

# INVESTIGATION OF CALCITE AND VOLCANIC ASH FOR THEIR UTILIZATIONS AS CEMENT FILLING AND ADDITIVE MATERIALS



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*Investigation of Calcite and Volcanic Ash for Their  
Utilizations as Cement Filling and Additive Materials*

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## **ABSTRACT**

The purpose of this study is to use calcite and volcanic soil as cement filling and additive materials in order to maximize cement productions in Ethiopia. In this study the characteristics of calcite and volcanic soil, suitable mix design of OPC raw materials, sources of calcite, chemical properties of calcite, volcanic soil, basic cement raw materials and clinker, and the effect of calcite and volcanic soil on mechanical performance of concrete were investigated. The additions of calcite up to 15% by weight improves early strength and additions above 15% results little decreasing early strength but develop high lateral strength. Use of volcanic soil from 28% to 35% by weight results a decrease of early strength and develops lateral strength. The additions of these materials did not affect quality of cement and mechanical performance of concrete.

The investigation shows that up to 15% Calcite filled cements have superior properties to the current Portland cement and Portland Pozzolanic Cements such as high early strength, excellent volume stability, minimum cost of productions and easy manufacture process.

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## 1. INTRODUCTION

Cement is a key to infrastructure industry and is used for various purposes and also made in many compositions for a wide variety of uses. Cements may be named after the principal constituents, after the intended purpose, after the object to which they are applied or after their characteristic property.

Cement used in construction are sometimes named after their commonly reported place of origin, such as Roman cement, or for their resemblance to other materials, such as Portland cement, which produces a concrete resembling the Portland stone used for building in Britain.

The term cement is derived from the Latin word *Caementum*, which is meant stone chippings such as used in Roman mortar not-the binding material itself. Cement, in the general sense of the word, described as a material with adhesive and cohesive properties, which make it capable of bonding mineral fragments in to a compact whole. The first step of reintroduction of cement after decline of the Roman Empire was in about 1790, when an Englishman, J.Smeaton, found that when lime containing a certain amount of clay was burnt, it would set under water. This cement resembled that which had been made by the Romans. Further investigations by J. Parker in the same decade led to the commercial production of natural hydraulic cement.

Joseph Aspdin, an English mason, made an important advance towards the manufacture of dependable hydraulic cement in 1824.[1,2,3] His product was called Portland cement because it resembled a building stone that was quarried on the Isle of Portland off the coast of Dorset, UK. Until the end of the nineteenth century, large quantities of this cement were exported to many parts of the world. The first factories for Portland cement outside the British Isles were opened in France in 1840, Germany in 1855, and the United States in 1871 [4].

Concrete is a composite material made by mixing coarse and fine aggregates, cement, water and sometimes admixtures are also essential when special properties are desired. A chemical reaction or hydration process takes place between the cement and water resulting in the formation of new compounds collectively known as cement paste, which bind the aggregates together into a coherent solid mass. Performance of concrete depends on the quality of the constituent materials as well as on their proportion and on the class of construction that comprises: placing, compaction, and curing.

In Ethiopia the first cement factory Dire Dawa was established in 1938 E.C, Addis Ababa Cement Plant in 1957 E.C, Mughar Cement Enterprise first line in 1976 E.C and second line in 1982 E.C and Messobo Cement Factory in 1992. Now there are many cement factories [5].

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, for which OPC is preferred, the demand for OPC is growing fast and is now taking a share of up to 25-30% of the total supply. Local contractors prefer to use OPC (as reflected in import data) but local production still leans toward PPC because of its relatively lower power requirements [6]. The very unsettled conditions being witnessed in recent years reflect Ethiopia's still limited supply of domestic cement as well as fast-growing demand. Until recently, cement was manufactured in only six factories, but this figure is now up to eight factories producing a total of 2.6 million tons table 1.1.

Per capital production of 33 kilograms is among the lowest in the world and well below levels found in, say, China (800 Kg per capita) and India (125 Kg per capita)[6].

Table 1.1 Cement productions in Ethiopia (in Tones)

Plant name	Max Capacity	Current Capacity		
		PPC	OPC	Total
Mugher Cement	900,000	775,000	89,000	864,000
Messobo Cement	900,000	845,000		845,000
National Cement	300,000	300,000		300,000
Jemma Cement	240,000		200,000	200,000
Abyssinia Cement	150,000		100,000	100,000
Midroc Dejen	90,000		90,000	90,000
Red Fox Intl.	150,000		150,000	150,000
CGOCC Cement	150,000	100,000		100,000
<b>Total</b>	<b>2,880,000</b>	<b>2020,000</b>	<b>629,000</b>	<b>2,649,000</b>

Despite the rising supply of cement, demand grows much faster rate than the supply, reflecting large-scale public sector infrastructure projects (roads, power plants) and private sector construction activity for residential housing, industry, and real estate developments. For both overall GDP growth (around 11 percent) and for construction sector growth (around 10 percent) by way of comparison, Ethiopia's cement consumption growth was roughly four times growth in global cement consumption [6].

However, Ethiopia is passing through a construction boom and huge property development schemes as a result the local cement producers and importers are not able to satisfy the demand for cement.

The cement consumption for the year 2006-07 is estimated to be around 2.05 million tonnes. The demand supply gap for cement has been estimated as given in table 1.2[7].

Table 1.2 Cement Demand and supply gap in Ethiopia.

<b>Year</b>	<b>Demand (million tones)</b>	<b>Supply (million tones)</b>	<b>Gap (million tones)</b>
2007	2.05	1.75	0.30
2008	2.66	2.01	0.65
2009	3.38	2.82	0.56
2010	4.19	3.50	0.69

Ethiopia spends million of dollars to meet its energy requirement for the purchase of furnace oil for Cement Sectors. See the annual utility of Mughher Cement Enterprise in table 1.3[8]. Water and Electrical power are also another utility required for various purposes.

Table 1.3 Annual utility requirement of Mughher Cement Enterprise.

<b>Description</b>	<b>Unit</b>	<b>Quantity</b>
Electricity	KWH	99,375,000
Water	m <sup>3</sup>	600,000
Fuel oil	Liter	63,000,000

In order to change the country's economic situation and to come-out of Poverty it is necessary to develop alternative techniques of low energy productions and utilize the country's widely available cheap materials.

The current amount of cement is much less than by a factory of eight the expected cement requirement of the country. There are also at least three large cement factories are being built which may achieve the demand. This may mitigate the existing dire situations; however, they fail to solve the critical cement shortage of the country.

Thus there should be other alternatives to meet the demand of the cement requirement of the country using available natural resources, and also, if possible, reduction of the energy consumption. Therefore, in this project it is planned to investigate for possible cement fillers, that will increase the cement output of the factories. By using Calcite for cement production it is possible to minimize the gap by increasing production of cement by 15-25%. If calcite was used for cement filler in 2007-2010 (table 1.4) the productions might be increased and would not be a gap between supply and demand.

Table 1.4 Gap and estimated production increment by calcite utilization.

<b>Year</b>	<b>2007</b>	<b>2008</b>	<b>2009</b>	<b>2010</b>
Gap (million tones)	0.30	0.65	0.56	0.69
Estimated increment by calcite (million tones)	0.3075-0.5125	0.399-0.665	0.507-0.845	0.6285-1.0475

## **1.1 Objectives**

### **General objectives**

The objective of this study is to investigate the suitability of the calcite material available near zway as cement filler.

Calcite is a well-known cement filler material in other countries around the world. Even if calcite is widely available in Ethiopia, it is not used as cement filler. So that investigations of this material for Cement productions in Ethiopia is the main objective of this research. It is also intended to analyse the properties of calcite and Volcanic Soil which is found in the Ethiopia and then to propose their appropriateness in the productions of blended cements with required strength of composite materials especially for concrete.

### **Specific objectives**

- Analysis the chemical compositions and the physical properties of the calcite materials and Volcanic Soils,
- Analyse the chemical compositions of ordinary Portland cement as well as pozzolanic Portland cement.
- Prepare test samples according to the specifications and carry out chemical and physical tests on calcite and volcanic soil,
- Based on the results obtained from chemical and physical analysis prepare composite and carryout physical tests, and
- Optimise the maximum percentage of filling materials or additives considering the chemical and physical properties.

## **2. THEORETICAL BACKGROUND**

### **2.1 Cement**

In the most general sense of the word, cement is a binder, a substance which sets and hardens independently, and can bind other materials together. And it is made from crushed rock with burnt lime as binder. The volcanic ash, pulverized brick and other additives which were added to the burnt lime to obtain a hydraulic binder were later referred to as cement [9]. The most important use of cement is the production of mortar and concrete the bonding of natural or artificial aggregates to form a strong building material which is durable in the face of normal environmental effects.

In a concrete mixture the function of the cement is to react with water forming a plastic mass when the concrete is fresh and a solid mass when the concrete is hard. The properties of the hardened paste are affected by the characteristics of the cement and, the completeness of chemical combination between the cement and water. Thus, it is essential to discuss about the prominent characteristics of cement and the logic behind the hydration of cement.

Types of Portland cement can be varied in type by changing the relative proportions of its prominent chemical compounds, by the degree of fineness of the clinker grinding and/or by adding some pozzolanic materials. As a result, there are several types of cements for different purposes. Some of them are:- Ordinary Portland Cement (OPC), Rapid Hardening Portland Cement, Sulphate Resisting Portland Cement, Low heat Portland Cement, Portland Pozzolana Cement (PPC). But, only Ordinary Portland Cement and Portland Pozzolana Cement are produced in Ethiopia. In this research I will collect the calcite type and volcanic soil pozzolanic materials which are found in Ethiopia near Zeway and between Wolenchite and Metehara and analyses the chemical compositions in the laboratory.

### 2.1.1 Portland Cement

Portland cement (often referred to as OPC, from Ordinary Portland Cement) is the most common type of cement in general use around the world, because it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. It is a fine powder produced by grinding Portland cement clinker (more than 90 percent), a limited amount of calcium sulfate which controls the set time, and up to 5 percent minor constituents (as allowed by various standards). Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates ( $3\text{CaO}\cdot\text{SiO}_2$  and  $2\text{CaO}\cdot\text{SiO}_2$ ), the remainder consisting of aluminium- and iron containing clinker phases and other compounds. The ratio of CaO to  $\text{SiO}_2$  shall not be less than 2.0. The magnesium content (MgO) shall not exceed 5 percent by mass.

Portland cement clinker is made by heating, in a kiln, a homogeneous mixture of raw materials to a sintering temperature, which is about 1300-1400°C for modern cements. The aluminium oxide and iron oxide are present as a flux and contribute little to the strength. For special cements, such as Low Heat (LH) and Sulfate Resistant (SR) types, it is necessary to limit the amount of tricalcium aluminate ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ ) formed. The major raw material for the clinker-making is usually limestone ( $\text{CaCO}_3$ ) mixed with a second material containing clay as source of alumina-silicate. Normally, an impure limestone which contains clay or  $\text{SiO}_2$  is used. The  $\text{CaCO}_3$  content of these lime stones can be as low as 80 percent. Second raw materials (materials in the raw mix other than limestone) depend on the purity of the limestone. Some of the second raw materials used are: clay, shale, sand, iron ore, bauxite, fly ash and slag [9, 10]. If a cement kiln is used by coal the ash of the coal acts as a secondary raw material.

As per the definition sited on the Ethiopian Standard ES C.D5.201, Portland cement means the product obtained by grinding clinker with the possible addition of a small quantity of calcium sulphates and/or water and it is manufactured by thoroughly mixing together calcareous or other lime bearing materials with argillaceous and/ or other silica, alumina or iron oxide bearing materials burning them at a clinkering temperature and

grinding the resulting clinker so as to produce a cement capable of complying with the requirements stipulated in the same standard. Portland cement is composed of four main oxides, namely: lime (CaO), Silica (SiO<sub>2</sub>), Alumina (Al<sub>2</sub>O<sub>3</sub>) and Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>). The Iron oxide added to the raw mixture is to aid in controlling the composition. Minor amounts of other materials, such as magnesia, MgO, and alkalis, Na<sub>2</sub>O, K<sub>2</sub>O are usually present in relatively small amount as impurities. The function of the gypsum is to control the time of setting of the cement when it is mixed with water [12, 13]. However, the principal compounds, in Portland cement exist not in the form of simple oxides but as minerals of more complex molecular structure [14, 15]. These four principal chemical compounds that make up Portland cement are: Tricalcium silicate (3CaOSiO<sub>2</sub>), Dicalcium silicate (2CaOSiO<sub>2</sub>), Tricalcium aluminate (3CaOAl<sub>2</sub>O<sub>3</sub>) and Tetracalcium aluminoferrite (4CaOAl<sub>2</sub>O<sub>3</sub>Fe<sub>2</sub>O<sub>3</sub>).

Therefore, depending on the relative proportions of its four prominent chemical compounds, the degree of fineness of the clinker grinding and/or by incorporating pozzolanic materials, it is possible to produce different types of Portland cements.

### **2.1.2 Chemistry of Portland Cements**

Portland cements are made by igniting a finely ground mixture of lime bearing materials such as calcium carbonate or calcium sulphate and aluminum silicate, such as clay or laterite, in some definite predetermined proportions, cooling the product or with the addition of some proportion of gypsum.

As stated earlier the raw material in Portland cement production consists of four main oxides namely: lime (CaO), Silica (SiO<sub>2</sub>), Alumina (Al<sub>2</sub>O<sub>3</sub>) and Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>). The names of oxide composition and abbreviation of the four principal reactive compounds present in clinker and anhydrate Portland cement are shown in Table 2.1

Table 2.1 Main Chemical Compounds of Portland cement.

Name of compounds	Oxide composition	Abbreviation
Tricalcium silicate	$3\text{CaOSiO}_2$	$\text{C}_3\text{S}$
Dicalcium silicate	$2\text{CaOSiO}_2$	$\text{C}_2\text{S}$
Tricalcium aluminate	$3\text{CaOAl}_2\text{O}_3$	$\text{C}_3\text{A}$
Tetracalcium aluminoferrite	$4\text{CaOAl}_2\text{O}_3\text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$

The range of oxide composition and constitution or compound composition of Portland cement clinker (except white cement clinker and oil well cement clinker) are given in table 2.2

Table 2.2 The range of oxide and compound compositions of Portland cement clinker.

Oxides	% Composition	Compounds	% Composition
$\text{SiO}_2$	$22\pm 4$	$\text{C}_4\text{AF}$	$11\pm 4$
$\text{Al}_2\text{O}_3$	$5\pm 2$	$\text{C}_3\text{A}$	$9\pm 4$
$\text{Fe}_2\text{O}_3$	$3\pm 2.5$	$\text{C}_3\text{S}$	$40\pm 10$
$\text{CaO}$	$64\pm 2$	$\text{C}_2\text{S}$	$35\pm 10$
$\text{MgO}$	$3\pm 2$	Free lime	$1\pm 1$
Alkalis	$0.8\pm 0.3$		
$\text{SO}_3$	$0.5\pm 0.2$		

The exact chemical composition of the clinker to be produced at the factory will depend up on the type of raw materials and fuel available. Alkalis and  $\text{SO}_3$ , always present in very small quantities in a raw mix or clinker have been ignored [7].

### 2.1.3 Clinker Compositional Parameters

Clinker Compositional Parameters based on the oxide composition are very useful in describing OPC clinker characteristics. The following stated parameters are widely used. Chemical formulae represent weight percentages.

### 1) Lime Saturation Factor (LSF)

The LSF is a ratio of CaO to the other three main oxides. Applied to clinker, it is calculated as:

$$LSF = \frac{\text{CaO}}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3}$$

The LSF controls the ratio of C<sub>3</sub>S to C<sub>2</sub>S in the clinker. A clinker with a higher LSF will have a higher proportion of C<sub>3</sub>S to C<sub>2</sub>S than will a clinker with a low LSF.

Values above 1.0 indicate that free lime is likely to be present in the clinker. This is because, in principle, at LSF 1.0 all the free lime should have combined with C<sub>2</sub>S to form C<sub>3</sub>S. If the LSF is higher than 1.0, the surplus free lime has nothing with which to combine and will remain as free lime. LSF 1.02 would mean 100% C<sub>3</sub>S in cement and 0.66 would mean 100% C<sub>2</sub>S.

### 2) Silica Saturation Factor (SSF)

It the combining efficiency of silica with lime left after forming C<sub>3</sub>A and C<sub>4</sub>AF. Which is maintained between 0.85 and 0.95 can give very satisfactory cement.

$$SSF = \frac{[\text{CaO} - (1.65\text{Al}_2\text{O}_3 + 0.35\text{Fe}_2\text{O}_3 + 0.7\text{SO}_3)]}{2.8\text{SiO}_2}$$

### 3) Silica Ratio (SR)

The silica ratio is defined as:

$$SR = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$$

A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite. SR is typically between 2.0 and 3.0. The silica ratio is sometimes called the 'silica modulus.'

#### **4) Alumina Ratio (AR)**

The alumina ratio is defined as:

$$AR = \frac{Al_2O_3}{Fe_2O_3}$$

This determines the potential relative proportions of aluminate and ferrite phase in the clinker. An increase in clinker AR (also sometimes written as A/F) means there will be proportionally more aluminate and less ferrite in the clinker [12].

In Ordinary Portland Cement clinker, the AR is usually between 1 and 4. The above four parameters are those most commonly used. A fifth, the 'Lime Combination Factor' (LCF) is the same as the LSF parameter, but with the clinker free lime content subtracted from the total CaO content. These factors have considerable effect on the burn ability of raw mix. In a correctly designed raw mix composed of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and MgO, during the process of burning all the Fe<sub>2</sub>O<sub>3</sub> and part of Al<sub>2</sub>O<sub>3</sub> first combines with a part of CaO to form C<sub>4</sub>AF; the remaining Al<sub>2</sub>O<sub>3</sub> then combines with a part of CaO to form C<sub>3</sub>A; which two (C<sub>4</sub>AF and C<sub>3</sub>A) act as fluxes to form silicates.

All the SiO<sub>2</sub> then present in raw mix combines with a part of CaO to form C<sub>2</sub>S and some CaO is still left uncombined. This uncombined CaO then combines with a part of C<sub>2</sub>S already formed to form C<sub>3</sub>S the ultimately desired compound.

In a correctly designed raw mix and under proper burning conditions, no free CaO should be left in the clinker; but in actual practice 0.5% to 2% free CaO is always left. The importance of LSF (Lime Saturation Factor), it takes in to account the potential combining power of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> with CaO. LSF should be between 0.66 and 1.02 in a Portland cement, the higher, up to a limit, the better.

If it is potentially near at about 1.0 in a clinker, it is very difficult to burn the clinker satisfactorily. So it is better to maintain to 0.9.

The factor  $\text{SiO}_2/\text{R}_2\text{O}_3$  is a measure for the fluxes in the clinker, the lower (up to the limit) it is, the better for burning. It should be maintained between 2.0 and 3.0.

A small variation in the composition or proportion of its raw materials leads to a larger variation in compound composition. Thus, to produce uniform cement, it requires stringent care in keeping the oxide composition of the raw materials uniform. In addition to the main compounds, there are minor compounds such as MgO, TiO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and K<sub>2</sub>O; which usually amount to not more than a few percent of the mass of cement.

Two of the minor compounds are of particular interest: the oxides of sodium and potassium known as the alkalis (although other alkalis exist in cement) [14, 17]. They have been found to react with some aggregates, the products of the reaction causing disintegration of the concrete, and have also been observed to affect the rate of the gain of strength of cement. It should, therefore, be pointed out that the term 'minor compounds' refers primarily to their quantity and not necessarily to their importance.

Knowledge of cement chemistry indicates that the major cement compounds have the following properties

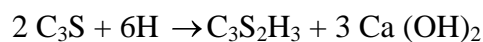
1. Tricalcium Silicate, C<sub>3</sub>S hardens rapidly and is largely responsible for initial set and early strength development because of the amount of CaO is more compared to C<sub>2</sub>S. The early strength of Portland cement concrete is higher with increased percentages of C<sub>3</sub>S.
2. Dicalcium Silicate, C<sub>2</sub>S hardens slowly and contributes largely to strength increase at ages beyond one week.

3. Tricalcium aluminate,  $C_3A$  liberates a large amount of heat during the first days of hardening. It also contributes slightly for early strength development. Cements with low percentages of this compound are especially resistant to soils and waters containing sulphates. Concrete made of Portland cement with  $C_3A$  contents as high as 10.0%, and sometimes greater, has shown satisfactory durability, provided the permeability of the concrete is low.
4. Tetracalcium aluminoferrite,  $C_4AF$  reduces the clinkering temperature. It acts as a flux in burning the clinker. It hydrates rather rapidly but contributes very little to strength development. Most colour effects are due to  $C_4AF$  series and its hydrates. The compounds tricalcium aluminate and tricalcium silicate develop the greatest heat, then follows tetracalcium aluminoferrite, with dicalcium silicate developing the least heat of all.

#### **2.1.4 Hydration of Portland Cement**

Hydration of Portland cement is the chemical reaction it undergoes when brought in contact with water. However, unlike the reaction of the other calcareous cements, hydration of Portland cement is a far more complex phenomenon. This is so because Portland cement is a heterogeneous mixture of several chemical compounds, which are complex in themselves.

The most important components of Portland cement from the strength development point of view are  $C_2S$  and  $C_3S$  which, on hydration, form the same compounds in differing proportions.  $C_3S_2H_3$  is the final product of hydration of both  $C_2S$  and  $C_3S$ , the reactions of hydration can be written for  $C_3S$  and  $C_2S$  respectively, as follows.



The rate of hydration of Portland cement is affected by a number of factors and is briefly discussed (listed 1 to 5) as follows.

## **1. Cement composition**

The speed with which the chemical reactions proceed depends on the affirmation of the individual compounds to water. The first to react are the aluminates.

The rate of hydration of the aluminates can be possibly retarded by varying the percentage of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The amount of gypsum to properly retard the setting varies mainly with the content of  $\text{C}_3\text{A}$  and the fineness of the cement. In very hot countries, cements that are used for making concrete should have reduced proportions of the constituents that hydrate rapidly ( $\text{C}_3\text{A}$  and  $\text{C}_3\text{S}$ ) with accompanying high rate of heat liberation. The rate of hydration accompanied by hot climatic conditions will lead to excessive expansion of the fresh concrete. At later ages, contraction takes place with resulting cracks that will seriously affect the structure.[13,17,18] The high heat liberation of the rapid hardening constituents can be put to advantage in very cold regions where freezing and thawing might adversely affect a freshly cast concrete.

## **2. Fineness of the cement**

The finer the grinding of the cement, the faster should be the hydration process and vice versa. However, the ultimate degree of hydration is not affected by the fineness of the cement. A finer cement will require not only more water to cover the higher surface area, but also relatively more gypsum to retard the speedy hydration of the decreased number of aluminates particles.

## **3. Water/Cement ratio**

Both the rate of hydration and the heat evolution are affected by the water/cement ratio. The water/cement ratio has practically no influence on the rate of hydration in the first 24 hours after mixing. Later on, the rate of hydration decreases with a decrease in a water/cement ratio.

#### **4. Age of paste**

It has been understood that the rate of hydration of cements, and hence the heat evolution, is highest at early age. Depending on the grain size distribution in the cement and the pressure of water, hydration may continue for several years after mixing but at a much-reduced rate.

#### **5. Ambient conditions**

The rate of hydration of Portland cement is influenced by the ambient temperature, and identical results cannot be expected from specimens that are subjected to different thermal histories. The rate of hydration increases with temperature and this is true only at earlier ages. Ultimately, however, the same degree of hydration is reached irrespective of the curing temperature

##### **2.1.5 Portland Pozzolana Cement**

In the Ethiopian Standard ES C.D5.210, Portland Pozzolana cement is defined as cement resulting from a homogeneous mixture of finely ground Portland clinker and less than 25 percent by mass of pozzolana and it does not necessarily satisfy the test for pozzolanicity [6]. Pozzolanicity is assessed by comparing the quantity of  $\text{Ca(OH)}_2$  present in a liquid phase in contact with the hydrated cement with the quantity of  $\text{Ca(OH)}_2$  capable of saturating a medium of the same alkalinity). Pozzolanic Cement means cement resulting from a homogeneous mixture of finely ground Portland clinker from 25 to 45 percent by mass of pozzolana and it satisfies the test for pozzolanicity [9]. In the same standard pozzolana is defined as a natural volcanic material having pozzolanic properties.

But the same standard also states that other natural and artificial materials such as diatomaceous earth, calcined clay and pulverized fuel ash which also have pozzolanic properties, but it does not include blastfurnace slag.

Pozzolanic properties mean the ability of a material to combine with lime at ambient temperature and in the presence of water in order to produce compounds that set and hardened with the formation of hydrated phases.

The Activity of Pozzolanas when mixed with cement is that the silica of the pozzolana combines with the free lime released during the hydration of the cement. Silicas of amorphous form react with lime more readily than those of crystalline form and this constitutes the difference in many cases between active pozzolanas and materials of similar chemical composition which exhibit little pozzolanic activity.

The most active of the natural pozzolanas are the diatomites, opaline cherts, and some shale. Volcanic materials such as pumicites and tuffs are generally less active, whilst many materials such as some clay require calcinations or heat treatment before they become reactive.

### **1) Lime-Pozzolana**

The addition of a pozzolana will decrease setting times and increase the strength of lime-based concretes, mortars and renders. It can produce hydraulic cement, which has the ability to set under water. While lime-pozzolana cements are unlikely to achieve the strengths of OPC they are more than adequate for all forms of low-cost shelter construction. Lime-pozzolana cements can often be produced for less than half the cost of OPC.

### **2) OPC-Pozzolana**

In OPC-based concretes pozzolanas are used to replace up to 30 percent of OPC for use in structural applications and up to 50 percent for non-structural purposes. As OPC is an expensive and sometimes scarce commodity, this can represent a significant cost saving.

In addition Portland-pozzolana blended cement has a number of significant technical advantages over plain OPC. Some of the advantages are: -

- Improved workability
- Improved water retention/reduced bleeding
- Improved sulphate resistance
- Improved resistance to alkali aggregate reaction
- Lower heat of hydration
- Enhanced long-term strength

The only disadvantage of these blended cements is that their early strength gain is slightly slower. This might mean that the dismantling of formwork on structural concrete may need to be delayed by a day or so, but this disadvantage is far outweighed by the advantages. These technical and economic advantages are well recognized and Portland-pozzolana blends are now commonly specified in both the developed and developing world.

## **2.2 Production and Reactions of Calcite Filled Cements**

Calcite or lime stone cements have been used in many countries since 1960's and EU CEM II/A 6 to 20% limestone cement are the largest single type of cement currently produced in the European countries. There are different sources of  $\text{CaCO}_3$  for cement filling materials like: Calcite (naturally burned limestone), limestone from Quarry by product and Caustic industry by product ( $\text{CaCO}_3$ ). Calcite (Limestone) filled cement can be produced by intergrinding, blending or by addition at the time of mixing concrete. Inter grinding of Calcite or limestone has several benefits. Calcite is a softer material than clinker and therefore takes less energy to grind to the same fineness. Figure 2.1 shows the energy required to grind each of the two materials to various specific surface areas.

As the content of calcite increases, the energy required to produce the same fineness decreases as shown in Figure 2.2.

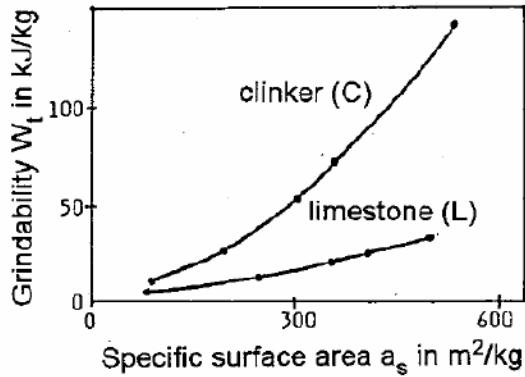


Figure 2.1 Grindability of clinker and calcite /limestone

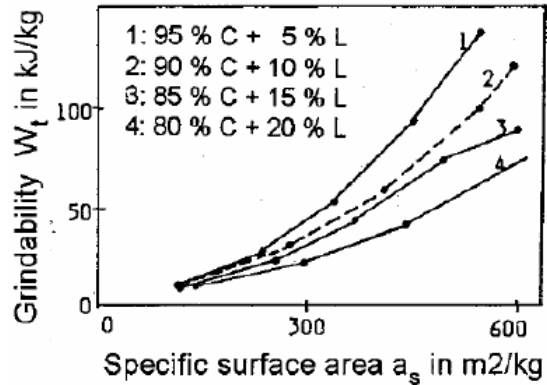


Figure 2.2 Grindability of calcite /limestone cement mixtures

### 2.2.1 Reactions in Calcite Filled (limestone) Cement

The reactivity of calcite has been debated, while most researchers have previously believed the calcite serves as inert filler, research shows that calcite does react to a limited extent. As the calcite particles become finer, this reaction is more likely [19, 20] found that at low concentrations limestone (calcite) reacts completely to form various carboaluminate phases.

The extent of calcite's reactivity is controlled by the amount of sulphate in the system. As the sulphate content increases, the likelihood of unreacted calcite increases. Increased calcite or limestone additions decreased the optimum  $SO_3$  content in both fine and coarse cements as shown in Figure 2.3 [21]. However, the decreases in sulphate would not be sufficient for complete reaction at high calcite replacement levels. Significant amounts of calcite remain unreacted even after extended moist curing.

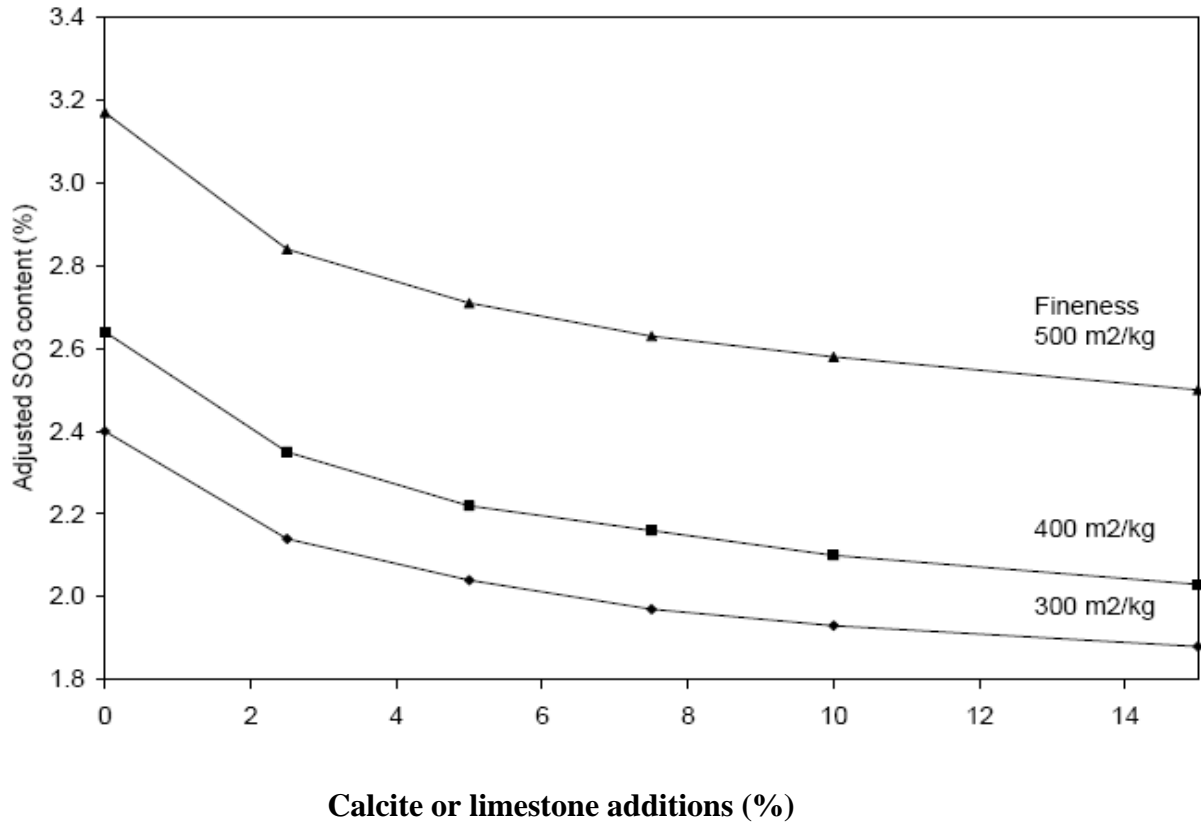
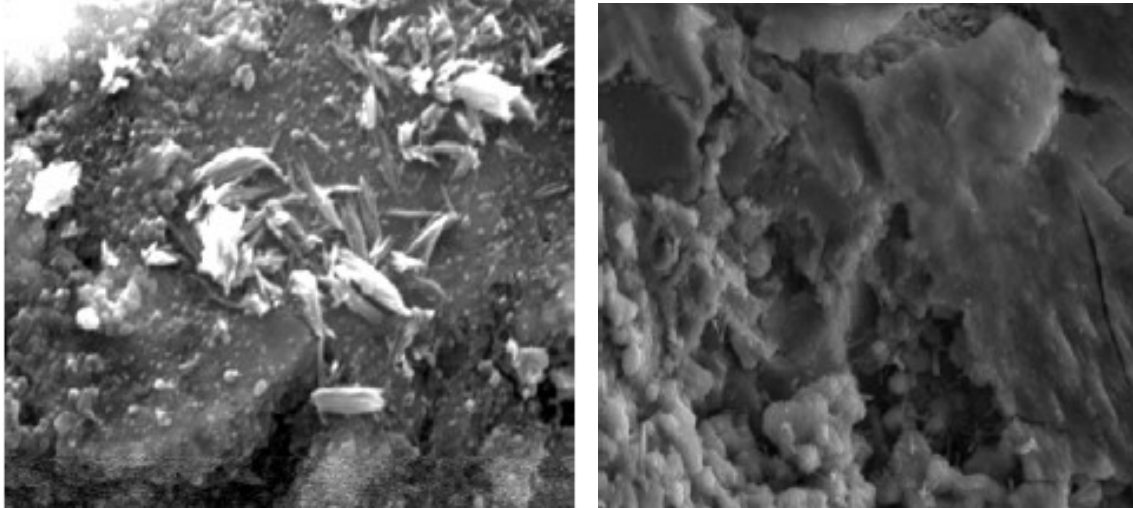


Figure 2.3: Optimum gypsum requirements with varying calcite addition and fineness.

Differences in the types and amounts of hydration products have been observed between Portland and Calcite filled cements. There is much agreement that Calcite reacts primarily with the  $C_3A$  component of the cement to form carboaluminates at the expense of hydrates see figure 2.4. The effect of reactivity with cements of varying  $C_3A$  compositions as observed by measuring compressive strength [22] clinker with lower  $C_3A$  (7.54%) and higher  $C_3S$  (65.15%) gave lower compressive strengths at all ages, grinding times and replacement levels than Calcite with higher  $C_3A$  (11.74%) and lower  $C_3S$  (57.99%). However, these results must be interpreted with caution as the latter cement required less water for standard consistency.



a) Formation of the carboaluminates crystals in concrete at 7 days.

b) Formation of CSH in concrete in 28 days

Figure 2.4. Observation of blended concrete microstructure by SEM.

Production of CH seems to be enhanced at early ages partially due to dissolution of Calcite and also due to Calcite's ability to act as nucleation sites [23]. The CH crystals forming in Calcite filled cements to have different morphology than those in Portland cements. The crystals were found to be well dispersed, smaller in size and have a tubular structure [23] However, beyond the first 2 to 3 days, calcium hydroxide concentrations decrease.

### **2.2.2 Effects of Calcite on Fresh Concrete Properties**

#### **1. Workability**

In regards to the effect of calcite additions on water demand and workability, there are conflicting results in the published literature. Much of these effects can be related to the particle size distribution of the calcite in relation to the cement. Generally, fine calcite particles can enhance the overall particle packing of the binder materials resulting in less space for water between the solid grains.

Decreasing the average particle size of calcite used as a partial replacement for cement gave better early-age rheological properties [26]. Increasing the fineness, as measured residue on 90 $\mu$ m sieve, decreased water demand by approximately 1.5% in cement paste mixtures containing 5% calcite [27].

## 2. Bleeding

Particles absorb water onto their surfaces. Therefore, it is not surprising that bleeding is highly dependant on the surface area of the binder particles. As the surface area increases, the affinity for water absorption increases. As shown in Figure 2.5 bleeding rate was highly correlated to the overall specific area of the binders, but independent of the amount of calcite addition. Increasing fineness of calcite fillers would decrease tendency for bleeding.

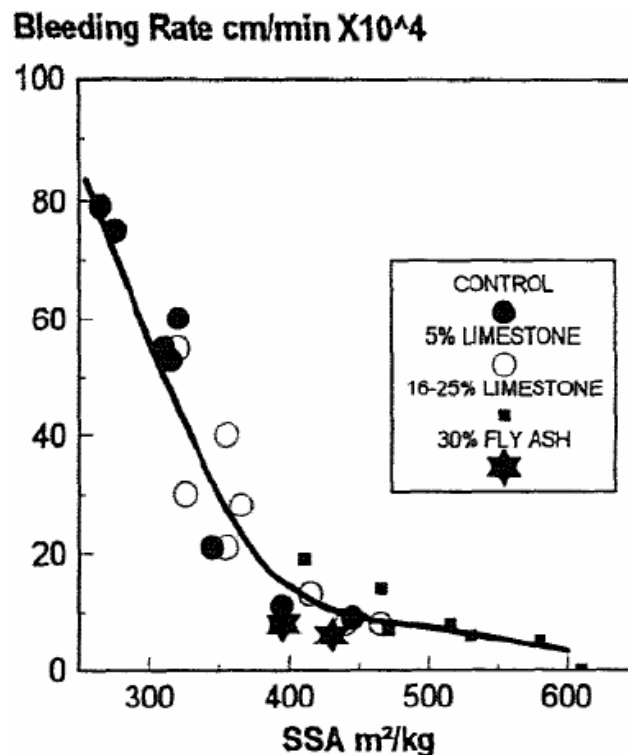


Figure 2.5: Bleeding rate vs. specific surface area.

### 3. Setting time

The general consensus is that the fineness of the Calcite is a factor influencing set time of cement pastes. However, the magnitude of this effect differs among various studies. Initial and final set times were found to decrease as fineness increased. The decrease was more pronounced in cements with low  $C_3S$  [27].

Increasing limestone additions decreased the set time of cement pastes (as also shown in Figure 2.6 [28]). To a lesser extent, and limestone affected both initial and final set to a minor degree generally decreasing as fineness increased [22]. The setting time of pastes varied with the fineness, but no clear trend was observed [25]. On the other hand, increasing fineness gave longer initial set times at 20% limestone replacement. In regards to limestone content, minor decrease in set times as replacement increases and while little correlation [22, 29]. For mixtures containing a total of 20% ground brick and limestone, initial set time was not significantly affected. Final set in these mixtures slightly decreased as limestone percentages increased [30].

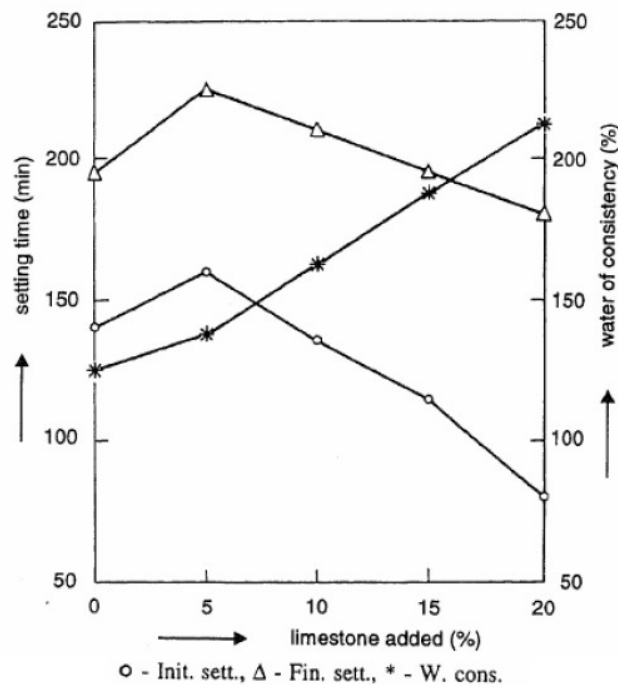


Figure 2.6: Water of consistency and setting of limestone cement pastes.

#### 4. Mechanical Properties (Compressive Strength)

The strength of concrete produced with calcite filled or limestone cement is strongly influenced by the quality of the calcite or limestone used, the manufacturing process (blending versus inter grinding) and the final particle size distribution of the cement. Calcite is softer than Portland cement clinker and will, therefore, be finer than the clinker if the two products are ground together. For cements of equal surface area (Blaine), the clinker particles in Portland-Calcite cement or Portland- Lime cement (PLC) will be coarser than those in Portland cement (PC).

To compensate for this, calcite cements are ground finer. Typical particle size distributions for PC and PLC from German cement works (Cilas) are shown in Figure 2.7[31].

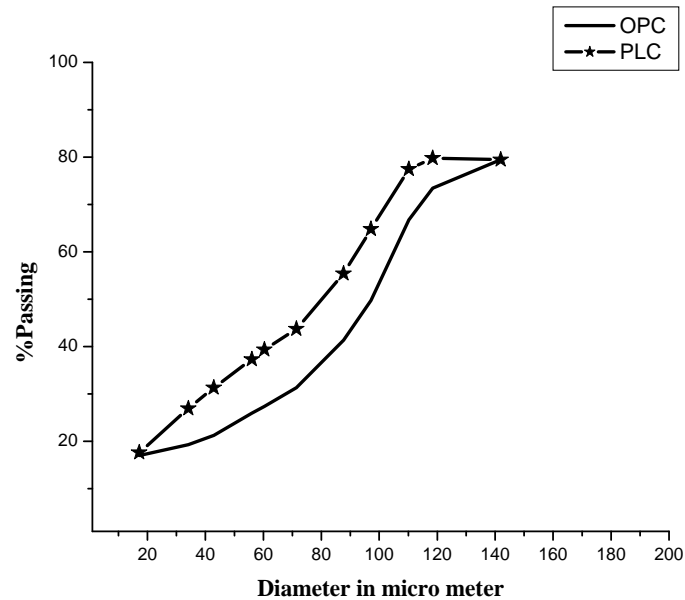


Figure 2.7 Particle Size Distributions for PC and PLC.

Additions of Calcite up to 5% may actually increase early-age strength as a combined result of improving particle packing [32]. Increasing the rate of cement hydration [27, 33]; and early production of calcium carboaluminate [34]. Even when ground limestone is blended with PC (as opposed to inter grinding), the strength is relatively unaffected up to 5% Calcite [35, 36]. At higher replacement levels the loss of strength due to dilution must be compensated for by finer grinding. For example comparable strengths for PC and PLC with 15% limestone, when the PLC was ground with specific surface of 511 m<sup>2</sup>/kg compared with specific surface 303 m<sup>2</sup>/kg for the PC [34].

See the three cements with 0, 8.3 and 18.1% interground limestone having Blaine finenesses of 317, 372 and 420 m<sup>2</sup>/kg, respectively [33]. Concretes (w/cm = 0.5) produced with these cements achieved 28-day, water-cured compressive strengths of 40.2, 38.1 and 36.3 MPa (for 0, 8.3 and 18.1% limestone, respectively). Early-age strengths were increased in the concretes produced with the calcite filled cements and, as a result, the 28-day strengths of concretes that were air-cured after 1 day, were greater for the mixes with PLC.

The performance of industrial cements PC and PLC with 20% limestone was compared in Table 2.3 shows the fineness of cements and the strength of concrete mixes produced with these cements. There is little significant difference in the strength of the concrete produced. The strength of concrete is reduced significantly when high a level (= 25%) of calcite is blended with Portland cement (as opposed to intergrinding the calcite with clinker and gypsum) [36, 37].

The performance of concrete produced with cement having 25% Calcite (blended) was equivalent to what would be expected due to a 25% replacement of the Portland cement with inert diluents [36]. There was an only minor difference in the performance of concrete with PC and PLC containing 15% limestone, but that above 15% limestone the water to cement ratio (w/cm) of the concrete should be reduced by 0.08 for every 10% limestone to achieve the same 28-day compressive strength [37].

Table 2.3 Strength of Concrete with different fineness and with and without calcite.

Cement types	OPC	PLC
Calcite or Limestone in cement (%)	0	20
Fineness of cement ( $m^2/kg$ )	345.0	482.5
Strength of concrete with 270 $kg/m^3$ cement at 28 days (MPa)	30.70	30.0
Strength of concrete with 330 $kg/m^3$ cement at 28 days (MPa)	39.70	38.0

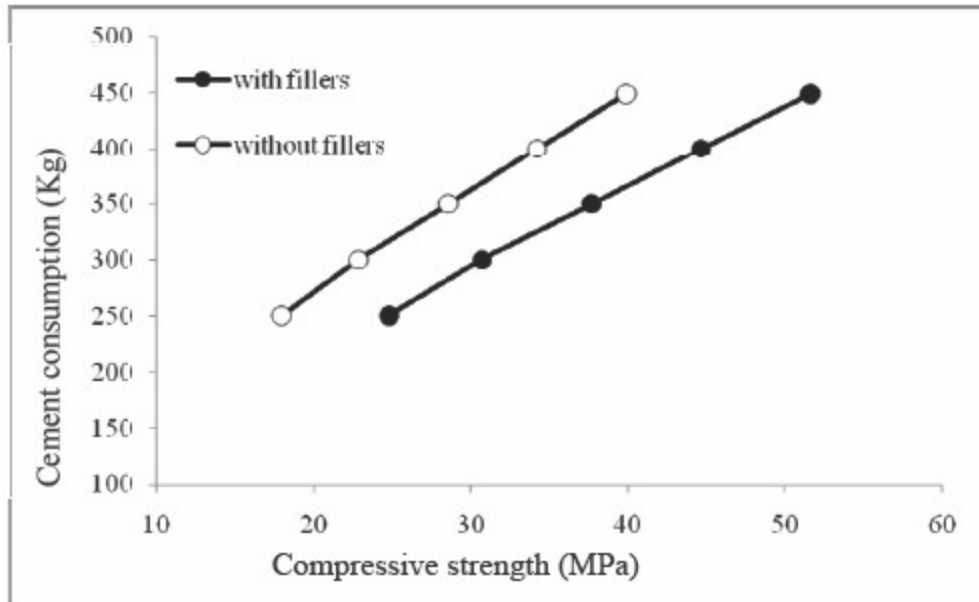


Figure 2.8 Cement consumption and compressive strength.

Up to 40% by mass replacement of OPC with reagent grade limestone improved sulphate resistance, with the best improvements occurring with limestone having high fineness (Blaine of 960-1120  $m^2/kg$ ) [38]. They attributed this to the increased likelihood of very fine limestone reacting to form carboaluminate hydrates. However the OPC plus limestone filler mixtures were not equivalent to expected sulphate resistance cement (SRPC) performance. With regards to the impact of PLC on the compressive strength of concrete, “that the appropriate choice of clinker quality, limestone quality, % limestone content and cement fineness can lead to the production of a limestone cement with the desired properties” at least for cements with up to 15% limestone [22].

The benefits of calcite filled Portland cements are:

- Reduce greenhouse gas emissions due to CO<sub>2</sub> resulting from reduced clinker factor in cements.
- Improved workability and pumpability.
- Comparative marginal decrease in water requirement due to filling of void spaces by the calcite particles in the resultant cement.
- The softer grinding of calcite resulted increase in cement fineness, hence there is an improvement in grinding behavior of clinker resulting saving in grinding time.
- The addition of calcite (% by weight) in OPC and PPC clinker grinding results relative increase in cement fineness keeping the constant time of grinding, the finer the cement higher the rate of hydration and so the faster the development of strength. This is due to finer cement offers greater surface area of particle for hydration.
- Similarly performance to current Portland cement when the cements are properly optimized.

Potential weakness:

- Increase susceptibility to the sulphate attack
- Increased potential to carbonation.

## 2.3 Pozzolanic Materials

Pozzolanas are materials containing reactive silica and/ or alumina, which on their own have little or no binding property but, when mixed with lime in the presence of water, will set and harden like cement [10]. They are an important ingredient in the production of alternative cementing material to Ordinary Portland Cement (OPC).

Cement or some form of binding agent is a vital element in almost all types of construction and in recent years the cement market has been dominated by one product, OPC. OPC is an expensive and sometimes scarce commodity and this has severely limited the construction. Alternative cements provide an excellent technical option to OPC at a much lower cost and have the potential to make a significant contribution towards the provision of low-cost building materials and, consequently, affordable shelter.

A wide variety of siliceous or aluminous materials may be pozzolanic. Pozzolanas can be divided into two groups: natural pozzolanas such as volcanic ash and diatomite, and artificial pozzolanas such as calcined clays, pulverized fuel ash and ash from burnt agricultural wastes. Pozzolanas can be used in combination with lime and/ or OPC.

In concrete, pozzolans are added to reduce cost and to improve long-term strength and durability of the hardened mass. Although pozzolans help to improve the packing density of the solids, the primary role of the pozzolan is to provide additional CSH-phases through reaction with water and the calcium hydroxide contributed by the reaction of portland cement. This pozzolanic reaction is slow for most pozzolans that are used in high proportion. Thus, the benefits of the pozzolan are seen within the time frame of a week to several weeks after casting.

Some of the finer, more highly reactive pozzolans, such as silica fume, are added in smaller proportions and help to improve early strength as well as durability at later ages [39]. The pozzolanic reaction in most pozzolans becomes significant after the seventh day, when enough cement reaction products exist and the alkali concentration is high enough to break chemical bonds and enable the formation of cement reaction products.

In most cases, and depending on the reactivity of the pozzolan, most of the reaction is finished in the first 60 days [9, 39]. However, the use of large volumes of pozzolanic additions increases the risk of self-neutralization because of excessive consumption of CH during the pozzolanic reaction. A significant drop in pH can result in the dissolution of the other reaction products and destruction of the cementing matrix [11].

The addition of a pozzolana in either a lime or OPC-based product has two major advantages. Firstly, the properties of the cement will be improved, and secondly, as the costs of a pozzolana are usually low and certainly well below that of lime or OPC, overall cost will be significantly reduced assuming the pozzolana does not have to be transported too far.

### 2.3.1 Volcanic Ash

Deposits of volcanic ash or tuffs are likely to be found wherever there are active or recently active volcanoes. The natural state of these deposits varies considerably as does their pozzolanic reactivity.

Volcanic ashes normally require no heating to enhance pozzolanic reactivity and, if they are already in a powdered state, may need little or no grinding. Volcanic ash pozzolanas are commercially exploited in many countries. Other volcanic materials such as pumice may also be pozzolanic. The colour of deposits can vary from off-white to dark grey.

Table 2.4 Composition of volcanic ash suitable for use as a pozzolana

Constituents	% Contents by weight
Silica	45-65
Alumina + Iron Oxide	15-30
Calcium + Magnesium Oxide + alkalis	Up to 15
Loss on ignition	Up to 12

The pozzolanic reactivity of ash deposits can vary considerably. The quality of material may also vary within a single deposit or a single geologically consistent stratum, with variations in depth being common.

Once the deposits have been excavated most volcanic ashes will require only minor processing before use as a pozzolana. Many ashes are only loosely cemented and can easily be excavated by hand, although others may need mechanical or pneumatic equipment.

Some litchi tuffs may require blasting with explosives. The ash may require drying, and in dry sunny climates this can simply be achieved by spreading the ash in a thin layer on a specially prepared drying floor, similar to those commonly used to dry crops. Alternatively, in wet climates, and for large quantities, inclined rotary driers are normally used. If the ash is cemented it will need to be crushed before entering the dryer.

Some volcanic ashes will already be in a very fine, loose powdered form and may not require crushing or grinding. Other ashes may be of sufficient fineness but be cemented together. These will require milling or crushing. Coarse ashes and lithic tuffs will need to be ground in a ball mill or similar.

### **2.3.2 Utilization of Pozzolanas**

Fineness similar or slightly greater than that of OPC is usually recommended for pozzolanas although some have been ground considerably finer. The minimum fineness recommended by the Indian standards for pozzolana (IS 1344. 1981. Calcined clays) is 320 and 250cm<sup>2</sup>/kg for grade 1 and 2 pozzolanas respectively, measured by the Blaine air permeability test. Once the pozzolana has been ground, it must be blended with lime and/or OPC to produce pozzolanic cement. This can be accomplished by human or animal-powered methods but full homogeneity is unlikely to be achieved and the strength and consistency of cements blended in this manner will be variable.

Mechanical techniques preferably inter grinding in a ball mill or, as a second option, dry blending in a pan or concrete mixer, will give better results in terms of both strength and consistency.

Pozzolanas can be used with either lime and/or OPC. With the latter, replacement of up to 25-35 percent is common, although suggested that for non-structural purposes replacement of up to 50 percent can be used. With lime pozzolana cements mixtures of 1:1 to 1:4 (lime: pozzolana) by weight are used. The addition of 5-10 percent of OPC will improve strength and decrease setting times. A larger percentage of OPC may be required if only poor quality pozzolanas are available. The exact ratio of the ingredients will depend upon the quality of the respective raw materials and on the required characteristics of the concrete or mortar made from the cement.

### **2.3.3 Effect of Pozzolana on Heat of Hydration**

A comparison of the temperatures generated with normal, modified, Pozzolanic and low heat cements, it is seen that pozzolanic cement has a similar heat of hydration to that of low heat cement. The gain is in both the lower total amount of heat generated and the slower rate of evolution.

### **2.3.4 Effect of Pozzolana on Strength of Concrete**

At early ages the replacement of cement by a pozzolana usually results in a decrease in the compressive strength, but the difference in strengths becomes less and may disappear at ages of three months or more. See the figure 2.9[9].

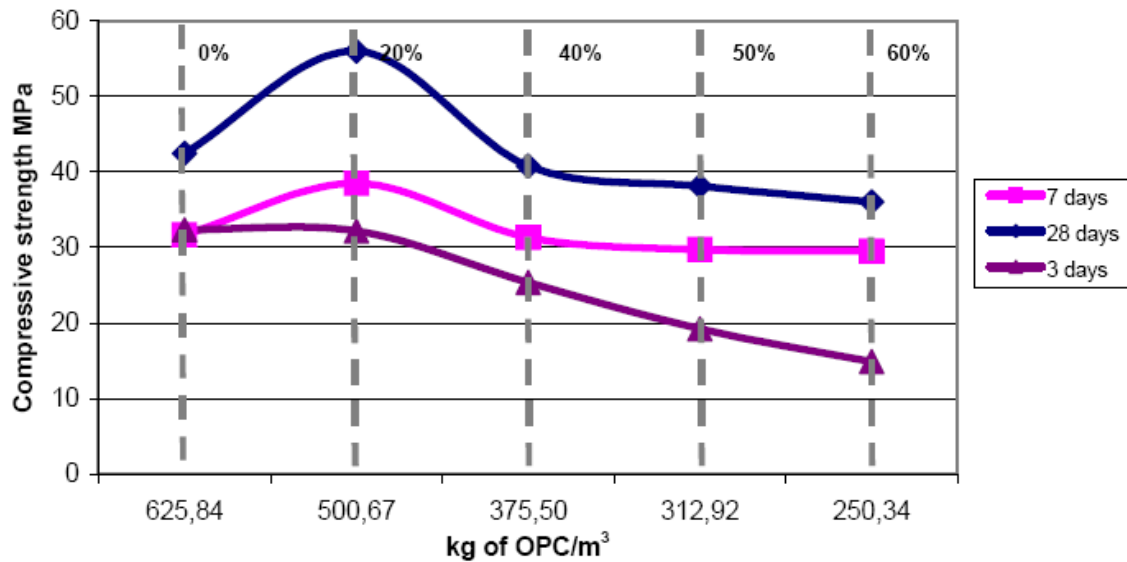


Figure 2.9 Compressive strength of PPC with different compositions of pozzolana.

## 2.4 Proportioning and Raw Mix Design for OPC Clinker Production

The most common raw materials used in cement production are: Limestone (supplies the bulk of the lime), Clay (supplies the bulk of the silica, alumina and ferric oxide), and other supplementary materials such as sand, pozzolanic and calcite, ground limestone to achieve the desired bulk composition. These materials must be mixed in the correct proportions.

The purpose of calculating the composition of raw mix is to determine the quantitative proportions of raw components in order to give the clinker the desired chemical and mineralogical composition. Once the type of clinker to be produced at the factory, with the process, raw materials and fuel available is fixed.

It will be necessary to calculate the proportion of raw materials required in preparing the raw mix. For example in Mughar Cement Enterprise for Portland cement clinker manufacturing by using different method of proportioning mix %R1 lime stone, %R2 clay and %R3 sand with given LSF and SR. The raw mix proportions are calculated based on the values of major oxides of each raw material like values in table 2.5

Table 2.5 Oxide compositions of Portland cement raw materials (Practical values).

Raw materials	%CaO	%SiO <sub>2</sub>	%MgO	%Fe <sub>2</sub> O <sub>3</sub>	%Al <sub>2</sub> O <sub>3</sub>	%LOI	%H <sub>2</sub> O
Lime stone	46.77	9.21	0.32	1.16	2.01	38.13	3.0
Clay	0.99	42.92	0.45	16.21	27.74	10.69	20.0
Sand	2.10	85.36	0.64	2.99	6.02	2.11	8.0

Before igniting the materials in the kiln for clinker production the proportioning of raw mix should be designed to get quality clinker with the required clinker compositional parameters such parameters are: LSF, SSF, SM, AM, the percentages of basic cement compounds and major oxides. The design of raw mix is based on the clinker compositional parameters and the value of major oxides from complete chemical analysis of the raw materials (lime stone, clay and sand).

## 2.5 Methodology

- Collecting Calcite (cement filler) and volcanic soils (pozzolanic materials) near Zeway and between Wolenchite and Metehara.
- Acquiring Portland cement and Pozzolana Portland cements from Cement Industries.
- Prepare composites as per the specification of cement factories.
- Carryout physical tests on the prepared composites.

### **3. EXPERIMENTAL PART**

This section has two parts. In the first part, the chemical test results of collected volcanic soil and calcite were summarized and/or analyzed. Then the literature survey on cement filling and additive properties and the summarized test results of these materials are used to propose properties of additives and fillers that could be used for Cement productions.

In the second part, the physical laboratory conducted compressive strength test results on different composites made of different proportions of calcite and volcanic soil were analyzed and discussed. Besides, composite properties analyzed using the laboratory test results and proposed using cement additives and filling material properties for cement productions.

#### **3.1 Chemical Analysis**

There are various testing methods available for determining the physical and chemical properties of cement basic raw materials, additives and filler materials. Those which are particularly suitable for use by small-scale industries, Cement industries and other users of cement filling and additive materials.

In chemical analysis the characteristics (oxide and compound compositions) of materials can be determined. The contents determined include Silica, Ferric oxide, Alumina, Calcium oxide, Calcium carbonate, Magnesia, Sulphuric anhydride, Loss on ignition etc. These chemical tests are performed using specified reagents and results of chemical content are given as a weight percentage.

#### **Apparatus and Instruments**

In these chemical analysis for the determinations of different chemical concentrations we used many apparatus such as: watch glass, graduate cylinder, burette, glass rod, Erlenmeyer flask, pipette, wash bottle, drying oven, digital balance, dropper, spatula, muffle furnace, desiccators, crucible, funnel, beaker, coarse filter paper (black band), red, blue-band filter paper, electric furnace, lid, Porcelain dish, evaporating dish, sand or

water bath, 500ml volumetric flask, , platinum crucible, crucible tong, Florence flask, funnel, cover, (Sieve No 4900, 90 μm), Blain testing machine, Stop watch, small brushes, LeChatelie ring, sample mixer, ruler, Vicat set, compressive strength testing machine, prism molds (40 mm x 40 mm x 160 mm) size, table vibrator, incubating machine and water sink.

## Chemicals

The chemicals used in this analysis are: hydrochloric acid (HCl), Phenolphthaline indicator, Sodium hydroxide (NaOH), Ethyl glycol, Nitric acid (HNO<sub>3</sub>), Ethanol, Acetic acid, Bromocresol green indicator, Fusion mixture (NaKCO<sub>3</sub>), Barium chloride (BaCl<sub>2</sub>) and Congo-red.

### 1) Determinations of calcium carbonate content

In chemical Laboratory work every sample will better at dry conditions. To determine the concentration of calcium carbonate take some part of calcite sample to dry in an oven at 105 °C for 30 minutes, grind, sieve and take exactly 0.5038 g of calcite sample. In this sample 25 ml 0.5N HCl was added for digestion. The mixture was diluted by 120 ml of distilled water, cover the flask by watch glass and boil for 3 minutes.

After boiling wash the watch glass and inner surface of the flask with cold distilled water. Use Phenolphthaline indicator for titration, titrate with 0.25 N NaOH until pink color stable and record the volume of 0.25 N NaOH consumed by titration. The concentration of CaCO<sub>3</sub> is determined using the formula

$$\% \text{CaCO}_3 = \left( 25 - \frac{V_{\text{titration}}}{2} \right) \times 5$$

Where  $V_{\text{titration}}$  is the volume of 0.25N NaOH consumed in ml.

## 2) Determinations of Sulphates

Exactly 0.50 g of sample was weighed. In this sample added 25 ml of distilled water and 13 ml of Conc. HCl for digestion. Break the lumps with glass rod, heat to boil and 100 ml of boiled distilled water was added. Immediately filtered with a medium (red band) filter paper and wash it several times with hot water. This filter used for SO<sub>3</sub> analysis while the residue (precipitate) used for insoluble residue (IR) analysis. Heat the filtrate to boil, while placing a glass rod and piece filter paper in it. After adding 10 ml of BaCl<sub>2</sub> solution slowly removed from the hot plate and stirred very well. In this solution added 50-60 ml of Congo-red carefully and leave it for 20-25 minutes for settlement.

Clear upper layer shows enough amount of Congo-red is added, other wise additional amount might needed. After the settlement filtered with fine (blue band) filter paper, washed the residue several times with hot water and placed the precipitate in previously weighed porcelain crucible. Placed this crucible on one of the hole of rapid incinerator or hot plate until the paper became blacken and then ignited in the muffle furnace controlled at 950 °C ± 50 °C for an hour. Finally cool in desiccators and weighed.

Sulphate ions dissolved by the decomposing the sample with hydrochloric acid is precipitated at a pH between 1 and 1.5 by a solution of barium chloride. The precipitation is carried out at a boiling point.

$\text{SO}_4^{2-} + \text{Ba}^{2+} \longleftrightarrow \text{BaSO}_4 \downarrow$  the determination is then completed gravimetrically and expressed as SO<sub>3</sub>. The sulphate content expressed as %SO<sub>3</sub> is calculated from the formula.  $\% \text{SO}_3 = \frac{(A - B) \times 0.343}{W} \times 100$

Where *A* is the weight of crucible and precipitate, *B* is the weight of empty crucible and *W* is weight of the sample. And 0.343 is the factor between BaSO<sub>4</sub> and SO<sub>3</sub> from:

$$\frac{\text{SO}_3}{\text{BaSO}_4} = \frac{80 \text{ g / mole}}{233.33 \text{ g / mole}}$$

### 3) Determinations of loss on ignition (LOI)

This is the loss of weight due to release of volatiles on ignition. A sample is ignited in a furnace under controlled conditions and the weight loss measured. This applies to materials which have to be calcined for use.

To determine the LOI weighed exactly 1.0 g of the sample; put this sample into a crucible which has been previously ignited and tarred. Placed the covered crucible in the electric furnace controlled at 1000 °C and after heated for 5 minutes removed the lid and left the crucible in furnace for further 20minutes. Cooled the crucible to room temperature in desiccators, weighed and determined the mass. The observed loss on ignition is determined from the formula:

$\%LOI = (A-B) \times 100$ , where *A* is the mass of the crucible and sample before ignition and *B* is the mass of the crucible and sample after ignition.

### 4) Determinations of major oxide contents

In order to get appropriate results mix the sample very well and take some part of the sample and let it to dry in the oven at 105 °C this helps to remove the moisture contents. After dried cool in desiccators and weigh 2.5 g fusion mixture (NaKCO<sub>3</sub>) was put in to platinum crucible and 0.5 g of sample over the fusion mixture again cover the surface of the mixture with 0.5 g NaKCO<sub>3</sub>. The mixture was placed in the Muffle furnace at 1000 °C for 20 minutes, removed from the furnace and gently swirls in order to spread the melt on the sides of the crucible. To make it cool placed and hold on porcelain basin about 50 ml cold distilled water of the basin. After cooled on the basin removed the crucible and the lid from the basin and places it in a clean dry porcelain dish.

In this solution added 20 ml of Concentrated HCl to loose the fuse and rinse with distilled water. After successful washing remove the crucible and lid. Put the dish on water bath and the contents of the dish evaporated to dryness wash with another 20 ml Concentrated HCl while it was dried.

Removed from the water bath, bake for an hour in a drying oven at 105 °C. Removed from the oven, cooled and 20 ml of 1÷1 HCl was added to digest for 10 minutes. Prepare 500 ml volumetric flask to filter the contents while hot with coarse filter paper (black band), wash repeatedly with hot water, cool and fill up to the mark.

*N.B.* The precipitate is used for SiO<sub>2</sub> analysis, while the filtrate is used for CaO, MgO, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>.

### 5) Determinations of silica contents

For this analysis the above major oxide determination procedures must be considered so dry and char the precipitate obtained above in dried and weighted porcelain crucible. This dried precipitate was ignited in a muffle furnace at 1000 °C for an hour and cooled in desiccators and weighed to nearest mg. The concentration of SiO<sub>2</sub> is determined from the formula:

$$\%SiO_2 = \left[ \frac{(A - B)}{W} \right] \times 100$$
 Where *A* is weight of crucible and precipitate, *B* is weight of empty crucible and *W* is weight of the sample.

### 6) Determinations of CaO content

Like silica content analysis major oxide determination procedures should be considered then take filtrate obtained above. (Filtrate placed in the 500 ml volumetric flask).

From the filtrate pipette out 25 ml of the filtrate in to 300 ml Erlenmeyer flask and dilute to about 100 ml with distilled water. In this solution 13 ml of 30% Tri-ethanol amine (TEA) was added and adjust the pH between 12 and 13 with 10% KOH (without formation of precipitate and check if by pH-meter). Again add about 50 mg of the mixed fluorexone indicator. Finally titrate with 0.01M EDTA from light green to pink and recorded the volume of EDTA consumed.

The concentration of CaO is determined from the formula:

$$\% \text{CaO} = (2.2432) \times (F_{\text{EDTA}}) \times (V_{\text{EDTA}}), F_{\text{EDTA}} = 1.00299$$

Where  $F_{\text{EDTA}}$  is factor of EDTA and  $V_{\text{EDTA}}$  is the volume of EDTA used to end point.

### 7) Determinations of MgO content

Similarly as CaO determination pipette out 25 ml of the filtrate and dilute to about 100 ml. In this solution 10 ml of 30% T.E.A added and adjust the pH between 10 and 11 with pH = 10 buffer. Add 5 drops of par and 5 drop of copper complexomate and titrate with 0.01M EDTA from red to orange yellow. The concentration of MgO is determined from the formula:

$$\% \text{MgO} = (1.6128) \times (F_{\text{EDTA}}) \times (V_{\text{EDTA}}), F_{\text{EDTA}} = 1.002976$$

### 8) Determinations of Fe<sub>2</sub>O<sub>3</sub> content

For this analysis also pipette out 100 ml of the filtrate prepared at above major oxide determination and add the Sulpho-Salicylic indicator about 50 mg. In this solution add drop wise 1+4 NH<sub>4</sub>OH solution till the yellow color is observed (the change observed is from colorless to violet and the yellow).

Return back the color to violet by adding 1+4 HCl solution and check the P<sup>H</sup> of the solution to between 1 and 2. Heat the solution gently to body temperature (do not exceed 50<sup>0</sup>C). Finally titrate with 0.01M EDTA from violet to colorless and recorded the volume of EDTA consumed. The concentration of Fe<sub>2</sub>O<sub>3</sub> is determined from the formula:

$$\% \text{Fe}_2\text{O}_3 = (0.7985) \times (F_{\text{EDTA}}) \times (V_{\text{EDTA}}), F_{\text{EDTA}} = 1.0030$$

### 9) Determinations of Al<sub>2</sub>O<sub>3</sub> content

Similarly pipette out 100 ml of the filtrate prepared at above major oxide determination and add the volume of EDTA consumed for Fe<sub>2</sub>O<sub>3</sub>. In this solution 40 ml of pH 3 buffer was added and heated just to boiling. To control the effect of other oxides add exactly three drops of copper complexomate. Add 10 drops of PAN indicator, boil and finally titrate while hot from red-violet to yellow.

Repeat boiling and titrating until yellow color became stable. The concentration of  $\text{Al}_2\text{O}_3$  is calculated from the formula:

$$\% \text{Al}_2\text{O}_3 = (0.5098) \times (F_{\text{EDTA}}) \times (V_{\text{EDTA}}), F_{\text{EDTA}} = 1.0029$$

### **10) Determinations of Free lime (CaO)**

The main aim of the kiln operator is to produce a clinker that have highest possible  $\text{C}_3\text{S}$  and the lowest possible free lime, keeping in mind about production costs. Inside the kiln at about  $800\text{ }^\circ\text{C}$  -  $900\text{ }^\circ\text{C}$  the  $\text{CaCO}_3$  dissociated and combination of CaO with  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . Around  $1200\text{ }^\circ\text{C}$  all  $\text{Fe}_2\text{O}_3$ , some of  $\text{Al}_2\text{O}_3$  and some of CaO combined to form  $\text{C}_4\text{AF}$ , all  $\text{SiO}_2$  combine with some of CaO to form  $\text{C}_2\text{S}$ . The remaining  $\text{Al}_2\text{O}_3$  combined with some of CaO to form  $\text{C}_3\text{Al}$ .

In actual clinkerizing zone  $\text{C}_4\text{AF}$  and  $\text{C}_3\text{A}$  act as flux to form  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  combine with some CaO to form  $\text{C}_3\text{S}$ . After all these reactions very little free lime is left uncombined or free. There is no free CaO in clinker on a correctly designed raw mix and proper burning but in practice always it present 0.5–2% values. Between 2-3% taken as a sign for improper condition of the kiln and above 3% it is completely out of statical control and the quality of the clinker become poor. In this analysis the value of free lime is 1.12% so it indicates that the clinker is good in quality.

To determine the free lime transfer 1.0 g of sample in to 300ml flask and add 50 ml of ethyl glycol and 1.0 g -2.0 g of laboratory sand and after shake well place it in a water bath at  $70\text{ }^\circ\text{C}$  for 20 minutes. Filter with suction and rinse with 10ml of ethyl glycol or absolute alcohol. The filtrate is titrated with 0.1N HCl in the presence of 5 drops of bromocresol green indicator. The end point is attained when dark blue colour changed to light green. The concentration of free lime in gram is determined from the formula:  $\% \text{CaO} = (V_{\text{titration}} \times 2.8 \times 10^{-3}) \times 100$ ; where:  $V_{\text{titration}}$  is the volume of 0.1N HCl consumed for titration.

### 3.2 Physical Analysis

Before starting the physical analysis the chemical properties of the materials (chemical composition values) should be considered. As shown in the chemical analysis data all materials were in the required ranges. The physical analysis also done in Mughher Cement Enterprise and it was based on their laboratory procedures and specifications.

In physical analysis properties like finess, coppressive strength, spesific surface, soundness, flexural strength, setting time, Permeability, Pozzolanicity Activity Index, drying shrinkage can be analysed or tested.

#### 1) Fineness

**For Sieve method:** - to measure the finess of cement following the correct procedures helps to achive the correct residue. A mass of 25 g of cement is put on the selected Sieve, sieving until the the final residue and weigh the residue.

**For Blain method:-** put 2.320 g of cement in to the Blain sample holder, adjust the level of the oil at the correct position, set the stop watch and take the time taken in seconds from initial level to the final level of the oil travels repeat for three times and take the average. It is possible to calculate the percent of residue (Sieve method) and specific surface (Blaine method) as:

$\% \text{ finess} = \frac{(r \times 100)}{W}$  ; Where  $r$  is the mass of residue and  $W$  is mass of cement sample.

$\% \text{ Specific surface} = k \sqrt{t_{av}}$  ; Where  $k$  is constant ( $527.96 \text{ cm}^2/\text{gS}$ ) and  $t_{av}$  is average time in second.

## 2) Soundness

Soundness is a measurement of its tendency to crack, distort, pit or disintegrate. In this experiment 500 g of cement and 150ml of water was mixed well with mixer for the preparation of good cement paste, accurately mold the paste in the Le Chatelier' ring, after waiting in water for 24 hours measure the distance between two ends of ring, put in boiling water for 2 hours and again measure the ends of ring.

The percentage expansion of the composite sample is calculated using the formula

$$\% \text{Expansion} = \frac{(L_o - L)}{L} \times 100 ; \text{ where } L_o \text{ is initial length and } L \text{ is final length.}$$

## 3) Setting time

Simple tests with Vicat method was carried out to determine the initial and final setting time of cement.

Prepare the paste from 500 g of PPC and 150 ml of water and fill in to the sample holder and put in to the vicat machine. The machine plots the graph of both initial and final setting time. By counting the graphs plotted by the machine and multiply them by 15 and recored as initial and final setting time in minute.

## 4) Compressive strength

For the composite preparation 450 g cement, 1350 g of standared sand and 225 ml of water or in the ratio of 0.5:3:1 (water:sand:cement) are mixed well and fill in to the molds. After waiting the mold in the incubator for 24 hours put in to water sink for other 24 hours. Test the compressive strength of composite samples at 2, 7, and 28 days (results in N/mm<sup>2</sup>).

## 4. RESULTS AND DISCUSSIONS

### 4.1 Chemical Analysis Results and Discussions

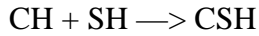
Chemical analysis of all the collected samples was carried out in Mughar Cement Enterprise Chemical Laboratory with the procedures stated above. The chemical analysis results of volcanic soil and calcite were recorded, summarized and given in table 4.1 and table 4.2 respectively. Chemical compositions of volcanic soil are in the oxide range of pozzolanic materials suitable for use as pozzolana. This chemical analysis data is important to decide about the material for PPC additives. From the result it is possible to propose to use as pozzolana for PPC.

Table 4.1 Practical values of chemical compositions of volcanic soil.

Oxides	% Composition test 1	% Composition test 2	% Composition average	Theoretical %compositions
SiO <sub>2</sub>	59.74	60.72	60.23±0.50	45-65
Al <sub>2</sub> O <sub>3</sub>	10.64	10.79	10.71±0.08	15-30
Fe <sub>2</sub> O <sub>3</sub>	6.81	6.67	6.74±0.07	
CaO	4.50	4.27	4.39±0.12	Up to 15%
MgO	0.65	0.66	0.655±0.01	
SO <sub>3</sub>	0.21	0.22	0.215±0.01	
LOI	7.98	7.79	7.89±0.10	Up to 12 %

Out of the active oxides, silica is normally considered to be the most important and should not normally fall below 45% of the total. Because silica is the basis of the pozzolanic reaction which stands a simple acid-base reaction between calcium hydroxide, also known as portlandite, or (Ca(OH)<sub>2</sub>), and Silicic acid (H<sub>4</sub>SiO<sub>4</sub>, or Si(OH)<sub>4</sub>).

For simplifying, this reaction can be schematically represented as following:  
 $\text{Ca(OH)}_2 + \text{H}_4\text{SiO}_4 \longrightarrow \text{Ca}^{2+} + \text{H}_2\text{SiO}_4^{2-} + 2 \text{H}_2\text{O} \longrightarrow \text{CaH}_2\text{SiO}_4 \cdot 2 \text{H}_2\text{O}$  or summarized  
 in abbreviated notation of cement chemists:



The product of general formula ( $\text{CaH}_2\text{SiO}_4 \cdot 2 \text{H}_2\text{O}$ ) formed is a calcium silicate hydrate, also abbreviated as CHS in cement chemist notation.

To use calcite as cement filling materials the calcite shall contain more than 75%  $\text{CaCO}_3$  by mass. The chemical compositions of collected calcite sample has about 89.50%  $\text{CaCO}_3$ , see the values in table 4.2. Based on these values it is possible to use as cement filler (for the productions of Portland calcite filled cement or Pozzolanic Calcite filled cement).

Table 4.2 Practical values of chemical compositions of calcite.

Oxides	% Composition test 1	% Composition test 2	% Average composition
$\text{SiO}_2$	3.10	3.60	$3.35 \pm 0.25$
$\text{Al}_2\text{O}_3$	0.35	0.32	$0.34 \pm 0.02$
$\text{Fe}_2\text{O}_3$	1.12	1.20	$1.16 \pm 0.22$
$\text{CaO}$	51.07	53.66	$52.37 \pm 1.30$
$\text{MgO}$	0.65	0.53	$0.59 \pm 0.06$
$\text{SO}_3$	0.19	0.21	$0.20 \pm 0.01$
LOI	41.97	40.43	$41.20 \pm 0.77$
$\text{CaCO}_3$	89.25	89.75	$89.50 \pm 0.25$

Finally chemical analysis results of calcite and volcanic soil are within the required range so they can be used as cement filling and additive materials.

## 4.2 Raw Mix Design for OPC Clinker Production

Based on clinker compositional parameters the desired raw mix would be possible to calculate the proportion of different raw materials in the mix. For example in Mughar Cement Enterprise for Portland cement clinker manufacturing by using different method of proportioning From the chemical analysis values (the oxide compositions) of these raw materials in table 4.3.

Table 4.3 Oxide compositions of Portland cement raw materials (Practical values).

Raw materials	%CaO	%SiO <sub>2</sub>	%MgO	%Fe <sub>2</sub> O <sub>3</sub>	%Al <sub>2</sub> O <sub>3</sub>	%LOI	%H <sub>2</sub> O
Lime stone	46.77	9.21	0.32	1.16	2.01	38.13	3.0
Clay	0.99	42.92	0.45	16.21	27.74	10.69	20.0
Sand	2.10	85.36	0.64	2.99	6.02	2.11	8.0

The design of raw mix is based on the clinker compositional parameters here we took (LSF 0.93 and SR 2.2) and the value of major oxides from complete chemical analysis of the raw materials (lime stone, clay and sand) in table 4.3. The percentages of raw materials mixed in the raw mix are R1 for % lime stone, R2 for % clay and R3 for % of sand. These ratios are calculated and the results: R1 = 89.79%, R2 = 7.29% and R3 = 2.91% The designed raw mix using the derived formula and the clinker compositional parameters (SR= 2.2, LSF =0.93) and raw materials in table 4.3 as an input and finally the values shown in table 4.4 are the theoretical and practical outputs. The calculations were done computationally by mathematica V.5.1 software.

Table 4.4 Theoretical and practical major oxide values of the raw mix and clinker

Major oxides	%CaO	%SiO <sub>2</sub>	%Fe <sub>2</sub> O <sub>3</sub>	%Al <sub>2</sub> O <sub>3</sub>
Theoretical clinker compositions considering LOI	64.90	21.39	3.56	6.16
Practical clinker compositions test-1	65.39	21.50	3.62	6.15
Practical clinker compositions test- 2	65.51	20.44	3.92	6.30

This raw-mix was ignited in the Kiln with the temperature of 1300 °C-1450 °C and form Portland cement clinker. The composition of the manufactured clinker from practical chemical analysis is given in table 4.5.

Table 4.5 Complet analysis of oxide compositions of OPC clinker from practical analysis

Oxides	% Composition test 1	% Composition test 2	Average %compositions
CaO	65.39	65.51	65.45
SiO <sub>2</sub>	21.50	20.44	20.97
Al <sub>2</sub> O <sub>3</sub>	6.15	6.30	6.23
Fe <sub>2</sub> O <sub>3</sub>	3.62	3.98	3.80
MgO	2.73	2.73	2.73
SO <sub>3</sub>	0.38	0.38	0.38
Free CaO	1.12	1.12	1.2
Total	99.89	98.46	99.18

The material shown in table 4.5 is used for the manufacturing of Ordinary Portland Cement by adding 4-5% of gypsum and for Portland Pozzolanic Cement and Calcite filled cements manufacturing by blending with other filling materials and additives like calcite, volcanic ash, pumice, fly ash etc in different proportions. Manufacturing of Portland cement using only Portland cement clinker is not economical and productive. The addition of supplementary materials is important to manufacture different varieties of cements with different properties for many applications and other economical benefits.

### 4.3 Physical Analysis Results and Discussions

In physical analysis properties like fineness, compressive strength, specific surface, soundness, flexural strength, setting time, Permeability, Pozzolanicity Activity Index, drying shrinkage can be analysed or tested.

#### 1) Fineness

In Muger Cement Enterprise especially in Addis Ababa laboratory fineness is measured with 90  $\mu\text{m}$  mesh and specific surface is measured with Blain method. Fineness is important physical properties of cement because fineness can affect strength, bleeding, and hydration rate. As fineness increases hydration of cement increases, improve workability and develop early strength of composites because the surface area of particles increases for water contact for hydration. In this analysis for 7% calcite filled cement with fineness 2.12% and 7.9% (using 90  $\mu\text{m}$  mesh) with 0.5 water to cement ratio; the compressive strength at 2 days was 24.31  $\text{N}/\text{mm}^2$  and 20.24 $\text{N}/\text{mm}^2$  for fineness 2.12% and 7.9% respectively. The results indicate increasing fineness of cement helps to increase compressive strength and rate of hydration. See in table 4.6.

Table 4.6 Compressive strength of 7% calcite with different fineness

Fineness PCC (7% calcite OPC) by 90 $\mu\text{m}$ mesh	Compressive strength ( $\text{N}/\text{mm}^2$ ) at 2 days
2.12%	24.31
7.9%	20.24

## **2) Soundness**

Soundness is a measurement of its tendency to crack, distort, pit or disintegrate. Either of the following tests can be used to establish soundness:

- ‘Le Chatelier’ method uses a simple expandable ring to indicate the expansion of a sample over a set period of time by boiling method.
- The autoclave method tests for expansion after a certain period of time at elevated temperature in an autoclave.
- Cake test method prepare two similar samples and by colliding each other.

In this experiment Le Chatelier method is used to test the soundness of the composites all the specimens have no visible expansions. The result indicates that the sample become stable in dimensions and durable.

## **3) Setting time**

Initial setting time should not less than 60 minutes for low-heat cement (LHC) and should not be less than 30 minutes for PPC and all other cements. In this test only PPC (cement with 5% calcite and 30% volcanic soil) was tested and initial set 1.25hours and final set 2.75 hours was recorded. This setting time is enough for the cement to have good workability with out affecting early strength.

## **4) Compressive strength**

Of the various strength properties of concrete, it is generally the compressive strength, which attracts the greatest interest since it is this property which is made use of in designing building units of structural or of simple load bearing quality. In addition, it has a great practical and economic significance because the sections and sizes of the concrete structures are determined by it. Since most concrete structures are designed to resist compressive stress, it is this property which is usually prescribed by codes or standards.

One should know the compressive strength standard values and the minimum required compressive strength. The Standard of Compressive Strength is given as in table 4.7. After evaluate and compare the results based on standards it is possible to propose the composites for functions. All the specimens prepared were class 32.5N cements and it is possible to compare the result data with standard calss 32.5N.

Table 4.7. Standard compressive strength determined in BS EN 196-1.

Strength class	Early strength (N/mm <sup>2</sup> )		Standard strength (N/mm <sup>2</sup> )	
	At 2 day	At 7 day	At 28 day	
32.5N	-	≥16	≥32.5	≤52.5
32.5R	≥10	-		
42.5N	≥10	-	≥42.5	≤62.5
42.5R	≥20	-		
52.5N	≥20	-	≥52.5	≤72.5
52.5R	≥20	-	≥62.5	-

**NOTE 1:** The standard strength of cement is the compressive strength determined in accordance with BS EN 196-1 at 28 days. Four class of standard strength are covered: class 32.5, class 42.5, class 52.5 and class 62.5. The classification of cement according to standard strength is indicated by the figure 32.5, 42.5, 52.5, or 62.5.

**NOTE 2:** The early strength of cement is the compressive strength determined in accordance with BS EN 196-1 at either 2 days or 7 days. Two subclasses of early strength are defined for standard strength classes 32.5 and 42.5, a class with ordinary early strength and a class with high early strength.

The letter N or R indicates the classification of cement according to early strength, for ordinary or high early strength respectively, following the figure indicating the standard strength class.

## **Factors Affecting Compressive Strength**

Compressive strength depends on cement paste, the bond between sand and surrounding cement paste and the overall adhesion and compaction of the particles. The cement paste characteristics depend on the characteristic of the cement, water/cement ratio (w/c), and the completeness of hydration.

### **i. Water/Cement Ratio**

Water is mandatory for hydration reaction to proceed. But if the amount of water added is exceedingly much, the excess water remains free in the concrete forming capillary pores. These pores remain the composite to be permeable and weak in strength. The strength of composite increases as the water/cement ratio decreases provided that there is sufficient water for hydration of cement. For all specimens used w/c ratio of 0.5.

### **ii. Degree of Compaction**

Immediate upon placement of mortar in the forms, it should be compacted to assure close contact of the constituent materials with themselves, as well as with other forms. This consolidation may be accomplished with the use of hand tools, vibrators are much preferred. This consolidation eliminates air pores and achieved maximum density, which gives the higher strength and durability. In these experiments I used vibrator and for each specimen the vibrations was for 60 seconds.

### **iii. Curing of Concrete**

The last step, and exceedingly important one in the preparations of composites, is curing. As hydration of cement takes place only in the presence of moisture and at favorable temperatures, these conditions must be maintained for a suitable time interval called curing time. Here my testing was carried out after 24 hours of placing and compaction, samples were removed from their molds and placed in to water pond for one, six and twenty seven days. And the compressive strength test has done at 2, 7, and 28 days including the first day in the mold.

Compressive test results obtained from Portland Calcite filled Cement and Portland Pozzolanic Cement shown in table 3.8.and table 3.9 respectively.

Table 4.8 Compressive strength of calcite filled cement

Wt % of calcite	Compressive strength (N/mm <sup>2</sup> ) at 2 days	Compressive strength (N/mm <sup>2</sup> ) at 7 days	Compressive strength (N/mm <sup>2</sup> ) at 28 days
0	23.66	33.89	48.23
7	24.31	37.57	51.35
10	23.79	35.97	51.81
14	21.26	34.94	50.08
20	20.43	30.65	47.12
25	17.20	26.65	45.98

Based on the compressive strength standards the compressive strengths obtained from calcite filled cement at 2 days and 7 days are much greater than the minimum required strength shown in table 4.8.

The composites develop high compressive strength through time (as the age of composites increases the compressive strength also increases). Results recorded from all proportions of calcite additions from 7% to 25% the specimens developed high strength through time. See the table 4.8 and figure 4.1. However, the proportions or the amount of added calcite is above 10% results in decreasing of early strength. See figure 4.2. But for the additions of calcite up to 10% by weight there is no decreasing of early strength, but further additions of calcite lowers early strength.

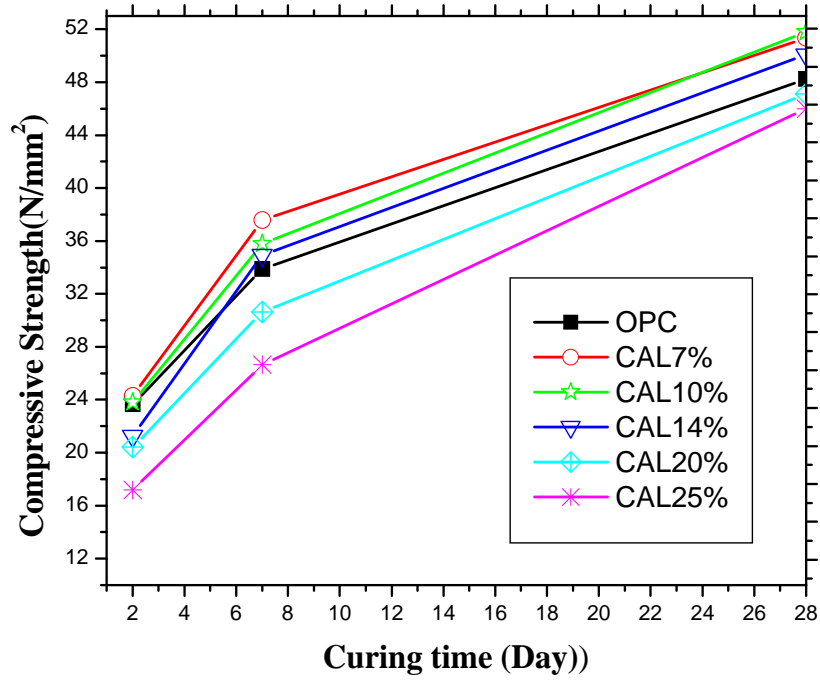


Figure 4.1 Compressive strength of calcite filled cement with time

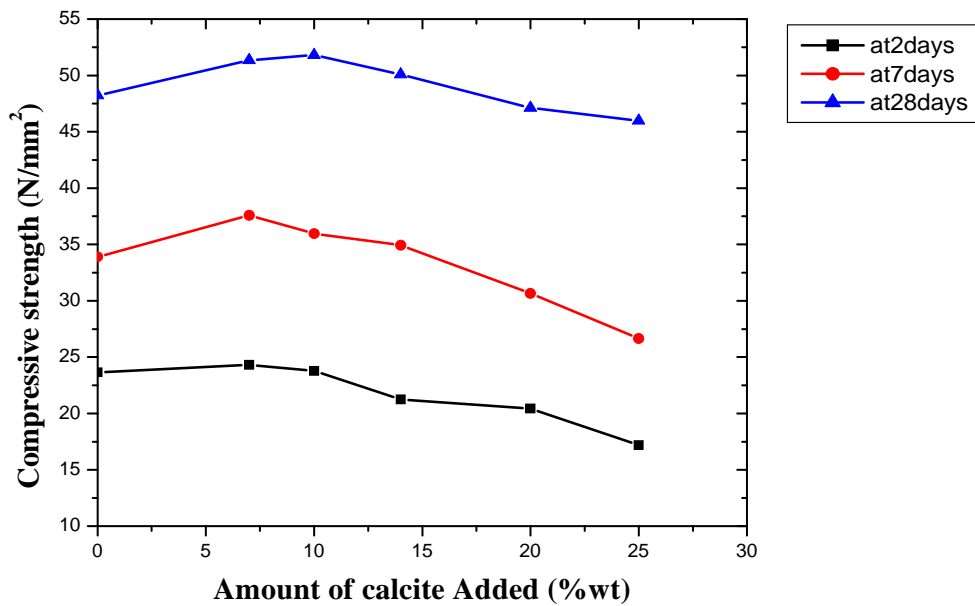


Figure 4.2 Compressive strength of calcite filled cement with varying calcite wt %

For this experimental analysis the amount of volcanic soil added and tested was very limited due to lack of time we could not analyze for bulk amount. The tests were done on 28%, 30%, 35% and 5% calcite and 30% volcanic soil proportions. Compressive strength results from these tests was given in table 4.9

Table 4.9 Compressive strength of PPC cement (with volcanic ash)

Wt % of volcanic ash	Compressive strength (N/mm <sup>2</sup> ) at 2 days	Compressive strength (N/mm <sup>2</sup> ) at 7 days	Compressive strength (N/mm <sup>2</sup> ) at 28 days
0	23.66	33.89	48.23
28	15.86	24.56	37.87
30	15.01	24.46	36.40
35	14.43	21.19	34.59
30% Volcanic ash + 5% calcite	15.103	23.95	36.57

As shown in table 4.9 additions of volcanic soil pozzolanic materials results decreases of early strength see also figure 4.3.

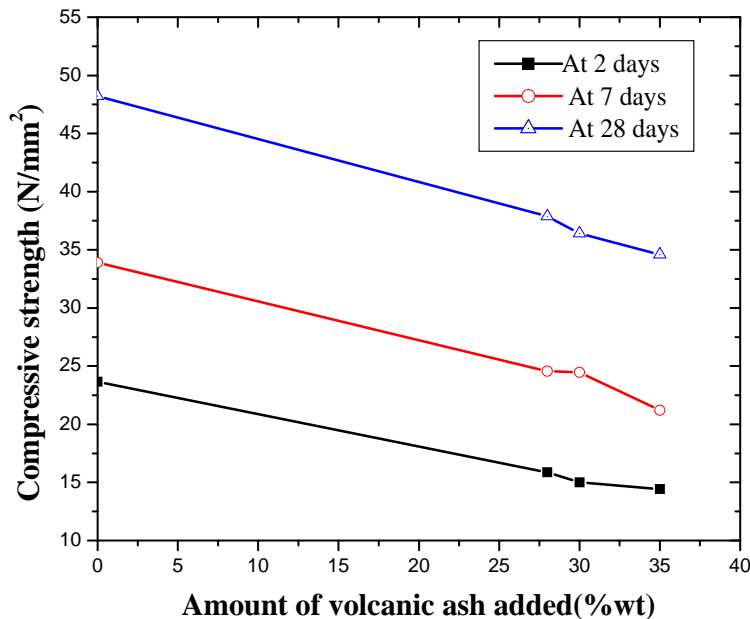


Figure 4.3 Compressive strength of PPC with varying wt % of volcanic ash.

However, through time the composites developed enough compressive strength (i.e. as curing time increases strength of composites increase) see figure 4.4.

Another one experiment was done by mixing 5% calcite and 30% volcanic soil with 65% OPC but the additions of 5% calcite on PPC (30% volcanic ash) there was no significant effect on compressive strength. It has almost similar compressive strength with 30% volcanic soil PPC. See figure 4.4.

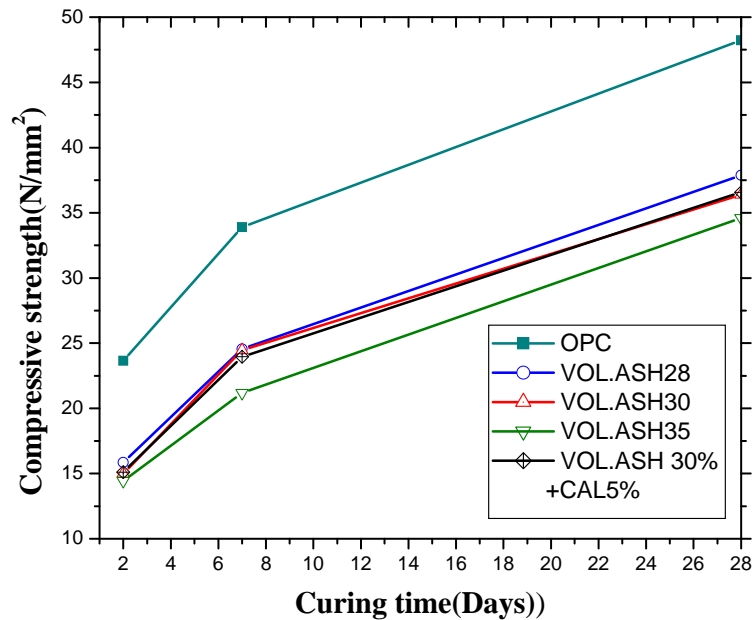


Figure 4.4 Compressive strength of OPC and PPC with time

The use of volcanic soil and calcite fillers to reduce the amount of cement used in normal and high performance concrete is an attractive proposition from an ecological viewpoint, because less energy is consumed in production, compared to OPC. Test results here have concentrated on compressive strength, but the principles are expected to also apply to higher-strength mixes. Results suggest that the quantity of cement can be reduced while maintaining equivalent strength by using a systematic procedure to optimize the amount of calcite and volcanic ash while maintaining a constant water/fineness ratio and constant consistency.

## **5. SUMMARY AND CONCLUSIONS**

### **5.1 SUMMARY**

As shown in Figures 4.1, 4.2, 4.3 and 4.4; generally, as the amount of calcite increases, the concrete containing calcite filler gives a higher strength than those of the cement especially with finely ground calcite. This behavior increases with the amount of calcite filler up to 15%. The incorporation of fines having a high specific area such as the finely calcite and up to 15% considerably improves the compressive strengths at early stages. Calcite content above 15% the concrete develops lateral strength. Concerning the coarse filler the compressive strength decreases for all amounts of substitution. The improvement of strength is essentially due to the acceleration effect of calcite filler related to the formation of calcium carboaluminate hydrates, which may be contributed to the overall increase in the rate of hydration. Also, the increased binding capacity of carboaluminate is likely due to its compact structure. Furthermore, the consumption of calcite in the formation of carboaluminate hydrates, the accelerating influence on the hydration of CA, the changes in the calcium aluminates hydrates between calcite filler and the cement constituents, in addition to the fineness of calcite are the different factors specific to the reactivity of calcite filler. Apparently, the surfaces of the individual filler particles provide sites for the nucleation cement hydration products such as the calcium silicate hydrate gel (CSH), which is the dominant hydration product in most hydrated Portland cements. The calcite filler acts primarily as an accelerator. It increases the rate of hydration and serves as crystallization nuclei.

The strengthening effect of filler on concrete paste is derived from the improvement of the pore structure. The number of small pores is increased at the same time as the number of large pores decreases, which has a positive influence on strength and durability. This study helped valorize local calcite fines, which may contain high calcium carbonate filler proportions, up to 25% of the OPC clinker or cement mass.

The fineness of calcite plays a considerable role in the improvement of mechanical performances of the concrete due to the formation the new compounds such as carboaluminates ( $C_3A.CaCO_3.11H_2O$ ), crystallized in fine hexagonal plates.

The chemical properties as well as mechanical property has been investigated simultaneously using varied experimental techniques.

The various experimental results obtained show that it is beneficial to use calcite fillers and volcanic soil. The following points may be drawn from this study:

- The chemical and physical roles of calcite filler addition lie in the formation of carboaluminates; crystal nuclei are due to the degree of fineness and particle size of fillers.
- The optimal calcite filler content that allows and obtaining of highest early mechanical resistance is up to 15% and lateral resistance above 15%.
- Concerning the cost, it is well known that the cement having filler and pozzolana is always the cheapest.
- The use of calcite fillers and volcanic ash as presented is not only beneficial to the cement industry, but also is friendly to the environment.
- The main sources of calcite used as cement filler are: calcite soil, limestone quarry fines and by products from caustic industries.

## **5.2 CONCLUSION**

This Thesis is the first ever from Materials Science Program in Addis Ababa University with these materials specially utilization of Calcite in Ethiopia to maximize the production of blended cement by reducing cost, energy consumptions, minimizing environmental hazardous and it is the art of improving Mechanical Performance of Concrete. In this study chemical properties of calcite and volcanic soil were analyzed and also their effects on the Mechanical properties of concrete. The Mechanical properties of concrete with the replacement cement by calcite from 7% to 25% by weight was studied and the result obtained shows high early compressive strength up to 15% and lateral compressive strength above 15% replacement. The volcanic soil replacement from 28% to 35% also gave some decreasing of early strength and good lateral compressive strength.

## **6. RECOMMENDATION**

We have found high compressive strength up to these limit of cement replacement it was not possible to study for further additions due to lack of time and shortage of research fund. Any industry after studies of the cost of productions of cement with the additions of these materials and it is possible to use calcite and volcanic soil for blended cement productions. In this study utilization of calcite is strongly recommended due to superior mechanical properties of concrete. The strength of the composites depends not only by the amount of filler but also highly on the fineness.

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## Declaration

This thesis is my original work and has not been presented for a degree in any other University and that all sources of materials used for this thesis have been dully acknowledged.

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This thesis has been submitted for examination with my approval as a university advisor.

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