC mortar compressive strength.

Fig.(4.9), (5.0), (5.1) shown that the compressive strength of Portland-limestone cement versus calcite content using different particle size of limestone powder. As shown in the Fig. compressive strength is obviously related to the limestone content. It was found that OPC filled up to 5% calcite increases the compressive strength at age 2, 7, and 28 days of curing. The graphs show that with the same particle size when the amount of limestone increases more than 5% in PLC, the compressive strength start to decreases at all age. However the result indicate that 20% calcite replaced OPC with fineness 6 μm, 15% calcite with fineness 12 μm, 10% calcite with fineness 18 μm and 10% calcite with fineness 24 μm have competitive compressive strength with the controlled OPC compressive strength (0.17%, 1.78%, 0.00%, 0.78% compressive strength reduction was observed respectively).

Sprung and Siebel [48] found that the use of inert material as a very fine filler can lead to an increase in strength due to improved packing of the particles (i.e., filling of voids between the cement grains). This effect is seen at early ages, does not produce additional increases in strength with continued curing.

Although there is a disagreement in many research areas about the role of limestone in OPC, this experiment shows that fined limestone participates actively in hydration process rather than being an inert filler [66, 67]. This participation improves the

compressive strength at all age by some degree with limited amount of calcite (up to 5%) filler. Moreover, for the same amount of calcite replacement when the fineness of calcite increases in OPC resulted in an increase in the compressive strength. This may be attributed to surface area, which results to, more reactive.

Further, due to the relative particle size of calcite with clinker the small particle size of calcite can fill the pore between cement particles in paste that is known as a filling effect. Thus, the fineness of limestone powder used has influence on the observed compressive strength values [68].

However, for more than 5% limestone powder in OPC caused a reduction in the compressive strength that can be explained as a result dilution of C_3S and C_2S, which are responsible for strength.

CHAPTER FIVE

5. Economical and Environmental Analysis

Cement production is one of the most energy intensive and carbon dioxide emitter industrial processes in the world. It contributes approximately five percent of the total CO_2 emitted worldwide, emitting nearly 810 kg of CO_2 for every 1000 kg of cement produced [69].

The clinker burning is the most important part of the process in terms of the key environmental issues for the manufacture of cement; energy use and emissions to air. The key environmental emissions are nitrogen oxides (NO_x), sulphur dioxide (SO_2) and dust.

In order to solve these problems and mitigate energy requirement as well as environmental emission in cement production process, it is necessary to explore, find and implement proper methods. For example, Gabel & Tillman [70] simulated nine scenarios of using recovered materials and alternative fuels. Simulations results showed that emissions of CO_2, NO_X, SO_2, CO, VOC, CH_4 and dust could be mitigated up to 80% due to use of recovered material and alternative fuel.

As mentioned above, the use of limestone as a partial replacement of Ordinary Portland Cement (OPC) has several advantages like Technical, Economical and Environmental. These, Technical, Economical and Environmental, advantages can be seen from two different perspective, one from the point of the cement factory and the other from the consumer part. The technical aspect of the filler was clearly present in chapter five. In this chapter the paper, focus on Economical and Environmental part of the filled cement.

5.1. Economical Analysis

The cement industry is an energy intensive industry. The dominant use of energy in cement manufacture is fuel for the kiln. On average, energy costs -in the form of fuel and electricity- represent 50% of the total production cost involved in producing a tone of cement. Electrical energy represents approximately 20% of this overall energy requirement [71].

The industry's energy consumption is estimated to be about 2% of global primary energy consumption and almost 5% of total industrial energy consumption [72]. Following energy price has risen, cement companies have adopted and continue to implement various approaches to reduced energy use considerably through improved technology, including a shift from wet to dry cement processing, introduction of preheaters, precalciners, improved burner design, process modeling and control [73].

Although economic investigation of a process is one of the most complexes, detailed and time consuming part of the research, it is essential to perform economic analysis to get a perspective whether or not a feasible process modification is economically attractive. Therefore, to assure the economic advantages of proposed scenarios in addition to their environmental benefits, economic comparison between proposed cases (calcite-replaced clinker, the so-called Portland limestone cement (PLC)) and base case (Ordinary portland cement (OPC)) in terms of fuel consumption, raw-mix design and additional facilities used and tabulated in table 5.1.

Table: 5.1. Economic Comparison between OPC and the proposed PLC

Cement Type	Mix-Design	Percentage by mass (%)	Fuel (HFO) consumption (l/tone)	Electrical Energy (KW/tone)	Strength Class as per EN-197-1 (MPa)
Ordinary Portland Cement (OPC)	Clinker	95	81	66	42.5
	-	-			
	Gypsum	5			
Portland Limestone Cement (PLC)	Clinker	75	64.8	60	42.5
	Limestone	20			
	Gypsum	5			

Using the above data into account, for example, MCE produce 5000 tons of clinker per day and this provide 5,250 tons OPC cement per day by consuming approximately 405,000 liters HFO. However, it is possible to produce the same tons of PLC cement (5,250 tons/day) with competitive compressive strength by using 324,000 liters of furnace (or with a reduction of 81,000 liters HFO which is in birr 1,215,000 from the control OPC).

5.2. Environmental Analysis

Since two past decades and due to dramatic increase of environmental threats, societies have pressured their governments to discuss environmental issues, and the accumulation of greenhouse gases (GHG) emissions in the atmosphere is one of these controversial debates. The Kyoto Protocol and Copenhagen Conference are two agreements made under the United Nations Framework Convention on Climate Change (UNFCCC). Under these agreements, some countries committed to reduce their Greenhouse Gas (GHG) emissions to the certain levels [74].

The clinker production system is the most important part of the manufacturing process in terms of main environmental issues. As mentioned above, the main use of energy is the fuel for clinker production. Electricity is mainly used by the mills and the exhaust fans. The emission to air derives from the combustion of fuel and the transformation of raw meal into clinker. Apart from nitrogen and excess oxygen, the main constituents of the kiln exhaust gas are carbon dioxide from the combustion of fuel and the calcination of limestone, water vapour from the combustion process. The exhaust gas also contains dust, sulphur dioxide, depending on sulphur content of the raw materials, small quantities of metals from the raw material and fuel, and remnants of organic compounds from the raw material.

Mass Balance for 1Kg Cement

Raw meal factor:	1.54	Fuel:	heavy fuel oil
Clinker factor:	0.75	Calorific value:	40000 KJ/Kg (on a dry basis)
Specific energy:	3.35 MJ/Kg Clinker		10 % excess air
Air:	10 – 11 Vol. % O_2		

Emissions:

CO_2	600 g (404 g CO_2 from raw material, 196 g CO_2 from burning
N_2	1566 g
O_2	262 g
H_2O	69 g + raw material moisture

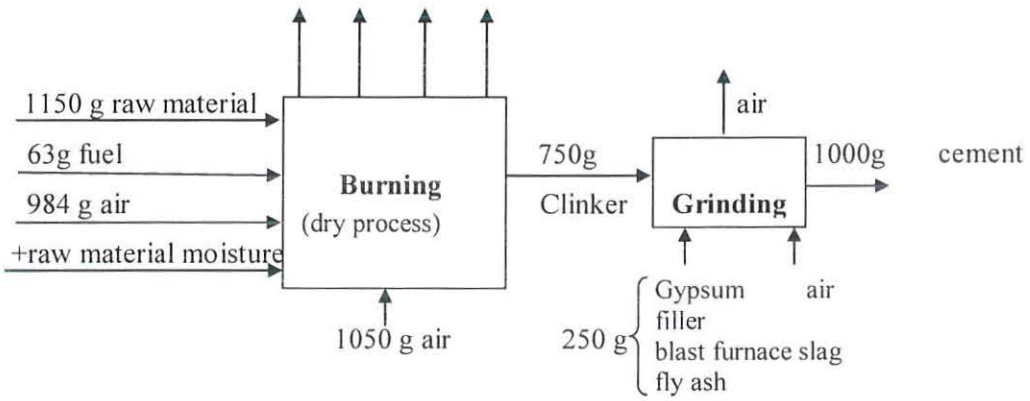


Figure: 5.1. Mass balance for the production of 1 kg cement [75]

According to the European Commission, the main environmental issues associated with cement production are emissions to air and energy use [76]. The key emissions are reported to be nitrogen oxides, sulphur dioxide, carbon dioxide and dust.

In 1999, a new type of cement, "building cement", was introduced on the Swedish market. Building cement is a blended cement with about 10 % of the clinker replaced with limestone filler. The environmental benefits of substituting limestone filler for clinker are a reduction in the amount of raw meal that has to be transformed into

clinker, and consequently, less environmental impact from the clinker production process, raw material and fuel preparation. The environmental impact per ton cement has been reduced by 10 % [77].

Means and Work Done to Minimize Negative Environmental Impact

The negative environmental impact from cement manufacturing and cement can be minimized in numerous ways. These can be grouped into four categories:

i. Substituting input, raw materials, fuels and cement additives, to the process
ii. Process development; optimize and develop the existing process
iii. End-of-pipe solutions; adding emission reduction systems
iv. Product development; develop new products or change cement composition and performance

Many of these solutions have consequences outside the actual cement manufacturing plant both upstream, as well as downstream.

Therefore, following the above-suggested point and research result, the research ascertained that it is possible to reduce environmental impact up to 20% by using fined calcite as filler in OPC.

CHAPTER SIX

6. Conclusions and Recommendation

6.1. Conclusions

The following conclusions have been drawn from the results presented and discussed in this thesis.

I. The consistency of PLC paste increase with increasing fineness of calcite. However, when the amount of calcite in PLC increases the amount of water required by the paste to get standard consistency was decreased.

II. Both initial and final setting times were decreased with an increase the amount of limestone. Moreover setting time of the PLC paste at the same level of calcite more reduced for more fined limestone.

III. Fined limestone participates actively in hydration process rather than being inert filler. This participation improves the compressive strength at all age by some degree with limited amount of calcite (up to 5%) filler. Further, due to the relative particle size of calcite with clinker the small particle size of calcite can fill the pore between cement particles that is known as a filling effect. Thus, the fineness of limestone powder used has a physical influence on the observed compressive strength values. However, for more than 5% limestone powder in OPC caused a reduction in the compressive strength that can be explained as a result dilution of C_3S and C_2S, which are responsible for strength.

6.2. Recommendation

Based on the result presented in this thesis the following recommendations are presented for cement industry:

Fined calcite as a filler of OPC has technical, environmental and economical advantages.

According to the research, using blended method, fined calcite with particle size 6μm at amount of 30%, 12μm at amount of 25%, 18μm at amount of 20% and 24μm at amount of 20% by mass of clinker in OPC gives strength at a standard class of 42.5Mpa PLC cement.

The environmental impact of cement manufacturing will be addressed in a joint approach between ourselves, the cement industry and key stakeholders, working together to improve the sector's environmental performance.

This study has worked to reduce the environmental impact nearly to 20% by using fined calcite as filler up to 25%.

As far as economical aspects, it is possible to reduce fuel consumption by 15 - 20% using fined calcite as a filler of OPC.

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Appendex:A Photo Attachments