ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

OPTIMUM UTILIZATION OF COAL ASH AS ADDITIVE FOR BLENDED CEMENT PRODUCTION

By
Mulatu Tadesse

A Thesis Submitted to the School of Graduate Studies of Addis Ababa University, Institute of Technology, in Partial Fulfillment of the Requirements for the Degree of Masters of Science in Chemical Engineering (Process Engineering)

Advisor
Whasik Min (Prof.)

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Addis Ababa
Ethiopia

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Approved by Board of Examiners

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LIST ABBREVIATIONS

ACAA	American Coal Ash Association
ASTM	American Society for Testing and Materials
CCP	Coal Combustion Product
CIC	Chemical Industry Corporation
COMPLANT	China National Complete Plant Import and Export Corporation
EDTA	Ethylene Diamine Tetra Acetic Acid
EN	European Standard
ES	Ethiopian Standard
FGD	Flue Gas Desulfurization
GTP	Growth and Transformation Plan
LOI	Loss On Ignition
MCF	Mugher Cement Factory
OPC	Ordinary Portland Cement
SCM	Supplementary Cementing Material
SEM	Scanning Electron Microscope
TEA	Tri- Ethanol Amine
XRD	X-Ray Diffraction
XRF	X- Ray Florescence

CEMENT CHEMISTRY ABBREVIATIONS

A	Aluminum Oxide, Al_2O_3
C	Calcium Oxide, CaO
F	Ferric Oxide, Fe_2O_3
H	Water, H_2O
S	Silica, SiO_2
Š	Sulfur Trioxide, SO_3
C_3A	Tricalcium Aluminate, $3CaO \cdot Al_2O_3$
C_4AF	Tetracalcium Aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
C_2S	Dicalcium Silicate, $2CaO \cdot SiO_2$
C_3S	Tricalcium Silicate, $3CaO \cdot SiO_2$
CH	Calcium Hydroxide, $Ca(OH)_2$
$CŠH_2$	Gypsum, $Ca_2SO_4 \cdot 2H_2O$
CŠ	Anhydrite, Ca_2SO_4
C-S-H	Calcium Silicate Hydrate, $nCaO \cdot SiO_2 \cdot mH_2O$
$C_6AŠH_{32}$	Ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
$C_4AŠH_{12}$	Monosulfoaluminate, $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$

ABSTRACT

The government of Ethiopia has given a great attention for establishment of chemical industries since 2011. The establishments of this chemical industry begin with coal based urea plant with an integration of a 90MW coal based thermal power plant for electric source. This power plant produces 75,000 ton per annum of coal ash as a waste during the production process. Using this ash, as raw material is an enormous opportunity both for cement and thermal power industries to reduce their environmental impact.

The aim of the research is to stress the characterization and optimum utilization of coal ash as additive for blended cement production. In this study coal sample was collected from Yayu and burned at home to get ash. The characteristics of coal ash and cement raw materials were investigated by classical and analytical testing methods. 15 types of blended cements having a solid residue of ≤ 10, (10-16], and (16-20]% on 45μm sieve were produced by inter-grinding of coal ash, clinker and gypsum in laboratory ball mill, with the clinker replacement levels of 20, 25, 30, 35, and 40% by mass. The performance of the cements was evaluated by conducting the following tests: setting time, soundness and compressive strength. The results showed that Yayu coal ashes possess sufficient pozzolanic characteristics to be used in production of blended cement, and the optimum clinker replacement level by this ash can range between 20-25% by mass.

Key words: setting time, soundness, compressive strength, pozzolanic, coal ash, blended cement,

CHAPTER ONE

1. INTRODUCTION

1.1BACKGROUND

In the process of generating power from coal, large quantities of Coal Combustion Products (CCPs) are produced. CCPs are the solid residues that remain after the combustion of coal within a furnace, and are collected in emission control processes. These are mainly boiler slag, bottom and fly ash and desulfurization products like spry dry absorption products and flue gas desulfurization (FGD) gypsum.

Coal combustion products have been used in the construction industry since the 1930's. Although the utilization of these products was limited to small scale applications in the early days, the use of coal combustion products has gained increasing acceptance in the construction industry in the last few decades. The interest in coal combustion products significantly increased during the 1970's because of the rapid increase in energy costs and the corresponding increase in cement costs [1].

In the early days of the power generation industry, coal combustion products (CCPs) were considered to be a waste material. The properties of these materials were not studied or evaluated seriously and nearly all of the coal combustion products were land filled. In the course of time, the cementitious and pozzolanic properties of bottom and fly ash were recognized and studied by several individuals and institutions. The products were tested to understand their physical properties, chemical properties and suitability as a construction material. During the last few decades these "waste" materials have seen a transformation to the status of "by-products" and more recently "products" that are sought for construction and other applications.

In the 1920's, more effective methods of firing power plant boilers were invented. These new processes involved burning pulverized coal instead of lump coal. While the process was a more efficient method of firing, the process generated an increased stream of fine combustion products and lower quantities of cinders. This fine combustion product is called fly ash, and the cinders that are relatively coarser are called bottom ash. As environmental awareness and land filling costs have grown, CCP generators and government regulators have encouraged the beneficial use of industrial by-products, including coal ash [2].

According to World Coal Ash Association 2011 report the worldwide production of coal combustion products was approximately 780 Million metric tons (Mt). The largest coal combustion product producing countries and reigns were; China 395 Mt, North America 118Mt, India 105Mt, European union (EU15) 52.6Mt, Africa 31.1Mt and Middle East as minor contributor. In Africa 92% of production coal combustion products was produced in South Africa. From 780Mt of the global CCPs produced, some 415Mt or 53% were reported as utilized. Utilization rate varies widely from country to country depending on the quality of CCPs produced, technological capability and degree of awareness on utilization possibilities. Japan had the highest reported effective utilization rate of 96.4% and Africa with lowest at 10.5% [3].

The American Coal Ash Association (ACAA) survey reported that the usage included a number of applications, with construction industries and civil engineering at 32.0%, followed by mining applications with 9.9% and other applications with 1.1%. These percentages are expected to increase, as a result of the development of new uses for CCPs, increased awareness of proven technologies, and global focus on sustainable development. 57% of the total CCPs produced in the USA are being stockpiled or disposed in landfills. Due to continued research and marketing efforts, the world was able to utilize 53 % of coal combustion products in 2010 compared to only 18 % in 1980 [4].

The disposal cost of CCPs has escalated significantly during the last couple of decades due to significant changes in landfill design regulations. Utilization of CCPs helps preserve existing licensed landfill capacity and thus reduces the demand for additional landfill sites.

Increased commercial use of CCPs translates to additional revenues and reduced disposal costs, which in turn translates to lower electric bills for electric customers. The use of CCPs in construction reduces the need for quarried raw materials, manufactured aggregates and Portland cement. Replacement of these virgin and manufactured materials with CCPs helps to conserve energy and reduce emissions associated with manufacturing and processing. When fly ash and bottom ash are used beneficially as engineered backfill material, these materials are replacing sand or gravel that would otherwise have been quarried and transported from various locations. The use of CCPs helps preserve mineral materials from sand and gravel pits and quarries as well as provides construction cost savings associated with operation. It is also important to keep in mind that every time Portland cement is replaced or displaced with fly ash, CO_2 and other

emissions to the atmosphere from cement production are reduced by decreasing the need for limestone calcinations as well as the fossil fuel that is consumed for production [2].

In Ethiopia, the Chemical Industry Corporation (CIC) was established with Council of Ministers Regulation No. 280/2012, on 7th January 2013 with the initial capital of birr 21.7 billion with the intention to develop the sector and enhance its contribution to the development of the country. The corporation integrated a public enterprise and two governmental projects namely; Mugher Cement Enterprise, Coal Phosphate Fertilizer Project and the National Rubber Nucleus Project.

A comprehensive investigation on the possibilities of establishing a fertilizer plant in Ethiopia had been made by China National Complete plant Import & Export Corporation (COMPLANT) in 1997. A Detailed Techno-economic Viability Study of Yayu Coal-mine completed under a contract awarded to COMPLANT in 2007.

A coal based fertilizer project is being undertaken to establish urea fertilizer production plant of annual capacity of 300,000 metric tons in the first phase. A coal fired co-generation thermal power plant of 90 MW capacity was also under construction. According to the techno-economic viability study of the project, the coal fired plant will produce 75,000 metric tons of ash per year [5].

The aim of this study is to investigate the suitability of Ethiopian Yayu coal ash as a cement additive in blended cement production. Currently coal ash (especially fly ash) widely used as cement additive all over the world. The properties of coal ash mainly fly ash vary significantly with coal composition and plant operating conditions. Each fly ash from different place has different quality, where quality requirements for fly ash vary depending on the intended use. In this study the properties of cement and coal ash is examined to establish optimum level of replacement for blended cement production.

Therefore, using this coal ash as cement additive will add to the competitiveness of the chemical industry corporation in environmental pollution control, as well as the reduction of both cement production and ash damping cost.

1.2 STATEMENT OF THE PROBLEM

The establishment of a coal based urea fertilizer integrated with the 90MW coal fired power plant for electrical energy source is in the Oromia regional state in the Ilubabor Zone in Yayu Wereda. It is expected that the power plant will produce 75,000tons of coal ash annually. Many researches on the effective utilization of coal ashes have been done all over the world, such as aggregate for road construction, brick and tile fabrication, land filling, filler in plastics and paint, and raw materials for cement industry [6].

However, the effective crucial and economical application has been varies from place to place on the quality of coal ash produced and its intended use. In these circumstances, the effective utilization of coal ashes is strongly desired from environmental, ecological and economical points of view.

The major aim of this research is to stress the characterization and optimum utilization of Ethiopian Yayu coal ash as additive for blended cement production. If this coal ash is proven compatible for the cement additives, more than 75% by mass of ash produced will be utilized. This will have dual advantages for CIC in green technology and reduction of cement production the damping cost.

1.3OBJECTIVES OF THE STUDY

The general objective of this study is to investigate the suitability of Yayu coal ash as a cement additive and optimum utilization in blended cement production.

Specific objectives:

The specific objectives are:

- Analysis of the chemical compositions and physical properties of the cement raw materials including Yayu's coal ash
- Determination and characterization of the optimum percent replacement of clinker with coal ash without affecting cement quality.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 COMPONENTS AND PROPERTIES OF CEMENT

Cement is a common construction material; a binder in mortars and concretes that hardens in the presence of water. Cement is called *hydraulic*, when the hardened product is stable in an aqueous environment. The most widespread hydraulic cement today is *portland cement* – a finely ground gray-to-white powder composed primarily of calcium silicates, calcium aluminates, and calcium ferrites, derived from mineral ingredients.

The European prestandard ENV 197-1 states that: Cement is a hydraulic binder, a finely ground in organic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which after hardening ,retains its strength and stability even under water[7],[12]. The cement as we know today is a specialized building material which is a result of various innovations over the past and is made in sophisticated manufacturing facilities.

The oldest use of cement dates back to the thousands of years of old Egyptian civilization. The Egyptians used natural cement made by combining limestone and gypsum for the construction of their massive and highly impressive pyramids. The fact that the Egyptian Pyramids have proudly stood the test of time over such a long period of human history is a testimony to the phenomenal strength of cement. However, it must be stated that the ancient Egyptian cement was very different from the cement in use today. Later in the Roman era, the concept of cement advanced further. Romans used a combination of slaked lime with Pozzolana, a volcanic ash from Mount Vesuvius. The Romans made many impressive structures using this cement. The Basilica of Constantine is one popular example of Roman construction in which they used such cement mortar. In eighteenth century England, John Smeaton, a British engineer, was assigned the task of re-constructing the Eddystone Lighthouse, a structure that had witnessed repeated structural failure. In 1756, Smeaton conducted a number of experiments that led to the discovery that cement made from limestone containing a considerable proportion of clay would harden under water. Based on this discovery, Smeaton rebuilt this lighthouse in 1759 and this time, it stood strong for 126 years.

Cement went through many more improvements and developments in the nineteenth and twentieth century. The industrial revolution and the subsequent development of the rotary kiln paved the way for huge and sophisticated cement manufacturing plants. These plants possess the capability of a homogenous mixing and intense heating of the raw material thus vastly improving the quality of the cement produced. The sophisticated quality-testing equipment employed by modern cement plants further helps in ensuring the quality of the cement produced [8],[9].

Basically there are two types of cement manufacturing processes. Wet process is grinding and mixing of cement raw materials in the existence of water; while dry process is done at their dry state.

Table 2.1 Comparison of Wet and Dry Cement Manufacturing Process (adapted from Dr. Basil Salah, "Concrete Technology" chapter one) [10].

Criteria	Wet process	Dry process
Hardness of raw material	Any type of raw material	Quite hard
Moisture content of	Slurry 35-50%	Raw mix less than 12%
Fuel consumption	High	Low
Time of process	higher	Lesser
Quality of product	Superior and more consistent	Inferior and less consistent
Size of kiln needed	Bigger	lower
Overall cost	higher	lower

Three production steps are distinguished in the description of the production of cement as shown figure 2.1

- ✓ Preparing raw materials: Mixing/homogenizing, grinding and drying produces the raw meal.
- ✓ Burning of raw meal to form cement clinker in the kiln: The components of the raw meal react at high temperatures (900-1500 °C) in the precalciner and in the rotary kiln, to give cement clinker.
- ✓ Finish grinding of clinker and mixing with additives: After cooling the clinker is ground together with additives to produce different types of cement

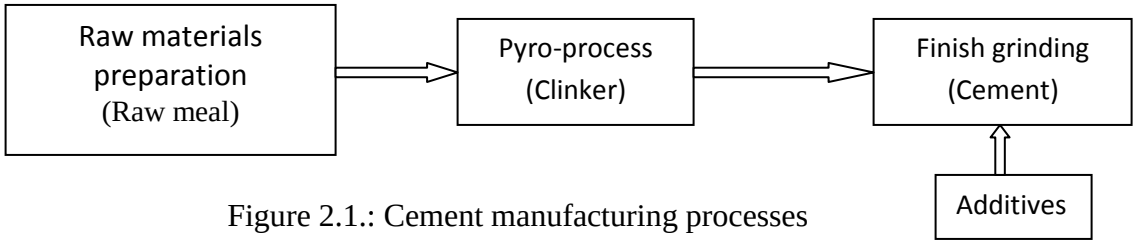


Figure 2.1.: Cement manufacturing processes

2.2 BLENDED CEMENT

Cement mixtures containing ordinary Portland cement clinker and at least one supplementary cementing material (SCM) are called blended cements. Blended cements blended or interground at cement plants are generally more uniform and produce better results than blended concrete mixtures combined at the concrete mixer

Climate change is an important issue all over the world. Carbon dioxide emission has been a serious problem in the world due to the greenhouse effect. Today many countries agreed to reduce the emission of CO_2. Many phases of cement and concrete technology can affect sustainability. Cement and concrete industry is responsible for the production of 7 % carbon dioxide of the total world CO_2 emission [11]. The use of supplementary cementing materials (SCM), design of concrete mixtures with optimum content of cement, and enhancement of concrete durability are the main issues toward sustainability in concrete industry.

During the past thirty years the use of by-product materials in concrete, either as components of blended cements, or as admixtures, has been increased significantly. One advantage offered by blended cement is the possibility of using less clinker to produce the equivalent amount of cement, thereby reducing energy consumption and CO_2 emissions. Manufacturing blended cement can save as much as 40% of the fuel and increase cement production by 50-100% without reducing the quality or performance of the product. Secondly, the incorporation of pozzolans can significantly improve the basic properties of fresh and hardened concrete. These include improve the workability; control of alkali silica reactivity; improved resistance to sulfates and dilute acids, and reduced heat evaluation which is the particular concern in hot weather and mass concrete. [12]. Possible disadvantages include slower rates of strength gain, particularly at lower curing temperatures, and greater sensitivity to poor curing, which can be mitigated by proper proportioning, increasing the fines of the cement to be milled, and appropriate additions of chemical admixtures.

Blended cements contain Portland cement clinker and other inorganic materials, both natural and industrial, that are used in quantities of 5% or more by mass of cement. The production of blended cements incorporating pozzolanic materials began in Italy in 1929. Cements containing granulated blast furnace slag have been produced in Germany, France, Luxemborg, Belgium, and other countries for more than half a century. In Ethiopia up to know natural pozzolan is used as

supplementary cementing materials for production of blended cement. Production history of blended cement in Ethiopia goes more than 40 years [13].

2.2.1 CEMENT CLASSES

Two approaches are normally used to classify cements - the first is in respect of their composition, and the second is in terms of their performance-related properties.

The two major international contributions to the classification of cement have been made in the USA through the American Society for Testing and Materials (ASTM) and European committee for standardization (ENV). ASTM has a number of prescriptive standards for the use of SCMs in blended cements and concrete: C618, C989, &C1240.ASTM C150 &C595 are the prescriptive standard for Portland & blended cement respectively. The European prestanderd ENV 197-1 on the types and composition requirements has also been proposed by European Committee for Standardization as in Table 2.2

Portland cements are made in many parts of the world but go by different names. Portland cement is denoted per ASTM standard C-150 as:

- Type I: general use portland cement. In some countries, this type is known as ordinary portland cement.
- Type II: general use portland cement exhibiting moderate sulfate resistance and moderate heat of hydration.
- Type III: high early strength portland cement.
- Type IV: portland cement having a low heat of hydration.
- Type V: portland cement having high sulfate resistance.

Table 2.2 Types and composition requirements (% by mass) for European Cements[1] adapted from PCA R&D bulletin RD112T [14]

Cement types	Designation	Notation	Cllinker	Granulated blast furnace slag	Silica fume	Nature pozzolan	Industrial pozzolan	Siliceous fly ash	Calcareous Fly ash	Burnt shale	limestone	Minor additional constituents[2]
			K	S	D[3]	P	Q[4]	V	W	T	L	
CEM I	Portland cement	CEMI	95-100	-	-	-	-	-	-	-	-	0-5
CEM II	Portland Slag Cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	0-5
	Portland- Silica fume Cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	0-5
	Portland- pozzolan Cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	0-5
	Portland fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	0-5
	Portland Burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	0-5
	Portland Limestone Cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	0-5
	Portland Composite Cement	CEM II/A-M	80-94	6-20[5]								
		CEM II/B-M	65-79	21-35[5]								
CEM III	Blast furnace Cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-
CEM IV	Pozzolanic Cement	CEM IV /A	65-89	-	11-35				-	-	-	-
		CEM IV/B	45-64	-	36-55				-	-	-	-
CEM V	Composite Cement	CEM V/A	40-64	18-30	-	18-30			-	-	-	-
		CEM V/B	20-38	31-50	-	31-50			-	-	-	-

[1]The value in the table refers to the cement nucleus, excluding calcium sulfate and any additives. [2]Minor additional constitutes may be filler or may be one or more of the main constitute unless included as main constitutes. [3]The proportion of silica fume is limited to 10%. [4]The proportion of non ferrous slag is limited to 15%. [5]The proportion of filler is limited to 5%.

Table 2.3 Mechanical and physical requirements given as characteristic value from Ethiopian Standard (ES 1177-1:2005) [15]

Strength class	Compressive strength in MPa				Initial setting time in Min.	Soundness (expansion) in mm.
	Early strength		Standard strength			
	2days	7days	28 days			
32.5N	-	≥16.0	≥32.5	≤ 52.5	≥75	≤10
32.5R	≥10.0	-				
42.5N	≥10.0	-	≥42.5	62.5	≥60	
42.5R	≥20.0	-				
52.5N	≥20.0	-	≥52.5	-	≥45	
52.5R	≥30	-				

2.2.2 HYDRATION REACTION OF CEMENT

In strictly chemical terms hydration is a reaction of an anhydrous compound with water, yielding a new compound, a hydrate. In cement chemistry hydration is understood to be the reaction of non-hydrated cement or one of its constituents with water, associated with both chemical and physico mechanical changes of the system, in particular with setting and hardening. A partial hydration of cement may even take place in humid air, whereas for a complete hydration the cement must be mixed with sufficient amounts of water.

As Portland cement is a multi-component system, its hydration is a rather complex process consisting of a series of individual chemical reactions that take place both in parallel and successively. The process gets under way spontaneously upon contact of the binder with water and is associated with liberation of heat [9].

The progress of hydration and its kinetics are influenced by a variety of factors, especially

- by the phase composition of the cement and the presence of foreign ions within the crystalline lattices of the individual clinker phases;
- by the fineness of the cement, in particular by its particle size distribution and specific surface;
- by the water-cement ratio used;
- by the curing temperature;
- by the presence of chemical admixtures, i.e. chemical substances added in small amounts to modify the hydration rate and properties of the cement paste;
- by the presence of additives, i.e. materials interground with cement in larger amounts, such as granulated blast furnace slag or pulverized fly ash.

The major components of cement that react with water to produce reaction products are tricalcium silicate (C_3S),dicalcium silicate (C_2S),tricalicum aluminate(C_3A), and tetracalcium alumionferite (C_4AF) [7].

The important strength-developing hydration reactions are those of C_3S and C_2S. Typical hydration reactions would be:

For C_3S: $2C_3S + 6H$ (water) $\rightarrow C_3S_2H_3$ ("tobermorite" gel) + 3CH (hydrated lime)

For C_2S: $2C_2S + 4H \rightarrow C_3S_2H_3 + CH$

The formula shown for tobermorite is only approximate, and some texts denote it as $C_3S_2H_4$, in which case both hydration equations above would need additional water (H) to start with. Actually, instead of just tobermorite, a whole family of similar calcium silicate hydrates (C-S-H) may be formed, and C-S-H is the preferred general term for these compounds. It is the C-S-H colloid or gel that is the actual binder in hydrated portland cement. The ultimate strength of the hardened cement paste will depend not only on the original total content of C_2S and C_3S but also on the completeness of their hydration.

Although the net hydration reactions for both C_3S and C_2S are similar, the reaction for C_3S is relatively fast, and C-S-H from it is responsible for virtually all of the early (e.g., within 3 days of curing) strength development of the cement. Typically, about 60% (by mass) of the C_3S has hydrated to C-S-H within the first 5 days of curing and about 70% has hydrated within about 10 days. Because of the formation of protective hydration shells, the remaining un reacted C_3S particle cores hydrate much more slowly, reaching about 75% hydration after 20 days of curing, about 80% hydration after 28 days (a standard measurement interval), and 85% after 60 days. Beyond 60 days, the rate of C_3S hydration slows dramatically and the incremental hydration and strength contribution is of little practical importance.

In contrast, the hydration of C_2S is relatively slow, with only about 20% hydration after 5 days of curing, about 30% after 10 days, 35% after 20 days, about 40% after 28 days, and only about 55% at 60 days. Its rate of hydration slows further after 60 days. Accordingly, the C-S-H derived from the hydration of C_2S, while making little contribution to the early strength of the concrete, contributes a significant proportion of the strength gain after the first week or so of curing.

As shown above, the C_3S and C_2S hydration reactions release free lime. Based on the typical clinker mineral proportions and their hydration reactions, it can be shown that the net free lime release during

clinker hydration, overall, is roughly 25%–33% of the original CaO content of the clinker. Free lime in hardened concrete is not particularly desirable because it increases the chemical reactivity of the surface (including along cracks) and can leach out in an unsightly fashion. On the other hand, by maintaining a high pH in the aqueous phase, free lime can help protect steel reinforcing bars (rebar) in the concrete from corrosion should water and oxygen reach the rebar via cracks. The lime is also available to react with any pozzolans that may have been added to the cement or concrete mix.

Alkalis, particularly sodium (Na_2O, or N in shorthand), can combine with C-S-H to form complex hydrates (e.g., C-S-N-H) that are unstable and prone to swelling compared with regular C-S-H. Alkalis can also react with forms (amorphous, opaline, or very fine grained crystalline) of silica in some aggregates used in concrete, forming highly hygroscopic alkali-silicate hydrates (e.g., N-S-H), and generally weakening the bond between the aggregates and the cement paste and forming higher-volume phases. These and similar reactions, collectively called alkali-silicate reactions (ASR) or alkali-aggregate reactions, can cause cracking of hardened concrete. The cracks not only weaken the concrete but render its interior susceptible to additional alkali or other chemical attack, and to freeze-thaw damage in cold weather regions. Approaches to controlling ASR reactions include selecting portland cements having lower alkali contents (e.g., ASTM C-150 provides for a low-alkali cement designation if the cement has a total alkali content [defined as $Na_2O + 0.658\ K_2O$] content of 0.60% or less), testing of aggregates for reactivity, and the incorporation of pozzolans into the cement paste. Pozzolans contain active silica which "sacrificially" combines with the alkalis in the paste (thus leaving less alkalis available to react with the aggregates), and significantly reduce the hardened concrete's porosity [16].

The other two clinker minerals, C_3A and C_4AF, have complex hydration reaction paths that are similar to each other, but those of C_3A are more important because they are much more rapid and exothermic. Having C_3A in the cement primarily enhances initial set and speeds, via release of heat, the hydration of C_3S (the presence of C_3A also has benefits to the cement manufacturing process because it speeds the overall formation of the clinker). In the absence of significant sulfate, C_3A very rapidly— almost instantaneously—forms C_3A-hydrates, many of which are unstable and may subsequently convert to other forms. One of the many possible sequential hydration reactions is:

$$2C_3A + 21H \rightarrow C_2AH_8 + C_4AH_{13} \rightarrow 2\ C_3AH_6 + 9H.$$

A minor, but lime-consuming, reaction is:

$$C_3A + 12\ H + CH \rightarrow C_4AH_{13}$$

The hydration of C_3A in the absence of sulfate can be so rapid as to cause the undesirable condition known as *flash set*. This is controlled through the addition of sulfate, usually as gypsum and/or anhydrite. Plaster is only rarely used because it hydrates so quickly back to gypsum that its use is rather counterproductive. The use of plaster also increases initial water consumption. A typical hydration reaction of C_3A in the presence of rate-controlling sulfate (here shown as gypsum) would be:

$$C_3A + 3\ C\bar{S}H_2 + 26\ H \rightarrow C_6A\ \bar{S}_3H_{32}\ (\text{“ettringite”})$$

Flash set is controlled because ettringite forms a shell around the C3A particles, which slows water diffusion to, and hence the hydration of, the residual C3A cores. Ettringite is stable only in the presence of excess sulfate. If this condition is not met (i.e. not enough gypsum present, or in the evolving conditions at the ettringite-residual C3A core interface), then ettringite reacts with C3A to form a monosulfate phase:

$$C_6A\ \bar{S}_3H_{32} + 2\ C_3A + 4H \rightarrow 3\ C_4A\ \bar{S}H_{12}\ (\text{“monosulfate”})$$

Alternatively, C_3A hydration under low sulfate conditions can be expressed by:

$$C_3A + 10H + C\bar{S}H_2 \rightarrow C_4A\bar{S}H_{12}$$

An important property of the monosulfate phase is that, in the presence of sulfate ions, it can re-form ettringite, such as by the reaction:

$$C_4A\ \bar{S}H_{12} + 2\ C\bar{S}H_2 + 16H \rightarrow C_6A\ \bar{S}_3H_{32}$$

Ettringite has a molar volume of about 735 cubic centimeters (cm3) per mole and monosolfate about 313 cm3 per mole. Because of this volume difference, re-formation of ettringite from monosulfate can cause expansion of the concrete. This is not much of an issue while the cement paste has yet to harden, but if ettringite re-forms in hardened concrete, the result can be cracking or spalling of the concrete. This process is known as sulfate attack and is prevalent in regions (commonly desert areas) having sulfate-rich ground water, or it can occur if too much gypsum is present in the cement. Thus the proportion of gypsum in the cement is important. Where sulfate attack from groundwater is likely, concretes are better made using a sulfate resistant portland cement, such as Type II, or better yet, Type V; both have low concentrations of C_3A. Type IV cement would also show resistance to sulfate attack, but would be less desirable for most applications because its relatively low C_3S content would

cause it to develop strength relatively slowly. Alternatively, sulfate resistance is improved by using a blended cement, as addition of pozzolans lowers the overall C_3A content of the cement paste and reduces the porosity (hence sulfate entry potential) of the concrete

The ferrite mineral C_4AF does not play a critical role in cement hydration. The chief value of ferrite is in its effects on kiln reactions to form C_3S (see process mineralogy discussion below). The hydration of C_4AF is broadly similar to that of C_3A, although the reactions tend to be slower and much less exothermic. The reaction stoichiometries will vary given the fact that, as noted earlier, C_4AF is merely a mean composition for the ferrite solid solution having end members C_6A_2F and C_6AF_2. In the absence of sulfate, the F partially substitutes for some of the A (partial substitution denoted as A, F) in the analogous C_3A hydration products, as shown in the reaction:

$$2C_4AF + 32H \rightarrow 2C_2(A,F)H_8 + C_4(A,F)H_{13} + (A,F)H_3 \text{ where total AF = total (A,F)}$$

In the presence of hydrated lime (from C_3S and C_2S hydration), however, the formation of $(A,F)H_3$ is suppressed and a stable AF-hexahydrate ($C_4(A,F)H_6$) is formed that is analogous to C_3AH_6, with a possible net reaction being:

$$C_2(A,F)H_8 + C_4(A,F)H_{13} + (A,F)H_3 + 6CH \rightarrow 3C_4(A,F)H_6 + 12H$$

2.3 COAL RESERVE AND ITS ASH PROPERTIES

Economic growth of countries is strongly associated with the use of energy. However, clean energy with minimum environmental impacts is vital for a sustainable socioeconomic development, particularly in the developing countries. Today in all corner of the globe, fossil fuels are the major source of energy generation. The demand for the fossil fuels has been increasing rapidly for the last two decades due to increased economic activities and changing lifestyles.

Contemporarily, Coal remains a major source for the global energy generation. Coal currently supplies around 30% of primary energy and 41% of total electricity generation; the remainder is used for the production of steel, cement, certain chemicals and domestic purpose. Coal use is forecast to rise over 50% by 2030, with developing countries responsible for 97% of this increase, primary to meet improved electrification rates [3]. Coal's dominant position in the global energy mix is largely due to the fact it is abundant, widely distributed across the globe and affordable [17].

Cement industry is said to be energy intensive together with steel, paper and petro-chemical industries. The primary fuel used in cement industries is fossil fuel, i.e oil, natural gas and coal. The cement industries in early fifties of the last century were using coal as a fuel in a wet processing and at that time environment pollution was not a key issue. In the following two decades, however, with the advent of dry process technology which required a uniform quality of raw materials for satisfactory operation and with increasing stress on environmental issues, a transformation took place and gradually the cement industries switched over to furnace oil. Since 1973, oil embargo, the steep rise in the cost of oil has caused many plants to convert back to the use of pulverized coal to serve as primary fuel. Since the last three decades and to date, cement plants converted from oil to coal and as of today almost 90 % of cement plants around the world are using coal for clinker burning [18].

2.3.1 COAL RESERVE AND PRODUCTION

Coal is a fossil fuel resource formed from peat and decayed vegetative matter from prehistoric swamps. Coal formation occurs over several hundreds of millions of years as the swamp humus degrades and is buried under layers of sediment. Increases in pressure and temperature compress the humus, reduce the moisture content and other organics, and create coal seams. Ultimately, coal is sedimentary rock comprised primarily of carbon, hydrogen, oxygen, sulfur, and nitrogen.

Coal resources are broadly dispersed across geographical locations with appreciable reserves on every continent except Antartica. In 2004, global recoverable coal reserves were estimated over 900 billion metric tons with major reserves in United States, China, India, Russia, and Australia [19]. Global coal production and consumption is expected to increase on average at 1% to 2% annually until 2030. China, India and the United States consume most of the world's coal. These countries, along with Australia and South Africa, are also the top coal producing countries.

2.3.2 CLASSIFICATION OF COAL AND ENVIRONMENTAL IMPLICATION

Coal seams are characterized by the coal type (rank), the presence of organic and inorganic matter, thickness and layering (banding), and fractures (cleats). In the US, the American Society of Testing and Materials (ASTM) standardizes methods to analyze coal for chemical and physical characteristics pertinent to industry use and coal bed science. An ASTM procedure to classify coal by rank (low to high) approximates the heating value, fixed carbon, moisture content and volatile matter in coal. Given the various characteristics and origins of coal, knowing the coal rank provides insight into coal behavior during extraction and conversion. Lignite and sub-bituminous are considered low rank coals, characterized by light brown or dull black color, high moisture content, and a low heating value. By comparison, bituminous coal and anthracite are high rank coals, black and reflective in appearance with less moisture and a higher heating value from more fixed carbon. Sub-bituminous and bituminous coals are the most plentiful types of reserves worldwide.

Table 2.4 Classification characteristics by coal rank[19]

Coal rank	Volatile matter (wt %)	Fixed carbon (wt %)	Heating value(MJ/Kg)
Lignite	27-35	65-73	26-28
Sub- bituminous	22-27	73-78	28-32
Bituminous	8-22	78-92	32-36
Anthracite	< 8	> 92	36-37

Although coal is economically affordable, coal mining and conversion pollutes the environment more than other fossil fuels. When utilized, coal is removed from its existing environment and converted to heat, gases and particulate emissions (ash). An array of pollutants such as dioxins, mercury, particulates, and greenhouse gases are released with coal conversion impacting the environment and atmosphere. Mining and preparation also immediately effects the local physical environment. Coal is mined from the surface (open cut) or underground depending on the depth of a coal seam. While surface mining is safer than underground mining, the scale of current surface mine operations alters the landscape, affecting soil and nutrient dynamics, animal and plant habitats as well as watersheds.

Surface mining accounts for about 40% of world production. Therefore mitigation of these pollutants must be applied when surface coal mining to protect the environment..

2.3.4 SOURCE AND CHARACTERISTICS OF ETHIOPIAN COALS

Ethiopia has discovered a significant potential of higher grade lignite resource at different places in the country the most promising resource areas are found at Yayu, Debre birhan, Delbi Moye followed by Chilga, Mush Valley and Wuchale with low grades lignite potential respectively. These lignite deposits are found in various parts of the central high lands of Ethiopia but at present Yayu deposit is mined in small quantity for different small scale industries. Proximate analysis and calorific value data show that the Ethiopian coals fall under the soft coal series (lignite to bituminous coal), A total of about 297,000,000 metric tons of coal reserve and registered in the country [20], [21].

Table 2.5 Proximate analysis and calorific values of coal deposits in different basins [20]

Basin	**Moisture in %**	**Volatile matter %**	**Fixed carbon in%**	**Ash in%**	**Calorific Value in cal/g**	**Reserve (X 10^6)tons**
Delibi –Moye	0.3 - 8.5	17.9 - 29	28.5-58.1	11.2 - 49.1	2,520-6,495	60
Yayu	***8.1- 20.7***	***28.3 - 46.5***	***11.3 – 28.1***	***24.6 – 42.2***	***3,795-5,930***	***200***
Chilga	5.9 - 10.7	21.1 - 31.8	34.4 – 45.2	16.6 – 41.6	3,072 – 4,560	19
Lalo-Sapo	9.1 – 13.4	18.2 – 32.4	20.9 – 58.3	11.5 – 33.1	2,626 - 4,120	7.5
Chida	11.2 - 18.9	15 – 29.5	19.6 -51	22.8 – 37.3	2,492 – 4,333	9
Mush Valley	21.3 - 21.4	31.8 – 40.4	10.6 -27.9	23.1-27.9	2,824 – 3,568	1
Nejo	14.4 - 16	35.2 – 40.4	10.6 – 28.8	23.1 – 27.6	3,400 – 3,987	3
Wuchale	10.4 – 12.3	18 – 29.7	22.6 - 45.4	35.2 – 48.7	3,700 – 5,445	3.3

The Yayu basins have the highest coal reserve in Ethiopia. This is the place where coal based fertilizer integrated with electric power generation plants are under establishment by the Ethiopian government. This coal based power generation plant will produce much coal combustions products (ash). And this by products should be utilized by other factories for both economical and environmental reasons.

2.3.5 ASH GENERATION

In the process of generating power from coal, large quantities of coal combustion products (CCPs) are produced. CCPs are the solid residues that remain after the combustion of coal within a furnace, and are collected in emission control processes.

In the coal combustion process, CCPs are also generated in direct proportion to the variety, quantity and ash content of coal consumed. The pulverized coal is burned in the furnace to generate heat, and the hot gases then pass around the bank of tubes in the boiler and are eventually cleaned and

discharged through the plant chimney. In large power plants that consume large quantities of coal, substantial quantities of coal ash are produced. The ash that is collected in electrostatic precipitators or bag houses is called fly ash.

In electrostatic precipitators the flue gas is passed between electrically charged plates where the fly ash particles are then attracted to the plates. Bag houses can also be used to collect ash with bags that filter the fly ash out of the flue gas stream. The fly ash particles are periodically knocked off the plates or bags and fall into the hoppers located at the bottom of the electrostatic precipitators or bag houses. The fly ash is then pneumatically transported to storage silos. The storage silos are equipped with dry un loaders for loading dry bulk semi tankers or rail cars, and wet un loaders for conditioned ash or disposal applications.

Bottom ash is formed when ash particles soften or melt and adhere to the furnace walls and boiler tubes. These larger particles agglomerate and fall to hoppers located at the base of the furnace where they are collected and normally ground to a predominantly sand size gradation. Some bottom ash is transported to storage dry, but most is transported wet from the furnace bottom to dewatering bins where water is removed prior to unloading and transports to construction sites or storage stockpiles. Figure 2-2 shows the typical ash generation process in a coal-fueled power plant.

The ash collected from pulverized-coal-fired furnaces is fly ash and bottom ash. For such furnaces, fly ash constitutes a major component (80 to 90%) and the bottom ash component is in the range of 10 to 20%. Boiler slag is formed when a wet-bottom furnace is used. The non-combustible minerals are kept in a molten state and tapped off as a liquid. The ash hopper furnace contains quenching water. When the molten slag contacts quenching water, it fractures, crystallizes, and forms pellets, resulting in the coarse, black, angular, and glassy boiler slag. The boiler slag constitutes the major component of cyclone boiler by-products (70 to 85%). The remaining combustion products exit along with the flue gases.

Flue gas desulfurization (FGD) material is the solid material resulting from the removal of sulfur dioxide gas from the utility boiler stack gases in the FGD process. The material is produced in the flue gas scrubbers by reacting slurried limestone or lime with the gaseous sulfur dioxide to produce calcium sulfite. Then the calcium sulfite is further oxidized to calcium sulfate (synthetic gypsum) which has the same chemical composition as natural gypsum. The dewatering system removes water from the calcium sulfate leaving the FGD absorber modules into hydro cyclone centrifuges and onto belt filter presses. Vacuum pumps beneath the belt siphon the water out of the material, leaving it

with about 10 percent moisture content. A belt conveyor system transports the dewatered materials from the dewatering building to an adjacent storage shed [3]. Figure 2.2 shows the ash production process flow diagram.

Currently, close to a billion tons coal is burned annually in the world to generate electricity and as a result, nearly 130 million tons of CCPs are produced. One –third of these CCPs are utilized, while the rest are disposed of mainly in landfills. Increasing costs and heightened environmental regulations are making the disposal of CCPs an undesirable option [22]. Utilization of CCPs as raw materials results in numerous benefits, including:

- A decrease in the demand for landfill space and handling costs
- Conservation of natural resources
- A cleaner safer environment
- Reduction CO_2 emissions
- A boost in economic development

Utilization of CCPs in cement and concrete industry has significant environmental benefits such as:

- Increasing the life of concrete roads and structures by improving concrete durability when fly ash use as concrete mix, bottom ash and sag as sub base for construction,
- Reduction in energy use and greenhouse gas and other adverse air emissions when fly ash is used to replace or displace manufactured cement,
- Reduction in amount of coal combustion products that must be disposed in landfills, and
- Conservation of other natural resources and materials when FGD used as cement retarded.

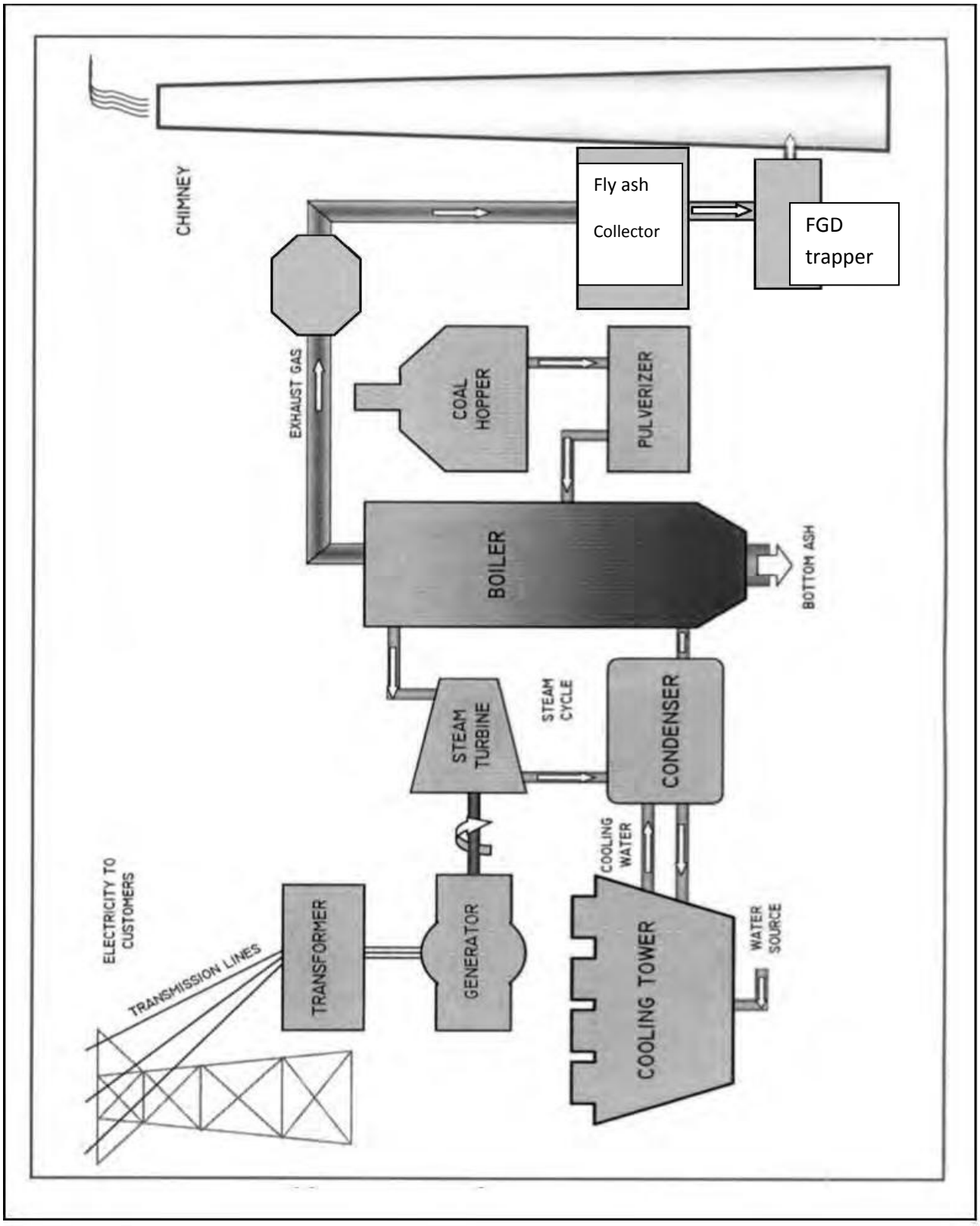


Figure 2.2. Schematic layout of a coal-fired electrical generating station [2]

Out of four CCPs mentioned above fly ash is widely and commonly used as supplementary cementitious materials (SCM) in concrete either as part of blended cement or a separate component added at stage of when the concrete mix is prepared around the world. A supplementary cementitious material, when used in conjunction with portland cement, contributes to the properties of the hardened concrete through hydraulic or pozzolanic activity, or both. As such, SCM's include both pozzolans and hydraulic materials. A pozzolan is defined as a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value, but that will, in finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperatures to form compounds having cementitious properties. Pozzolans that are commonly used in blended cement production include fly ash, silica fume and a variety of natural pozzolans such as calcined clay and shale, and volcanic ash. SCM's that are hydraulic in behavior include ground granulated blast furnace slag and fly ashes with high calcium contents (such fly ashes display both pozzolanic and hydraulic behavior) [23].

2.3.6 PROPERTIES OF FLY ASH

a. Physical properties

Fly ash particle size is finer than Ordinary Portland cement. Fly ash consists of silt sized particles which are generally spherical in nature and their size typically ranges between 10 and 100 μm [24]. The surface area of fly ash particles vary from 2,000-10,000 cm^2/g depending on the proportion of fine particles in the fly ash [7]. These small glass spheres improve the fluidity and workability of fresh concrete. Fineness is one of the important properties contributing to the pozzolanic reactivity of fly ash.

Fly ash colour depends upon its chemical and mineral constituents. It can be tan to dark gray. Tan and light colours are generally associated with higher lime content, and brownish colour with the iron content. A dark gray to black color is attributed to elevated unburned carbon (LOI) content. Fly ash color is usually very consistent for each power plant and coal source.

Fineness of fly ash is most closely related to the operating condition of the coal crushers and the grindability of the coal itself. Fineness of fly ash is related to its pozzolanic activity. For fly ash use in concrete applications, fineness is defined as the percent by weight of the material retained on the 45 μm (#325) sieve. ASTMC618 limits the maximum amount of fly ash retained on the 45 μm (#325) mesh sieve on wet sieving as 34%. Generally, a large fraction of ash particle is smaller than 3 μm in

size. In bituminous ashes, the particle sizes range from less than 1 to over 100 μm. A coarser gradation can result in a less reactive ash and could contain higher carbon content.

The specific gravity of fly ash is related to shape, color and chemical composition of fly ash particle. In general, specific gravity of fly ash may vary from 1.3 to 4.8.

Any amount of moisture in Class C fly ash will cause hardening from hydration of its cementitious compounds. Even surface spraying may cause caking. To prevent caking and packing of the fly ash during shipping and storage and to control uniformity of fly ash shipments, a 3.0% limit on moisture content is specified in ASTM C618. Therefore, it is important that such ashes have to be kept dry before being mixed with cement [25].

b. Chemical properties

Although several dozen minerals are present in coals, most occur in trace amounts. The majority of coal minerals that influence fly ash composition may be classified in to five groups: aluminosilicates (clays), carbonates, sulphides, chlorides, and silica (quartz). With the exception of quartz, all other minerals are substantially decomposed during coal combustion. Chemical reactions at high temperatures result in the formation of new glassy and crystalline phases. The bulk chemical composition of fly ash glassy and crystline phases consists mainly (95-99% by mass) of oxides of silica, alumina, iron, and calcium with smaller amounts (0.5-3.5%by mass) magnesium, sulfur, sodium, and potassium [26].

ASTM Standard C-618 specifies two classes of fly ash based on chemical composition. Class F fly ashes, which were at one time the only class, are required to have a minimum sum of three major oxides (SiO_2 +Al_2O_3 +Fe_2O_3) of 70% by mass. This requirement was designed to ensure adequate pozzolanic reactivity. Class F fly ashes are typically derived from burning anthracitic and bituminous coals.

Fly ashes derived from burning liginitic and subbituminous coals were found to enhance concrete quality even though therir silica, alumina, and ferric oxide contents were relatively low. Therefore, an additional fly ash class was added, Class C. Class C fly ashes are required to have a sum of three major oxides (SiO_2 +Al_2O_3 +Fe_2O_3) of 50-70% by mass.

Since Class C fly ashes have relatively low proportion of silica, alumina, and ferric oxides, they have relatively high proportions of the fourth major oxide, calcium. Class C fly ashes are often referred to as high –calcium ashes while Class F fly ashes are often referred to as low –calcium ashes.

A compilation of reported chemical composition of Class F and Class C ashes is shown in Table 2.6. In addition to high calcium contents relative to Class F fly ashes, Class C fly ashes typically have higher magnesium oxide, sulfur trioxide and alkali contents. Differences in the bulk chemical composition of fly ashes are reflections of the different glassy and crystalline compound compositions. The composition of glass and the types and proportions o crystalline compounds influence fly ash reactivity.

Table 2.6 Ranges of bulk chemical compositions of fly ash produced in North America (wt. %) [26]

Oxide	Class F fly ash	Class C fly ash
SiO_2	38-65	33-61
Al_2O_3	11-33	8.0-26
Fe_2O_3	3.0-31	4.0-10
CaO	0.6-13	14-37
MgO	0.0-5.0	1.0-7.0
Na_2O	0.0-3.1	0.4-6.4
K_2O	0.7-5.6	0.3-2.0
SO_3	0.0-4.0	0.5-7.3
LOI*	0.1-12	0.2-1.4

* Loss on ignition

c. Mineralogical Characteristics

X-ray diffraction study of the crystalline and glassy phases of a fly ash is known as mineralogical analysis. Mineralogical characterization determines the crystalline phases that contain the major constituents of fly ash. Generally, fly ashes have 15–45% crystalline matter. The high-calcium ashes (Class C) contain larger amounts of crystalline matter ranging between 25 and 45%. Table 3.2 presents crystalline phases in fly ashes identified by XRD analysis [25].

Although high-calcium Class C ashes may have less glassy or amorphous material, they do contain certain crystalline phases such as anhydride ($CaSO_4$), tricalcium aluminate ($3CaOAl_2O_3$), calcium sulpho-aluminate ($CaSAl_2O_3$) and very small amount of free lime (CaO) that participate in producing cementitious compounds. Also, glassy phase in Class C ashes is usually more reactive. The glassy particles in Class C fly ashes contain large amount of calcium which possibly makes the surface of such particles highly strained, and probably, it is because of highly reactive nature of Class-C fly ashes

Table 2.7 Crystalline phases in fly ashes from North America [25].

Class of fly ash and code	Name	Nominal composition
Low-calcium/Class F		
Hm	Hematite	Fe_2O_3
Mu	Mullite	$Al_6Si_2O_{13}$
Qz	Quartz	SiO_2
Sp	Ferrite Spinel	$(Mg.Fe)(Fe,Al)_2O_4$
High-calcium/Class C		
Ah	Anhydrite	$CaSO_4$
AS	Alkali sulfate	$(Na,K)_2SO_4$
C2S	Dicalcium silicate	Ca_2SiO_4
C3A	Tricalcium aluminate	$Ca_3Al_2O_6$
Hm	Hematite	Fe_2O_3
Lm	Lime	CaO
Ml	Melilite	Ca_2 (Mg.Al) $(Al,Si)_2O_7$
Mu	Mullite	$Al_6Si_2O_{13}$
Mw	Merwinite	$Ca_3Mg(SiO4)_2$
Pc	Periclase	MgO
Qz	Quartz	SiO_2
So	Sodalite structure	$Ca_2(Ca,Na)_6(Al,Si)_{12}O_{24}(SO4)_{1-2}$

Anhydrite ($CaSO_4$) is formed from the reaction of CaO, SO_2 and O_2 in the furnace or flue. Quantity of anhydrite increases with the increase in SO_3 and CaO contents. It plays a significant role in fly ash hydration behavior because it participates along with tricalcium aluminate and other soluble aluminates to produce ettringite and calcium sulphoaluminate hydrate.

Tricalcium aluminate ($3CaOAl_2O_3$) is one of the most important crystalline phases to identify and quantify the fly ash because it contributes to ettringite formation, and also in self-hardening reactions as well as disruptive sulfate reactions in hardened concrete.

Periclase is the crystalline form of magnesium oxide (MgO). Presence of this form of MgO in fly ash affects the soundness of the resulting concrete through its expansive hydration to brucite, Mg $(OH)_2$. Crystalline iron oxide, ferrite spinel and/ or hematite are generally found in all fly ashes. In most of the fly ashes, about 0.33–0.50% of iron is present as crystalline oxide. The reactivity of fly ash is, however, dependent on the glassy phases of Fe_2O_3.

Table 2.8 Concentration Range of Minerals Commonly found in Fly Ash [12]

Minerals Present	Concentration range (%)
Mullite	6.5 – 9.0
Quartz	2.2 – 8.5
Magnetite	0.8 -8.5
Hematite	1.1 – 2.7
Free CaO	Up to 3.5

Table 2.9. ASTM C618-94 Chemical and Physical Requirements for Fly Ash Used as a Mineral Admixture in concrete [12].

	Class F	Class C
A. Chemical Requirements		
(SiO_2 +Al_2O_3+Fe_2O_3),min.,.%	70.0	50.0
SO3, max., %	5.0	5.0
Loss on ignition, max., %	6.0*	6.0
Supplementary optional chemical requirements		
Available alkalis, as Na_2O,max.,%	1.5	1.5
B. Physical Requirements		
Fineness: Amount retained when wet-sieved on No.325 (45μm) sieve, max.,%	34	34
Strength Activity Index: With Portland cement, at 7days,min.,% of control With Portland cement, at 28days,min.,% of control Water requirement, max.,% of control	 75 75 105	 75 75 105
Soundness: Autoclave expansion or contraction, max.,%	0.8	0.8
Uniformity Requirements: Density, max. variation from average,%** Percent retained on No.325(45μm) sieve max. variation, % points from average**	 5 5	 5 5
Supplementary optional physical requirements		
Multiple factor, product of L.O.I.,% and fineness,% ,max.	255	-
Increase of drying shrinkage of mortar bars at 28 d, max.,%	0.03	0.03
Uniformity requirements: In addition, when air-entraining concrete is specified, the quantity of air entraining agent required to produce air content of 18.0 vol.% shall not vary from the average of the previous 10 by more than,%	20	20
Effectiveness in Controlling Alkali-Silica Reaction: Expansion of test mixture as parcentage of low – alkali cement control,at 14 days,max.,%	100	100

*Reduced from 12%in 1984, with the provision that Class F pozzolan containing up to 12% loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available

**Average established by the ten preceding tests, or by all preceding tests if fewer than ten.

2.4 SUPPLEMENTARY CEMENTING MATERIALS

2.4.1 POZZOLANIC PROPERTIES

Fly ashes, blast furnace slags, and natural pozzolans are the most commonly used supplementary cementing materials in blended cement today. These materials may be blended or interground with Portland cement or added as admixtures to concrete. Each of these products is available in a very wide range of compositions and there is not necessarily a full correlation between physic-chemical characteristics and performance. The predominant reactive constituent in these additives is amorphous silica.

Most supplementary cementing materials have at least some pozzolanic properties. In the pozzolanic reaction the silica (SiO_2) in the pozzolan reacts with calcium hydroxide ($Ca(OH)_2$) and water to form calcium silicate hydrate, the main strength producing component of hydrated cement and concrete.

There are three characteristics of pozzolan that make it reactive. These are:

1. High silica content: Since silica is what participates in the reaction with calcium hydroxide.
2. High degree of amorphousness: On cooling from a disordered state such as gas or liquid, silica becomes ordered in crystals because that is its lowest energy state. However, when it is cooled rapidly it does not have time to order itself before solidifying, so that instead it solidifies in an amorphous structure (glass) or in a structure intermediate between crystalline and amorphous. Since this state has a higher free energy than the crystalline state, the silica is metastable and thus more reactive. Fly ash can be made to have a high degree of amorphousness by careful control of the temperature during burning process of the coal.
3. High specific surface, which provides more surface from which the material can react. Some fly ashes are naturally fine. Others can also be ground (probably interground with the clinker rather than separately), beneficiated by removal of the coarsest particle fractions.

In addition, the clinker can be formulated to enhance the reactivity of the pozzolan. Since alkalis activate pozzolans, the alkali content of the clinker can be adjusted for optimal reactivity. Heat can also activate the pozzolanic reaction and, in the case of Class C fly ash, the cementitious reactions as well. The hydration of C_3A generates the most heat of any of the hydration reactions. The hydration of C_3S also generates heats well as calcium hydroxide, one of the reactants in the pozzolanic reaction. In addition, the particle size distribution of the clinker portion of the cement can be adjusted for enhanced reactivity by adjustments to the grinding circuit or simply by finer grinding.

2.4.2 PHYSICAL EFFECTS

Supplementary cementing materials, whether pozzolanic or not, have physical characteristics that affect the properties of cement and concrete. The introduction of an additional component into the particle system will affect cement production and the properties of fresh and hardened concrete. Inter-grinding of clinker with materials that are harder to grind (such as slag) or easier to grind (such as lime stone) will affect the particle size distribution of both clinker fraction and the cement as whole. The material that is easier to grind will concentrate in the finer fractions, while the material that is harder to grind will concentrate in the coarser fractions. Depending on the choice of materials and their relative proportions, the net effect will be beneficial if it increases the width the particle size distribution. However, it is not possible to predict the exact effects. Trials would have to be conducted with the selected materials in the grinding plant in order to determine the specific result and optimize the particle size distribution for both workability and reactivity.

Materials that have a high specific surface –fly ash, silica fume, clay, rice husk ash, limestone, and cement kiln dust- will affect a number of the properties of the fresh concrete. If surfactant admixtures such as water reducers, super-plasticizers, or air entraining admixtures are used, the dosages will generally have to be increased because there is more surface with which to interact. However, once the additional surface forces have been counteracted by a water reducer or super-plasticizer, the water requirement for a mortar or concrete is a function of the space that must be filled rather than the surface that must be coated. Fine particles fit into the interstices between clinker particles, thus improving particle packing and displacing water that then becomes available to increase the flow. This advantage may be exploited ether by increasing the flow at the same water/cement ratio or by reducing the water/cement ratio while maintaining constant workability.

An additional physical effect when finely divided particles such as limestone, silica fume, or fine fly ash are present in the cement paste is that of nucleation sites for the products of the hydration reactions. In some cases the hydration reactions are accelerated because the products are more readily precipitated from solution. Also, the hydration products are more uniformly distributed throughout the hydrated cement paste matrix, leaving finer, less continuous pores.

2.4.3 POSSIBLE IMPURITIES

The various materials that could be used in the manufacture of blended cement are either natural or the by- products of industrial processes. In either case they are not reagent –grade chemicals. Thus they do not consist of 100% silica, but rather of combinations of materials. This section discusses only those impurities that can have negative effects on the properties of cement and concrete.

Carbon is always present in rice husk ash and fly ash, and may also occur in silica fume, clay and limestone. Carbon may have two effects. The more important of these is its interaction with air entraining admixtures and other surfactants, which are adsorbed on the surface of active carbon. In the case of fly ash, most of the carbon is concentrated in the larger particles because they are less likely to have been completely burned. These can be removed by air separation if desired. It should be noted that not all carbon has the same effect on the surfactants because it may be encapsulated and thus not available for surface interaction. Also, carbon detected by loss of ignition of limestone could be in the form of $CaCO_3$, which does not have any particular interaction with surfactants. Generally the effect of carbon on surfactants can be compensated by increasing the dosage of the surfactants. However, the air void system in hardened concrete should be checked to determine the dosage of air entraining admixture needed to produce acceptable spacing factors.

Another effect of carbon on cement and concrete is color. For normal structural use it is not of particular concern, but occasionally the dark color imparted by carbon can be a problem, particularly if the carbon content varies so that the color irregular. As mentioned earlier, fly ash can be beneficiated to remove most of the carbon. Limestone deposits may contain clay, which absorbs water. The effect on the fresh concrete is an increase in water demand, and the effect on hardened concrete is deleterious to frost resistance. Since the European prestandared ENV 197-1 allows up to 35% limestone in blended cement, it also specifies limits on the clay content which could be used.

Alkali present in fly ash or cement kiln dust could react with aggregates susceptible to alkali-silika or alkali-carbonate reactions. Supplementary cementing materials are more or less effective in controlling alkali-silica reactivity, and alkalis in fly ash do not contribute to alkali-silica reactivity in the same way that alkalis from clinker or cement kiln dust do [12].

2.5 BEHAVIOR OF CEMENT AND CONCRETE CONTAINING COAL ASH

The performance of fly ash in concrete is strongly influenced by its physical, mineralogical and chemical properties. The mineralogical and chemical compositions are dependent to a large extent on the composition of the coal and since a wide range of domestic and imported coals (anthracite, bituminous, sub-bituminous and lignite) are burned in different generating stations all over the world; the properties of the fly ash can be very different between sources and collection methods. The burning conditions within a power plant can also affect the properties of the fly ash [23].

2.5.1 WORKABILITY

Rheology is the science of flow and deformation of matter. The rheological properties of a fresh cement paste are of interest because of its role in determining the workability of concrete. In practice, the consistency of mortar or concrete is measured in tests where the material is deformed under the force of gravity (the slump test) or a combination of vibration and gravity.

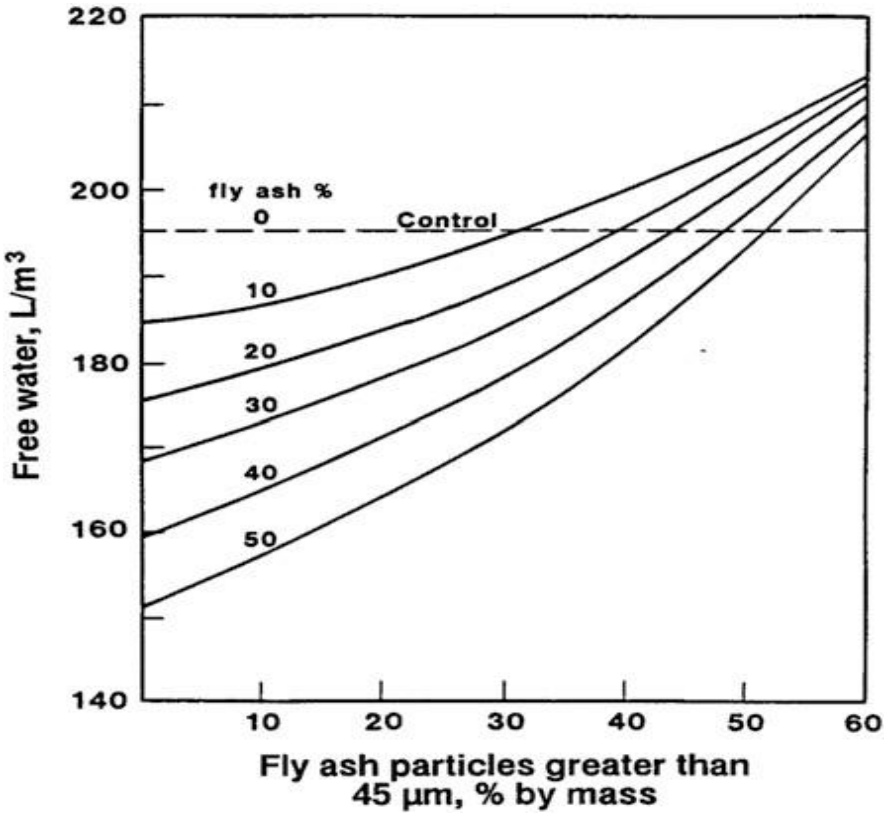
The water requirement for flow, hydration behavior, and the properties of the hardened state largely depends on the degree of dispersion of the cement in water. Parameters such as fineness, particle size distribution, and mixing intensity are the important in determining the rheology of a cement paste. Due to the charges that develop on the surface, cement particles tend to agglomerate in the paste and form flocs that trap some of the mixing water. Factors such as water content, early hydration reactions, water reducing admixtures, and mineral admixtures determine determines the degree of flocculation in cement paste. The loss of workability due to false set is generally attributed to the formation of fine interlocking gypsum crystals. These crystals also imbibe water that would otherwise be available to maintain flow. The gypsum crystals can be broken up by mild agitation. Flash set, on the other hand, occurs when the hydration reaction of C_3A is not properly controlled. Flash set causes rapid loss of workability and must be avoided for proper placement of concrete.

The use of good quality fly ash with a high fineness and low carbon content reduces the water demand of concrete and, consequently, the use of fly ash should permit the concrete to be produced at a lower water content when compared to a portland cement concrete of the same workability (Figures 6 and 7). Although the exact amount of water reduction varies widely with the nature of the fly ash and other parameters of the mix, a gross approximation is that each 10% of fly ash should allow a water reduction of at least 3% [12].

A well-proportioned fly ash concrete mixture will have improved workability when compared with a portland cement concrete of the same slump. This means that, at a given slump, fly ash concrete flows and consolidates better than a conventional portland cement concrete when vibrated. The use of fly ash also improves the cohesiveness and reduces segregation of concrete.

Several investigations have been conducted to study the role of Class F fly ash on the rheology of fresh concrete . Brown (1982) conducted several studies with fly ash replacing cement and fine aggregate at levels of 10–40% by volume. He concluded that for each 10% of ash substituted for cement, the compacting factor or workability changed to the same order as it would by increasing the water content of the mix by 3–4%. When fly ash was substituted for sand or total aggregate, workability increased to reach a maximum value at about 8% ash by volume of aggregate. Further substitution caused rapid decrease in workability. Owens (1979) reported that with the use of fly ash containing large fraction of particles coarser than 45μm or a fly ash with high amount of unburned carbon, exhibiting loss on ignition more than 1%, higher water demand was observed. Water demand was noticeably increased to maintain the desired level of fluidity. Figure 3.4 shows the effects of coarse fly ash particles on the water demand of concrete mixtures.

Figure 2.3 Influence of coarse-particulate content of fly ash on the water required for equal workability in concrete [11].



2.5.2 SETTING TIME

With the addition of water to concrete, hydration reaction start and the cement paste begins to stiffen accompanied by heat release. The rate of stiffening of cement paste is expressed in terms of setting time.

Investigations have revealed that the addition of low calcium Class F fly ashes generally show some degree of retarding effect on cement setting. Generally, the effect of fly ash on the time of setting depends on the characteristics and amount of fly ash used. The interacting effects of fly ash with other chemical and mineral admixtures used in concrete may also influence the setting of concrete. It has been observed that all Class F fly ashes, especially low calcium fly ashes with high carbon content or LOI, increase the setting time.

High calcium fly ashes, generally low in carbon and high in reactive and/or cementitious components sometimes exhibit opposite behavior of reduced setting time. Not all Class C fly ashes cause rapid setting.

The impact of fly ash on the setting behavior of concrete is dependent not only on the composition and quantity of fly ash used, but also on the type and amount of cement, the water-to-cementitious materials ratio (w/cm), the type and amount of chemical admixtures, and the concrete temperature. It is fairly well-established that low-calcium fly ashes extend both the initial and final set of concrete.

The hydration or setting of Portland cement paste is accompanied by an evolution of heat that causes a temperature rise in fresh concrete. Replacement of cement by fly ash results in a reduction in the temperature rise in fresh concrete. This is of particular importance in mass concrete, where cooling following a large temperature rise can lead to cracking.

2.5.3 COMPRESSIVE STRENGTH

The strength of a porous material is governed largely by its pores. Unlike permeability, this is governed by the continuity of the pore system. Strength is governed by the size of the largest pores, which act as local stress concentrations from which failure will begin. This concept first demonstrated on glass specimens, but it also applied to other brittle materials such as cement pastes and concrete. On the submicroscopic scale, hydrated cement paste is held together by Vander Waals forces. However, in cement paste the pores that weaken the material are much larger, and in concrete the areas of weakness, can be larger still. Thus the strength of the cement is not necessarily a good predictor o the strength of concrete made from it.

Concrete considered being a three- phase material comprising hydrated cement paste, aggregate, and an interfacial region between them. The interfacial region the weak link, as it is the most porous of the three. The porosity arises primarily from the accumulation of bleed water under aggregate particles and reinforcing bars. As hydration proceeds, solid hydration products begin to fill in the space, but generally they will be less dense than in the bulk cement paste. In low-strength concretes, on the other hand, the cement paste matrix is so weak that the weakness of the interfacial region does not make much difference.

Cracks form in concrete when the local tensile stress exceeds the local tensile strength of the material. Although applied loads cause stress in the concrete, they are only one possible cause off cracking. Volume changes resulting from temperature changes, thermal gradients, drying, creep, and various chemical reactions will generate stresses if they are restrained. In cases where only the paste is affected, such as in drying shrinkage, the aggregate acts to restrain the volume change.

The strength of hardened concrete is the fundamental importance to structural designers. It is also extensively used as index of other properties and concrete quality.

The measured compressive strength of concrete depends on the intrinsic properties off the concrete. Many variables influence the strength development of fly ash concrete, these being:

- fly ash characteristics such as its chemical and mineralogical composition, fineness, pozzolanic reactivity
- type of cement;
- replacement level of cement with fly ash;
- mixture proportions;
- Ambient temperature and curing conditions

The pozzolanic reaction has several characteristics that affect the strength

1. The reaction is slow, so that the rates of both heat libration and strength development are correspondingly slow.
2. The reaction consumes lime rather than producing it.
3. The reaction products are efficient in filling up space and subdivided pores

Lowering the rate of heat liberation reduces thermal gradients that lead to cracking; however, the reduced rate of strength gain may not be acceptable in all application. The consumption of CH is beneficial to strength because large deposits of CH tend to form in voids and along the interfaces of aggregate particles and reinforcing bars. Generally large crystals form parallel to the interface.

Since their cleavage planes are also parell to the interface, these large, oriented crystals serve as areas of weakness in the concrete. The consumption of CH in the pozzolanic reaction thus replaces a weak material with a stronger one, C-S-H, which has the additional advantage of filling more space with solid material. All supplementary cementing materials, given good curing conditions for sufficient time, will provide these benefits to the strength of concrete [12].

The main components of fly ash contributing to its pozzolanic reactivity are its reactive silicates and aluminates (contained in the glass phase), whereas mullite and quartz are ineffective. It has been suggested that the reactivity of fly ash depends on the temperature at which the coal is burned rather on than the quality of coal [27].

The highly pozzolanic fly ashes start their contribution to strength development almost from the onset of Portland cement hydration. But the low calcium fly ashes do not exhibit significant pozzolanic activity to affect strength until about two weeks after hydration. However, some high calcium fly ashes, with calcium oxide content more than 15%, may start contributing to strength development as early as 3 days after mixing because of their self hardening and pozzolanic properties.

The sulphate content of a fly ash has been reported to contribute significantly to the early hardening of fly-ash mortars Increased carbon content (indicated by high loss on ignition) is found to affect the strength of fly-ash concrete adversely. This is attributed to an increased water requirement and an increased amount of air-entraining agent (needed to maintain the same workability and air content as in control concretes) as the carbon content of fly ash increases.

Because of its fineness as well pozzolanic reactivity, fly ash in cement concrete significantly improves the quality of cement paste and the micro-structure of the transition zone between the binder matrix and the aggregate. As a result of the continual process of pore refinement, due to the inclusion of fly ash hydration products in concrete, a gain in strength development with curing age is achieved. When high calcium Class C fly ash is used, the strength development with time is likely to be different from the one using Class F fly ash. The self-hardening reactions in the Class C fly ashes are likely to occur within the same time frame as the normal Portland cement hydration reactions, giving equal or sometimes greater strengths at early ages. The pozzolanic activity of such cementitious fly ashes further enhances strength at later ages [28].

CHAPTER THREE

3. MATERIALS AND METHODS

The aim of this chapter is to discuss the materials, equipments and testing methods used in the practical analysis of the physical and chemical properties of Yayu coal ash, clinker, gypsum and laboratory produced cement by performing test for particle size, chemical, and x-ray analysis. In addition cement performance like water consumption, setting time, soundness and compressive strength testing procedures are described. All physical and chemical tests used for this research are according to the Ethiopian Standard (ES 1176:2005) and European Standard (EN 196:1998) methods of testing. All experimental work was performed in Mugher Cement Factory quality control and assurance laboratory.

3.1 MATERIALS AND METHODS FOR CEMENT RAW MATERIALS ANALYSIS

3.1.1 MATERIALS, APPARATUS AND REAGENTS

Clinker, gypsum and coal ash are the direct materials used as cement raw materials for chemical compositions analysis.

The following basic apparatus and instruments used are watch glass, graduate cylinder, burette, glass rod, pipette, wash bottle, drying oven, digital balance, 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, volumetric flask, platinum crucible, Florence flask, funnel, cover.

The chemical reagents used in this analysis are: hydrochloric acid (HCl), Phenolphateline indicator, Sodium hydroxide (NaOH),EDTA(ethylene diamine tetra acetic acid),TEA(tri-ethanol amine), Ethyl glycol, Nitric acid (HNO_3), Ethanol, Acetic acid, Bromocresol green indicator, Fusion mixture ($NaKCO_3$), Barium chloride ($BaCl_2$) , Congo-red, and distilled water.

3.1.2 METHODS AND TEST PROCEDURES

- Clinker and gypsum are collected form Mugher Cement Factory
- Since Yayu coal based thermal power plant is under establishment the coal ash is prepared at home as follows:
    - A coal sample was collected from Oromiya regional state Ilubabor zone, Yayu coal mining area.
    - Coal was crushed in Mugher lab by P100 x 100 jaw crusher.
    - The crushed coal was burned by locally made burner.
    - The ash was collected from the burner and screened by locally made screen to separate the ash from unburned one. See below the coal ash prepared at home.

The cement made in laboratory was by intergrading of clinker, gypsum and coal ash in SM-500 ball mill which derived by motor having 48 revolution per minute. The mill grinding capacity was 5Kg per batch.

Figure 3.1 Raw Materials Used For Lab Cement Preparation.

Yayu coal Yayu coal ash Clinker Gypsum

The following test procedures are used for these experimental works; which were complying with Ethiopian standard and Mugher cement factory methods of testing cement and cement raw materials.
In chemical analysis the characteristics (oxide and compound compositions) of cement raw materials can be determined [29]. The contents determined include oxides of silica, ferric, alumina, calcium, magnesium, sulphate, and loss on ignition. The chemical tests for basic cement raw materials were performed using classical testing method.

The classical chemical analysis techniques/procedures to find out basic parameters are described in details as follows:

1. **Determinations of major oxide contents**

Ethiopian Standard (ES 1176-2:2005 and EN 196-2:1998) [30] stated the procedure as follow:

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 105^0C this helps to remove the moisture contents. After dried cool in desiccators and weigh 2.5 g fusion mixture ($NaKCO_3$) 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 $NaKCO_3$. The mixture was placed in the Muffle furnace at 1000^0C 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 50ml 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 lose 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 ^{0}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 The precipitate is used for SiO_2 analysis, while the filtrate is used for CaO, MgO, Fe_2O_3 and Al_2O_3

2. **Determination of silica oxide (SiO_2)**

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 ^{0}C for an hour and cooled in desiccators and weighed to nearest mg. The concentration of SiO_2 is determined from the formula:

$$\%SiO_2 = [\frac{T-C}{S}] \text{ x } 100$$

Where: T = mass of crucible and precipitate, C = mass of empty crucible and S = mass of sample.

3. Determination of calcium oxide (CaO)

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:

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

Where: F_{EDTA} = factor of EDTA and V_{EDTA} = the volume of EDTA used to end point.

4. Determinations of magnesium oxide(MgO)

Similarly as CaO determination pipette out 25 ml of the filtrate and dilute to about 100ml. 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:

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

5. Determinations of ferric oxide(Fe_2O_3)

For this analysis also pipette out 100 ml of the filtrate prepared at above major oxide determination and add the Sulpho-Salicilic indicator about 50 mg. In this solution add drop wise 1+4 NH_4OH 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 pH of the solution to between 1 and 2.Heat the solution gently to body temperature (do not exceed 50^0C). Finally titrate with 0.01M EDTA from violet to colorless and recorded the volume of EDTA consumed. The concentration of Fe_2O_3 is determined from the formula:

$$\% Fe_2O_3 = (0.7985) \times (F_{EDTA}) \times (V_{EDTA})$$

6. Determinations of aluminum oxide(Al_2O_3)

Similarly pipette out 100 ml of the filtrate prepared at above major oxide determination and add the volume of EDTA consumed for Fe_2O_3. 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 form red-violet to yellow. Repeat boiling and titrating until yellow color became stable. The concentration of Al_2O_3 is calculated from the formula:

$$\% Al_2O_3 = (0.5098) \times (F_{EDTA}) \times (V_{EDTA}), \quad F_{EDTA} = 1.0029$$

7. Determination of free calcium oxide(CaO)

Free calcium oxide the oxide left uncombined during clinkerization process. The value is directly related to the quality of clinker produced.

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 ^oC 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 color changed to light green. The concentration of free lime in gram is determined from the formula:

$$\%CaO = (V_{titration} \times 2.8x10^{-3}) \times 100$$

Where: $V_{titration}$ = the volume of 0.1N HCl consumed for titration.

8. Determination of sulfur trioxide (SO_3)

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 lamps 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_3 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 $BaCl_2$ 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, otherwise 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 1000 ^{0}C for an hour. Finally cool in desiccators and weighed. The sulphate content expressed as %SO_3 is calculated from the formula:

$$\% SO_3 = [\frac{T-C}{S}] \text{ x}34.3$$

Where: T = mass of crucible and precipitate, C = mass of empty crucible and S = mass of the sample.

9. 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 and ignite at 1000 ^{0}C for 5 minutes then removed the lid and left the crucible in furnace for further 20minutes. Cooled the crucible to room temperature in desiccators, and ascertaining whether constant mass is obtained by weighing the sample. The observed loss on ignition is determined from the formula:

$$\%LOI = [\frac{A-B}{A}] \text{ x}100$$

Where: A is the mass of the crucible and sample before ignition and B is the mass of the crucible and sample after ignition.

3.2 MATERIAL AND METHOD FOR CEMENT PERFORMANCE TEST

3.2.1 MATERIALS, APPARATUS AND REAGENTS

The basic materials used for cement performance analysis are lab cement, and standard sand.

The following basic apparatus and instruments are used for cement performance analysis such as: drying oven, digital balance, muffle furnace, desiccators, platinum crucible, XRF machine, sieve machine, blain testing machine, stop watch, small brushes, LeChatelie ring, sample mixer, ruler, Vicat apparatus, compressive strength testing machine, prism molds, jolting apparatus, humidity cabinet and water bath. Lithium tetra borate ($Li_2B_4O_7$) and distilled water are used as chemical reagents for the test.

3.2.2 METHODS AND TEST PROCEDURES

The cement used for performance analysis was produced in Mugher cement laboratory by intergrading of clinker, gypsum and coal ash in SM-500 ball mill which derived by motor having 48 revolution per minute, and grinding capacity was 5Kg per batch according to ES1176-7:2005 [31]. The laboratory cement produced as follows:

- Cement raw materials clinker and gypsum are crushed by lab jaw crusher for easy blending.
- Moisture is removed from gypsum and coal ash.
- Using 20,25,30,35 &40 % clinker replacement level and each level at three % residue on 45μm sieve 15 different cement types are produced by intergrounding with ball mill.
- Lab cement without coal ash is produced for reference purpose

The lab cement was produced according to the ES 1176-7:2005 and EN 196-7:1998

The chemical and physical analysis procedures of cement produced are as follows:

1. Chemical analysis with X- ray fluorescence spectroscopy(XRF)

An XRF spectrometer was used to investigate the characteristic spectra of elements present in the solid sample. For quantification analysis, the intensity of characteristic line of the element analyzed was measured. The powdered cement sample was calcined at 850^{o}C for 4 hours in order to remove all organic compounds and water contained in the sample. The calcined sample was converted into a solid solution by fusion with lithium tetra borate ($Li_2B_4O_7$). The prepared solid solution and standard

were placed in sample holders and placed in the sample compartment of the DY1507 Epsilon3 XRF spectrometer. The intensity of a characteristic line of the element to be determined was measured. The concentration of the element in the sample was calculated from the intensity measured.

2. Physical analysis

The effect of coal ash used as cement additives on the properties of cement produced was determined by physical analysis of cement properties like fineness, compressive strength, soundness, and setting time. All tests were complying with Ethiopian Standard of cement testing methods (ES 1176:2005) and European norm of testing method (EN 196:1998).

a. Testing method of cement fineness: As given in ES 1176-6:2005 [32]:

Cement fineness one of the physical properties of cement that mainly affect the hydration reaction of cement. Therefore controlling the cement fineness is mandatory for cement manufacturers. The cement fineness can be measured by two ways. These are by blain (specific surface area) and sieve (% residue) methods.

For Blain method**:** A mass 2.66 g of cement sample weighed and placed in to the blain sample holder of PC- Controlled Automatic Blaine apparatus. 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 repeated for three times and we taken the average. Specific surface area was calculated with the following formula:

$$\text{Specific surface area} = k\sqrt{tav}$$

Where: k = constant [$cm^2/g.s$], and t_{av} = average time in second.

For Sieve method: A mass of 25g of the cement sample weighed and placed on 45μm Hosokawa Alpine Ag sieve. Run the sieve machine that develops a pressure of 4KPa for four minute. Determine the mass percent of the residue by the following formula.

$$\%\ \text{residue} = \left(\frac{b}{a}\right) \times 100$$

Where a= mass of the sample, and b = mass of the residue

b. Consistency of Standard Cement Paste: As given in ES 1176-3:2005 [33]

A 500g of cement sample was weighed and 25% water content of the mass of dry cement was added as a start. The mixture was mixed for 3.0 minutes by using a trowel to give a paste and was immediately transferred into the mould lying on the steel plate. The top of the mould was smoothened off as quickly as possible with the aid of the trowel. The mould and paste were placed under the

plunger in the Vicat apparatus and the plunger lowered gently to contact the surface of the paste. This material was released quickly and allowed to sink into the paste.

The scale reading of the vicat apparatus was noted after 1 minute and recorded. If the plunger penetrates to a point 5 to 7 mm above the bottom of the mould, the water-cement ratio is taken as the consistency, if not, a new water-cement ratio is taken and the procedure repeated.

c. Setting Time Determination on Cement: As stated in ES 1176-3:2005

A sample of cement paste of standard consistency was prepared and the time of first mixing the water with cement was noted down. A slight excess of paste was immediately transferred into the mould in one layer by using hand trowel. The top of the mould was smoothened and leveled. The mould was placed under the initial set needle of cross-sectional area of 1mm and the needle was covered gently onto the surface of the paste and was quickly released by allowing it to sink to the bottom. These tasks were repeated several times at regular intervals of 10 minutes in different positions of mould until the paste has stiffened sufficiently for the needle not to penetrate deeper than 5mm above the bottom of the mould.

The time interval between the addition of water and the initial setting time was recorded. Finally, the needle was replaced with a 1mm square needle fitted with a metal annular attachment and this probe was allowed to come gently with contact with the surface of the invertied cement paste at an interval of 15 minutes. The final set was reached when the needle makes an impression on the surface but annular cutting edges fail to do so.

d. Soundness Test (Expansion Determination on Cement : As stated in ES 1176-3:2005

Soundness is a measurement of its tendency to crack, distort, pit or disintegrate.

The cement paste was prepared as of a standard consistency and filled in to the expansion mould, or Le Chatelier mould, placed on a glass plate. The split end of the mould was gently closed by tying it with a piece of cotton as the operation was being carried out. The surface of the paste was well smoothened and leveled with the blade of a gauging trowel and was covered with another piece of glass and was immediately immersed in clean water.

After 24 hours, the mould was removed from the water and the distance between the pointers measured by using a meter rule. The mould was re-immersed in water again and was brought to boiling point within 30 minutes and afterwards allowed to boil for one hour. This material was then kept in the water and allowed to cool. The distance between the pointers was again measured.

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

$$\% \text{ Expansion} = [\frac{Lo - L}{L}] \text{ x100}$$

Where: Lo is initial length, and L is final length

e. Compressive Strength Test

As stated on Ethiopian standard of cement testing method (ES 1176-1:2005) [34], the compressive strength was carried out as follows.

A 450g cement, and 1350g standard sand were weighed into the mixing bowl. Starting from 10% by mass of cement distilled water was added and mixing was carried out until a cement mortar of homogenous consistency was obtained. The test specimens (molds) used is 40mm x 40mm x 160mm prisms as seen figure 3.2

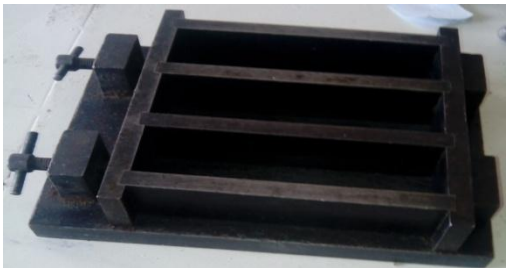


Figure 3.2 Test specimen used for compressive strength test

Molds were set on the working bench and all bolts were tightened using the spanners. The base of the mould was greased with a thin film of petroleum jelly and also the joints of the two halves. As quick as possible, the concrete mixture was scooped into each mould (to half the depth) in a single layer. The mortar mixture was tamped in each mould with 25 strokes of the tamping bar spread uniformly over the cross-section of the mould and exerting the same force in each case by raising the bar about 30mm above the surface of the concrete and guiding it as it is then allowed to fall under its own weight.

More mixture was scooped into each cube being completely filled to the brim. This material was tamped again 35 times for each mould. The assembled mould was placed on a vibrating machine and well secured in place, a suitable hopper was used to facilitate filling. The mould was vibrated on a jolting machine for 2 minutes. Afterwards, the prisms were covered with an impervious sheet to avoid evaporation and were allowed to cure at room temperature of 22^{o}C and relative humidity of 55% for 24 hours. The prisms were removed from their mould after 24 hours and were marked for identification. This material was then immersed in clean water to be removed for testing ages of 2 and 28 days.

The prisms were brought out of the water in due time and their surface was carefully wiped clean of water and adhering loose sand. The DY- 208MC compression machine was switched on 15 minutes before use. Prisms are supported on the supports 100mm apart and loaded with a point load at mid span. The prism was broken into approximately two equal pieces. The two halves of each prism are tested in the press and the average of the six results obtained is taken as the compressive strength. The compressive strength of each a prism is calculated as follows:

$$Rc = \frac{Fc}{1600}$$

Where: Rc = compressive strength (MPa), Fc= maximum load at fracture (N) 1600= 40mm x 40mm, area of the plates (mm^2)

3.3 EXPERIMENTAL PROGRAM

The following test programs were used for this project:

Table 3.1. The experimental programs used in this research

S.No.	Tests	Number of samples	Test method used
1	Coal ash preparation	1	-
2	Chemical analysis of coal ash, clinker and gypsum	4 each	ES 1176-2:2005 and EN 196-2:1998
3	Lab cement production with six clinker replacement level (0,20,25,30,35,40) and except 0 replacement level all are made at three different particle size on 45μm sieve residue. (≤ 5, 10-16 & 16-20%)	16	ES 1176-7:2005 and EN 196-7:1998
4	Fineness of cements	16	ES 1176-6:2005 and EN 196-6:1998
5	Chemical analysis of cement	16	Analytical method (XRF)
6	Setting time and soundeness of cement paste	16	ES 1176-3:2005 and EN 196-3:1998
7	Compressive strength of cement mortar	32	ES 1176-1:2005 and EN 196-1:1998

The most important factors that influence cement qualities are the chemical compositions of cement raw materials especially clinker, and gypsum, the grinding effect (fineness) and the amount of supplementary cementing materials added to the production [35]. The main aim the experiment was to know the performance of blended cement produced using of coal ash addition. Due to the material and the time resource limitation only two factors are chosen for the experiment. These two factors are cement fineness characterized by (C_R) and the coal ash addition percent characterized by (CA_P). To reduce the effect of clinker compositions on the cement performance the same clinker was used for cement production. The optimum and recommended amount of gypsum added for blended cement production is 4-5% by mass of cement [36]. For this experiment 4.5% by mass cement of gypsum was used for all cement produced.

Behavior of cement is strongly dependent on the properties of the individual particles, and the size effects become more important as the particles become smaller [37]. Using supplementary cementing material have many advantages on cement properties like increasing workability, reducing of heat of hydration etc, but increasing the amount of cementing additives have a

negative effect on the early strength of the cement [11]. Therefore, these two variables were selected as candidates for influencing the optimization of properties of blended cement. Three levels of cement fineness and five levels of clinker replacement percent were used. These levels of cement fineness on 45μm sieve residue of ≤ 10, (10-16], and (16-20) % characterized as C_{R5}, C_{R13}, C_{R18}, and levels of clinker replacement percent (addition of coal ash) that are 20, 25, 30, 35, and 40% by mass of cement characterized as CA_{P10}, CA_{P25}, CA_{P30}, CA_{P35}, and CA_{P40} respectively. Accordingly 16 types of cement produced in laboratory including control OPC. Sixteen cement pates were prepared according ES 1176-3:200 for consistency, setting time and soundness test of the cement. In addition thirty two prisms of size 40mm x 40mm x 160mm were also prepared according ES1176-1:2005 for 2 and 28 days compressive strength test.

Table 3.2 Characterization of cement produced and amount of raw materials used.

Cement Identification	Reside% on 45μm	% Coal Ash	Cement Raw Material [g] ®		
			Clinker	Gypsum	Coal ash
C_0 ©	≤ 20	0	4,775	225	0
C_1	≤ 10	20	3,775	225	1,000
C_2	(10-16]	20	3,775	225	1,000
C_3	(16-20)	20	3,775	225	1,000
C_4	≤ 10	25	3,525	225	1,250
C_5	(10-16]	25	3,525	225	1,250
C_6	(16-20)	25	3,525	225	1,250
C_7	≤ 10	30	3,275	225	1,500
C_8	(10-16]	30	3,275	225	1,500
C_9	(16-20)	30	3,275	225	1,500
C_{10}	≤ 10	35	3,025	225	1,750
C_{11}	(10-16]	35	3,025	225	1,750
C_{12}	(16-20)	35	3,025	225	1,750
C_{13}	≤ 10	40	2,775	225	2,000
C_{14}	(10-16]	40	2,775	225	2,000
C_{15}	(16-20)	40	2,775	225	2,000

© OPC for reference. ® The amount of cement raw materials was a dry base.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF CEMENT RAW MATERIALS

4.1.1 CHEMICAL ANALYSIS OF CLINKER AND GYPSUM

The chemical analysis of all three raw materials used for cement production was carried out in Mugher Cement Factory quality control and assurance laboratory prior to cement production. The chemical analysis results of raw materials were summarized on table 4.1.

Table 4.1 Chemical and Mineralogical Properties of cement raw materials

Compounds	Clinker	Gypsum
SiO_2	21.67	4.74
Al_2O_3	5.24	1.08
Fe_2O_3	3.41	0.77
CaO	65.28	33.98
MgO	0.74	0.9
SO_3	1.17	34.25
Free CaO	0.96	-
LOI	0.09	22.73
C_3S	60.94	-
C_2S	16.24	-
C_3A	8.12	-
C_4AF	10.38	-

Mineralogical compositions of clinker were calculated according to Bogue equations.

According to ASTM classification there are five types of cement. These are Type I to IV. The mineralogical value of clinker for modern Portland cement are C_3S =50 -70, C_2S =10 -30, C_3A = 3 - 13 and C_4AF = 5 -15. But the value of $C_3A \leq 5\%$ for cements Type IV and V [16]. Therefore, the mineralogical analysis of clinker indicated on the table 4.1 shows that it is suitable only for the production of Type I - III of Portland cement.

4.1.2 CHARACTERIZATION OF COAL ASH

The performance of coal ash in cement production is strongly influenced by its physical, mineralogical and chemical properties. The mineralogical and chemical compositions are dependent to a large extent on the composition of the coal and burning conditions.

The most widely used specification for coal ash especially fly ash in world is ASTM C618. This specification divides coal ash especially fly ash into two classes based on its source of origin and composition.

These are class C and F with the sum of $SiO_2+Al_2O_3+Fe_2O_3 \geq 50\%$ and $\geq 70\%$ respectively. Many fly ashes produced from lignite or sub-bituminous coals meet the chemical requirement of Class F fly ash.

Table 4.2 ASTM C618 and ES 1177-1 Chemical requirements for fly ash used as mineral admixture in cement production, and chemical analysis of Ethiopian Yayu coal ash.

Compounds	Coal ash	Class F	Class C
SiO_2	59.83	-	-
Al_2O_3	6.66	-	-
Fe_2O_3	8.48	-	-
$SiO_2+ Al_2O_3+ Fe_2O_3$	74.97	≥70	≥50
CaO	3.26	≤ 8	≥8
MgO	2.26	-	-
SO_3	3.82	≤ 5	≤ 5
Loss on ingestion	10.04	≤12®	≤6

® should be approved by the user

As described on table 4.2 the Yayu coal ash $SiO_2+ Al_2O_3+ Fe_2O_3$ is 74.97% which is greater than 70%, CaO is 3.26% which is less than 8% and loss on ignition is 10.04% which is greater than 6% and less than 12%. These values indicate that the Ethiopian Yayu coal ash is classified as class F fly ash. They are predominantly non crystalline silica, which is the determinant factor for pozzolanic activities. Therefore, the Ethiopian Yayu coal ash is suitable for utilizing it as cement additive for production of blended cement. Even if the 10.04% loss of ingestion is the range of requirement the higher the value has its negative effect on the cement properties by increasing the water requirement for hydration reaction.

4.2 EFFECT OF COAL ASH ON CEMENT PROPERTIES

In the previous sections, the pozzolanic properties of the Yayu coal ash were shown to be sufficient for using them in blended cement production. However, in order to propose that ash can be used in blended cements, the performance of the cements containing Yayu coal ash has to be investigated, too. Moreover, these cements have to satisfy the requirements given in standard specifications. For this purpose, the cements produced were tested to check their conformity with the three most widely used cement specifications given in ES, and EN standards. The cements investigated can be classified as ‘‘type Portland-fly ash’’ according to ASTM C 595, ‘‘type GU (General Use)’’ according to ASTM C 1157, and ‘‘CEM II/A-V 32.5 R’’ or ‘‘CEM II/B-V 32.5 R’’ according to EN 196-1 and ES 1177-1

4.2.1 NORMAL CONSISTENCY

Consistency refers to the relative mobility (ability to flow) of a freshly mixed cement paste or mortar. Five blended and one OPC cement pastes were tested for evaluation of normal consistency. The water of consistency of the cement pastes containing different ratios of coal ash are shown in table 4.3

Table 4.3 The normal water consistency of cement as coal addition

Paste Id.	P0	P1	P2	P3	P4	P5
% Coal ash	0	20	25	30	35	40
Consistency (%)	30	35	37	38	43	44

The results show that, the water of consistency of the blended cement pastes are higher than that of the control OPC paste and increases with coal ash content; this is mainly due to the unburned carbon content. LOI is a parameter that when done with coal ash mainly describes the carbon content in the substance. Carbon has a low density and can absorb significant amounts of water. This means that the maximum dry density and optimum moisture content of coal ash are influenced by the LOI. Higher LOI ash is lower in density, but has higher optimum moisture contents. This will increase the water demand for getting optimum workability of cement paste [38]. The ash analysis results show that the loss of ignition was 10.04% which has a significant effect on water demand. The results show that the water consistency of blended cement increase from control OPC by 16.7% for cement containing 20% ash and 46.7 % for cement containing 40% ash. The value of LOI of the ash was increased due

to the burning method used for this experiment. The value should be decreased when the coal burning done by thermal power plant boiler.

Figure 4.1 Effect of Yayu coal ashes addition on normal consistency of blended cement

The results described on table 4.4 shows that the LOI of all blended cements were greater than the control OPC cement and the results was increases with the coal ash addition. This indicates that the coal ash is main source of LOI in this blended cement production. Therefore The Ethiopian standard ES1177-1:2005 set the standard requirement for cement that limits its LOI. The value should be less or equal to 5%. As result the addition amount of 35% and above Yayu coal ash for blended cement production was causes the LOI of cement greater than 5% which is not allowed.

Table 4.4 Loss of ingestion of cement as coal addition

Cement Id.	C_0	C_{20}	C_{25}	C_{30}	C_{35}	C_{40}
% Coal ash	0	20	25	30	35	40
LOI of cement (%)	1.65	3.87	4.20	4.38	5.44	6.51

C_{20} – C_{40} the average results of cements at three fineness level

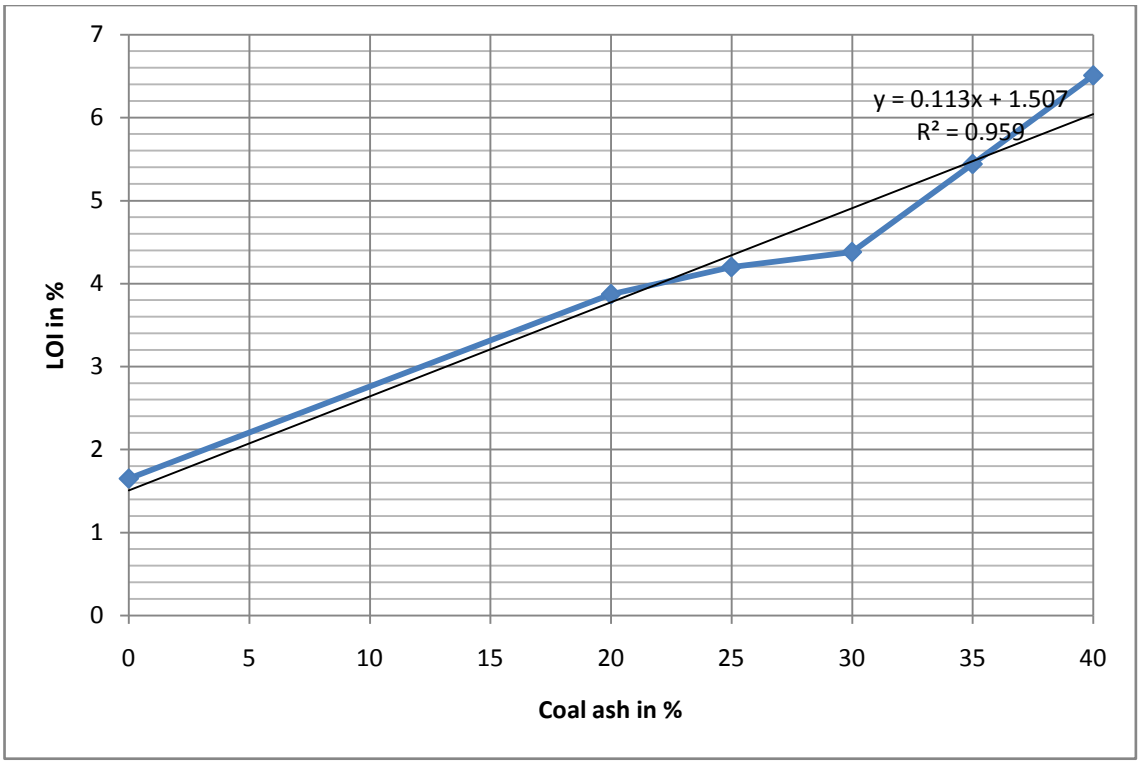


Figure 4.2 Effect Yayu coal ashes ignition loss on blended cement

4.2.2 SETTING TIME AND EXPANSION

The standard specifications ASTM C 595 and C 1157 limit the initial setting time to minimum 45 minute and final setting time to maximum 420 minute. On the other hand, ES 1177-1 and EN 197-1 specifies a limit only for the initial setting time. It is 75 min for the cements like those produced in this study. As seen from table 4.5, all cement types satisfied these requirements. Due to the lower clinker content, the setting time values of the blended cements were longer than that of control OPC. The results on table 4.5 show that as the fineness of the blended cement having the same compositions increases the setting time was decreasing. This due to the cement hydration reaction rate was increased with fineness. The setting time of the cement increases with the addition of coal ash. see table 4.6. This implies that the pozzolanic nature of the ash decreases the rate of hydration by decreasing heat of hydration.

Table 4.5 Experimental results of setting time and Le chatlier expansion of blended cement.

Cement Id.	Coal ash addition %	% residue on 45μm Sieve	Setting time(min.)		Le chatlier expansion (mm)
			Initial	Final	
C0	0	13.2	80	165	0.6
C1	20	17.92	112	191	0.3
C2		13.52	100	185	0.2
C3		2.24	94	180	0.4
C4	25	17.40	128	220	0.3
C5		12.36	120	198	0.3
C6		5.04	105	185	0.3
C7	30	17.6	158	258	0.2
C8		11.7	148	252	0.2
C9		7.72	120	220	0.4
C10	35	17.16	165	267	0.3
C11		12.76	152	245	0.4
C12		0.64	130	225	0.3
C13	40	16.2	188	269	0.3
C14		13.2	166	255	0.4
C15		0.44	142	230	0.3

.

Table 4.6 Average results of setting time of with coal addition

Cement Id.	C_0	C_{20}	C_{25}	C_{30}	C_{35}	C_{40}
% Coal ash	0	20	25	30	35	40
Initial setting time	80	102	118	142	149	165
Final setting time	165	185	201	243	246	252

The average test results summarized in table 4.6 shows that the minimum initial setting time was 102 minute; that was found on the cement that contain 20% coal ash. This result was greater than the minimum requirement 75minute by 36%. The highest final setting time 252minute was found for the cement that has 40% coal ash. This value was less than the maximum requirement 420 minute by 40%. Therefore adding Yayu coal ash as additive for blended cement production was not having an accelerating or retarding effect on setting of the cement. The workability of the produced cement was very good.

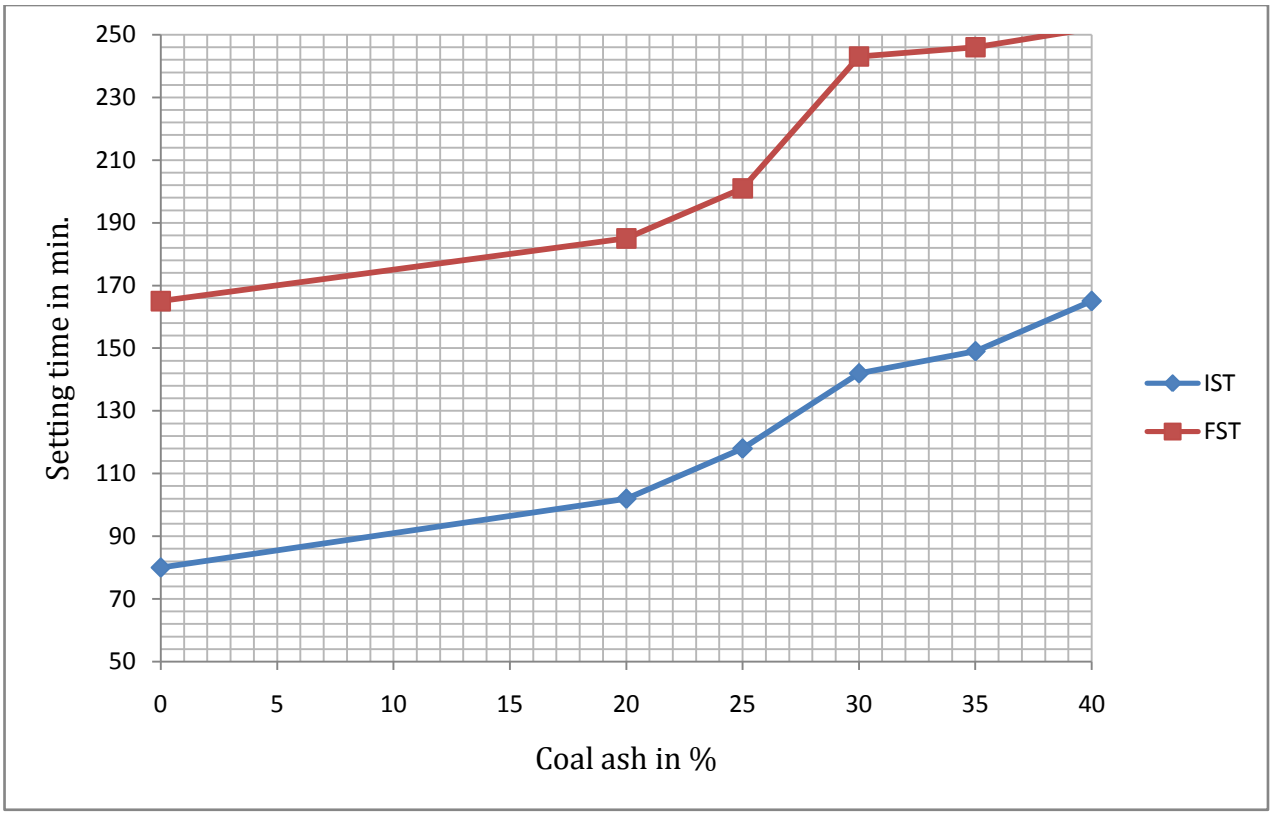


Figure 4.3 Effect of Yayu coal ash additions on cement setting time.

The standard specifications ES1177-1 and EN197-1 allow the Le chatlier expansion a maximum value of 10 mm. Table 4.7 shows that the results for the blended cements were below this limit and very small. It can be stated from this table that addition of Yayu coal ash reduces the expansions. The results on table 4.5 shows that increasing the coal ash content in the production of blended cement do not bring a significant change on cement paste expansion.

Table 4.7 Average test results of Le Chatiler's expansion of cement paste.

Cement Id.	C_0	C_{20}	C_{25}	C_{30}	C_{35}	C_{40}
% Coal ash	0	20	25	30	35	40
Expansion in mm.	0.4	0.3	0.3	0.27	0.33	0.33

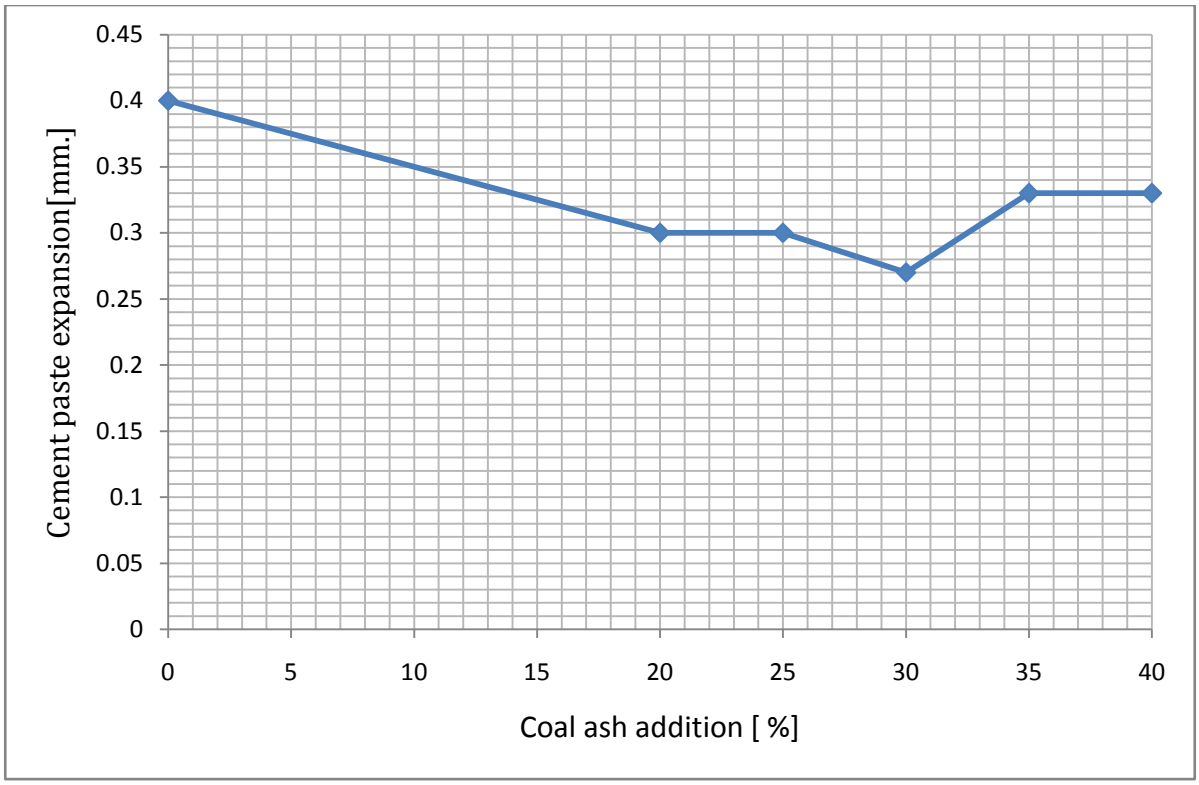


Figure 4.4 Effect of Yayu coal ash additions on cement paste expansion

4.2.3 COMPRESSIVE STRENGTH

Of the various 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 standards. The main constitutes of concrete that affect compressive strength is the cement quality. According to ES 1176-1:2005 test method, 450 gram cement and 1350gram EN standard sand and 0.5,0.51,0.52,0.53,0.54, and 0.55 water to cement ratio were used based on normal consistency of mortal of OPC, blended cement of 20,25,30,35, and 40% respectively. The prepared mortal specimens were tested for 2 and 28 days.

Table 4.8 Test Results of Compressive Strength of Blended cement

Mortar Id.	Ash addition [%]	% residue on 45μm	Water to cement ratio	Compressive strength (MPa)	
				2 days	28 days
M0	0	13.2	0.5	22.74	54.83
M1	20	17.92	0.51	13.83	46.66
M2		13.52		15.46	47.96
M3		2.24		21.26	49.94
M4	25	17.40	0.52	11.16	34.51
M5		12.36		12.16	36.45
M6		5.04		15.44	44.63
M7	30	17.6	0.53	7.94	29.09
M8		11.7		10.61	32.79
M9		7.72		20.3	40.36
M10	35	17.16	0.54	6.87	26.73
M11		12.76		7.89	30.71
M12		0.64		21.02	42.01
M13	40	16.2	0.55	7.06	24.93
M14		13.2		7.21	26.08
M15		0.44		20.48	37.27

The compressive strength of reference and blended cement are summarized on table 4.7.The results shows that as normally expected compressive strength test results of all blended cement are less than the reference OPC both at 2 and 28days. For all coal ash addition level the cement compressive strength increases with fineness and age. And it decreases with the coal ash addition amount. This is because of the hydration of cement increases with fineness and age. But the pozzolanic nature of coal ash slows the reaction rate.

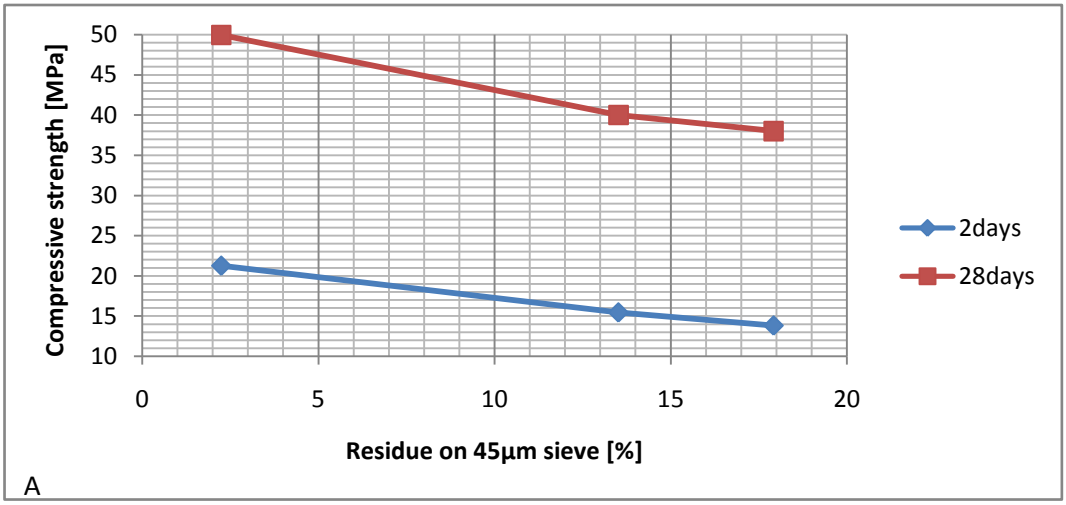
As we see from table 4.8 the slow compressive strength development of blended cement was compensated by increasing cement fineness. These cements were produced in laboratory. But in bulk cement production process making cement finer:

- ✓ It will incur more cost of production by increasing the electrical energy consumption, wear and tear of grinding media and mill internals.
- ✓ More gypsum is required for proper retardation because increased fineness makes more tricalcium aluminate available for early hydration.
- ✓ A higher early rate of hydration causes a higher early rate of heat liberation. If not properly dissipated, this heat may cause cracking – especially in mass concrete construction.

Therefore, optimization of cement fineness should be done for economical production of cement without affecting quality. The fineness of C_3, C_6, C_9, C_{12}, and C_{15} used only to know its effect on cement performance. But due to the above reasons it was not practically produced.

Table 4.9 Compressive Strength of More Fine Cements

Mortar Id.	Coal ash addition [%]	% residue on 45µm	Compressive strength (MPa)	
			2 days	28 days
M_0	0	13.2	22.74	54.83
M_3	20	2.24	21.26	49.94
M_6	25	5.04	15.44	44.63
M_9	30	7.72	20.3	40.36
M_{12}	35	0.64	21.02	42.01
M_{15}	40	0.44	20.48	37.27



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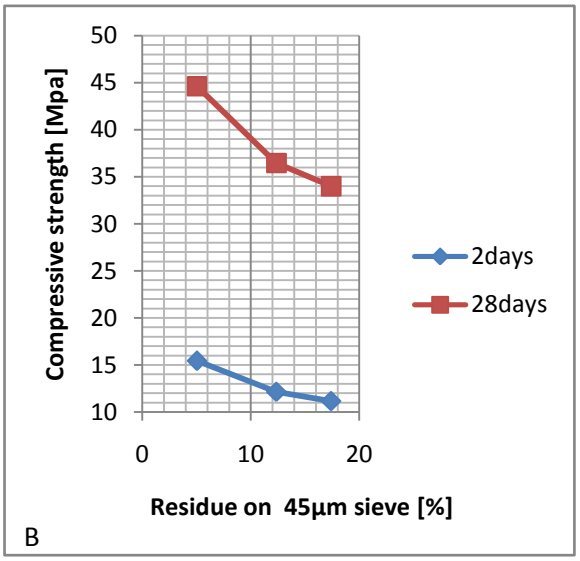

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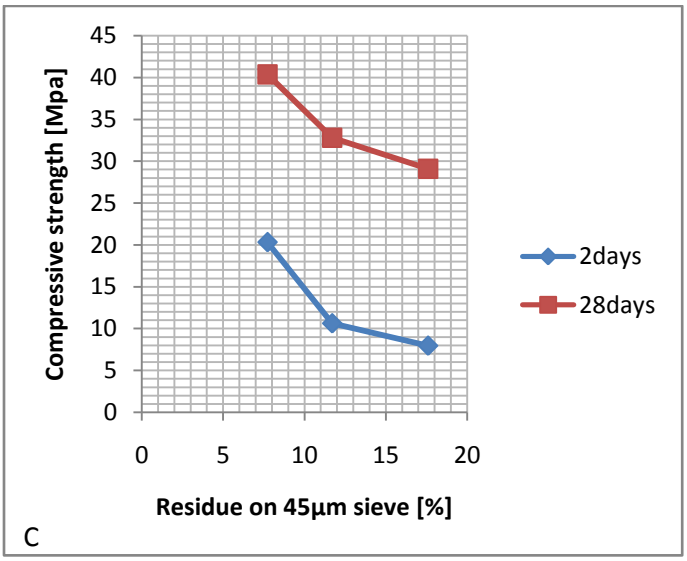

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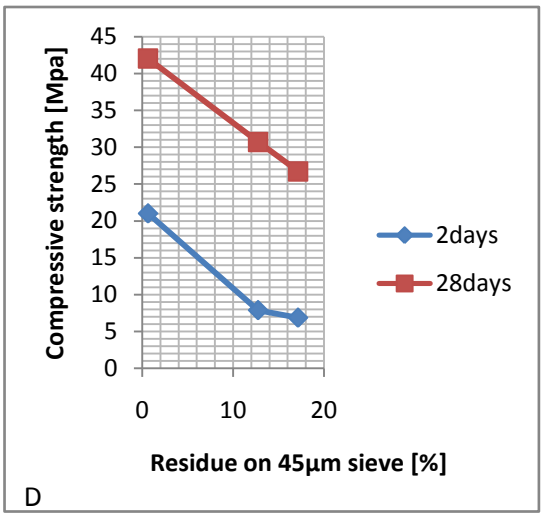

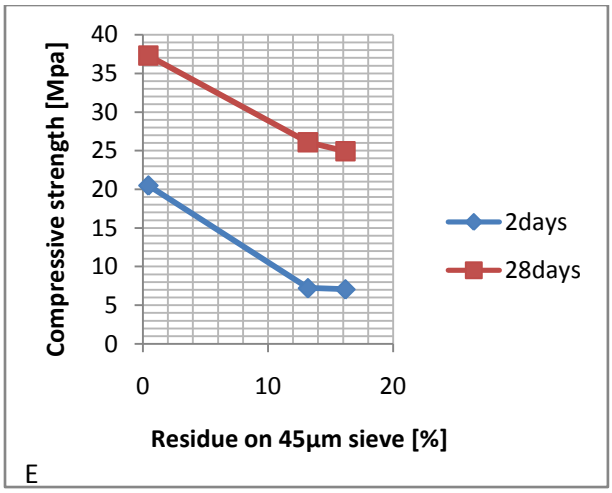

Figure 4.5 Effect of cement fineness on compressive strength. A is 20% coal ash addition, B is 25% coal addition, C is 30% coal addition, D is 35 % coal addition and E is 40% coal addition

For any cement application, one should know the compressive strength standard values and the minimum required compressive strength. The Ethiopian Standard requirements of compressive strength are given as in table 4.10.

After evaluate and compare the results based on standards it is possible to propose the optimum coal addition level for blended cement for bulk production. All the specimens prepared were class 32.5R cements and it is possible to compare the result data with standard class 32.5R.

Table 4.10 Mechanical and physical requirements of 32.5 classes cement (ES1177.1:2005)

Strength class	Early strength [MPa]		Standard strength [MPa]		Initial setting time[min.]	Final setting time[min.]	Soundness (expansion) [mm]
	At 2 day	At 7 day	At 28 day				
32.5N	-	≥16	≥ 32.5	≤ 52.5	≥75	≤ 420	≤ 10
32.5R	≥10	-					

As indicated on table 4.11 the results of all cement mortars having 20 and 25% coal addition was satisfy the minimum requirement of both early and lateral compressive strength. Except M_8, M_9, M_{12} and M_{15} all other cement mortars having 30 - 40% coal addition do not satisfy both early and lateral strength. Cement mortalr (M_8) very marginal to the minimum standard requirement. The results were greater by 6.1% and 0.9% form early and lateral age minimum strength respectively. But M_9, M_{12} and M_{15} including to M_3 and M_6 satisfy the requirement due to extreme fineness. Therefore, these samples were not used for determination of optimum coal addition level.

Table 4.11 Compressive strength test results as compared to ES requirements

Mortar Id.	Strength Class		Remark
	32.5R		
	2 day	28 day	
	≥10	≥32.5	
M_0	22.74	54.83	OPC 42.5R
M_1	13.83	46.66	Satisfy
M_2	15.46	47.96	Satisfy
M_3	21.26	49.94	Satisfy
M_4	11.16	34.51	Satisfy
M_5	12.16	36.45	Satisfy
M_6	15.44	44.63	Satisfy
M_7	7.94	29.09	Not satisfy
M_8	10.61	32.79	Satisfy
M_9	20.3	40.36	Satisfy
M_{10}	6.87	26.73	Not satisfy
M_{11}	7.89	30.71	Not satisfy
M_{12}	21.02	42.01	Satisfy
M_{13}	7.06	24.93	Not satisfy
M_{14}	7.21	26.08	Not satisfy
M_{15}	20.48	37.27	Satisfy

Table 4.12 Average test results of compressive strength

Coal ash addition [%]	Compressive strength (MPa)©	
	2 days	28 days
0	22.74	54.83
20	14.65	47.31
25	11.66	35.48
30	9.28	30.94
35	7.38	28.72
40	7.14	25.51

© Results of cement having extreme fineness that described on table 4.8 were excluded because if it included it may lead to wrong conclusions.

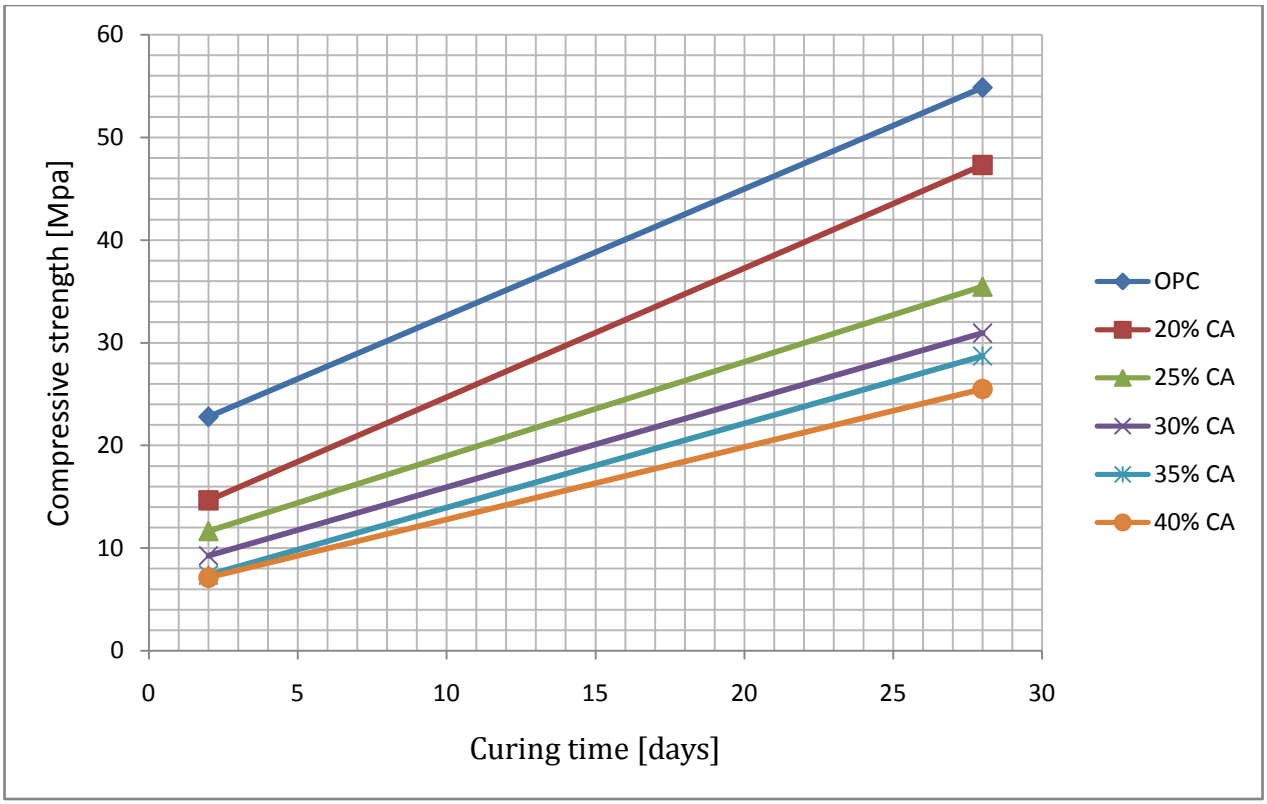

Figure 4.6 Effect coal ash additions on cement compressive strength

The average test results of compressive strength in table 4.12 and figure 4.5 shows that there is a reduction of early strength by 51.3% and lateral strength by 46.1% as coal addition raised from 20 to 40%. The compressive strength of cement produced by addition of 30 to 40% coal ash does not satisfy the minimum requirement set by Ethiopian standard. Therefore, the optimum Yayu coal ash addition level of for blended cement production must between 20 - 25% by mass of cement. The result indicates that, using Yayu coal ash one can able to produce blended cement that conforms to *ES1171-1- CEM II/B-V 32.5R* (Portland fly ash cement containing a total quantity of siliceous fly ash (V) between 21-35% by mass and strength class 32.5 with a high early strength.

4.3 ECONOMICAL ANALYSIS OF PRODUCING CEMENT AT YAYU

Mugher Cement Factory (MCF), one of the organizations under Chemical Industry Corporation which has a design capacity of 1.5million metric ton clinker or 2.1million metric tons cement per annum. The organization is monopolizing the cement market for the last 20 years. But as the new entrants in sector increases since last five years the cement market become stiffer.

Table 4.13 Mugher Cement Factory performances in clinker production and cement delivery for last five consecutive budget years. (Source: MCF annual reports)

S.No.	Fiscal year*	Clinker production (ton)			Cement delivery (ton)		
		Plan	Actual	Performance (%)	Plan	Actual	Performance (%)
1	2003	590,000	453,328	77	822,770	589,391	71
2	2004	1,114,800	544,870	49	1,446,860	864,958.16	60
3	2005	1,270,800	825,711	65	1,775,000	1,046,049.89	59
4	2006	1,335,000	789,403	59	1,895,000	1,002,847.53	53
5	2007	1,225,000	719,793	59	1,664,000	890,098.41	54

* Ethiopian calendar

The maximum capacity utilized in clinker production and cement delivery are 55 and 50 % respectively in 2005 fiscal year. See table 4.

This mainly due to:

- ✓ Electrical energy shortage and interruptions.
- ✓ Technical and technological problem encountered
- ✓ Cement market become stiffer

The third problem become increasing for time to time, therefore CIC is using different market strategy to increase the market share of Mugher Cement. Among these are reducing of sale price of cement, increasing the capacity utilization of the plant, increasing the distribution channels, intensive adverting the product qualities and service etc.

Yayu is found 600 kilo meters for capital city Addis Ababa at southern west of Ethiopia. There is no cement factory at this part of the country. All cement delivered to southern west of Ethiopia is by car transport mostly from central Ethiopia. But for CIC bringing coal ash from Yayu which is 600Km to Tatek by truck is expensive as compared to currently transporting pumice from Adama which is 100Km for production of blended cement.

Establish cement milling and packing plant at Yayu is one option for utilization of the coal ash from thermal power plant. As seen from table 4.13 MCF has large unutilized capacity of clinker production. Therefore, transporting clinker to Yayu for utilizing coal ash produced form thermal power plant.

For cost analysis of cement producing at Yayu and Tatek the following assumptions are used bellow, this assumptions are based on literature review and cement industrial benchmark.

- ✓ 85% by mass coal ash is used as cement additive
- ✓ Average moisture of coal ash, gypsum and FGD used is 5%
- ✓ Average process loss of materials is 1%
- ✓ Average gypsum & FGD used in cement production is 5% by mass
- ✓ Average pumice used in cement production is 28% by mass and average moisture is 10%
- ✓ Except direct material and transportation cost all other cost at Tatek and Yayu considered to be same.
- ✓ The synthetic gypsum is used in place of virgin gypsum at Yayu
- ✓ The cost of production of coal ash & FGD is 10 Birr/ton
- ✓ The working hours of mill 20hr/day and 360days/year
- ✓ The truck taking clinker to Yayu and in return will bring fertilizer to central market.
- ✓ Cement milling and packing plant established at Yayu will utilize the infrastructure constructed for fertilizer and thermal power plant.
- ✓ Establishing of cement milling and packing plant at Yayu will integrate the chemical sectors increase the awareness of utilizing coal ash in construction sector.

Annual coal ash production =75,000 Mt,

Using average of 80% by mass to be used for blended cement,

Total usable coal ash for cement additive is 60,000Mt

Considering average moisture 5% and process loss 1%

The dry coal ash used for cement additive is 56,400Mt.

Assuming 22% coal addition for blended cement production

The annual cement production using dry coal ash = $\frac{56{,}400\,\text{t}}{0.22} = 256{,}364 \approx 256{,}000$

Working hours of mill to be 20hr/day, 360 days/year

Total working hours per year = 7,200

The nominal mill capacity $=\frac{256{,}000\,\mathrm{t}}{7{,}200\ \mathrm{hr}} = 35.6\mathrm{t/hr} \approx 36\mathrm{t/hr}$

Table 4.14 Amount of raw materials required in metric tons for production of 256,000 Mt blended cement

Raw materials	Site of cement production		Source	Distance from source to site (Km)
	Tatek	Yayu		
Clinker	171,520	186,880	Mugher	70/690
Pumice	79,565	-	Adama	100
Coal ash	-	59,700	Yayu	0
Gypsum	13,440	-	Mugher	70
FGD(synthetic gypsum)	-	13,440	Yayu	0

Table 4.15 Current production and transport cost of raw materials
(Source: MCF 2008 E.C fiscal half year report)

Raw materials	Production cost (Birr/t)	Transportation cost (Birr/ton. Km)
Clinker	1620	0.86
Pumice	23	0.86
Gypsum	52	0.86
Coal ash	10®	0
FGD	10®	0

® assumed values

Table 4.16 Unit production cost of cement at Tatek site (considering direct material and transport)

Raw materials	Amount (t)	Direct material cost(Birr)	Transportation cost (Birr)
Clinker	0.65	0.65*1620 = 1053	0.65*0.86*70 = 39.13
Pumice	0.31	0.31*23 = 7.13	0.31*0.86*100 = 26.66
Gypsum	0.053	0.053*52 =2.76	0.053*0.86*70 = 3.19
Sum		1,062.89	68.98
Cost of cement at Tatek		1,131.87	
Cost to delivery at Yayu		1131.87+(1*0.86*600) = 1,647.87	

Table 4.17 Unit production cost of cement at Yayu site (considering direct material and transport)

Raw materials	Amount (t)	Direct material cost(Birr)	Transportation cost (Birr)
Clinker	0.73	0.73*1620 = 1182.6	0.73*0.86*690 = 433.18
Coal ash	0.23	0.23*10 = 2.3	0
FGD	0.053	0.053*10 =0.53	0
Sum		1185.43	433.18
Cost of cement at Yayu		1618.61	

Unit cost saving = Cost of cement at Yayu – cost of producing at Tatek and delivering at southern west Ethiopia.

Unit cost saving= 1,647.87 – 1,618.61(Birr/ton of cement)

= 29.26 Birr/ton

Annual saving =29.26 Birr/ton*256,000ton

= **7,490,560 Birr**

The results from above table and calculation shows that transporting clinker to Yayu and producing cement have annual saving of **7,490,560** Birr cost advantages than producing at Tatek and distributing at south west part of Ethiopia.

Establishing cement plant of nominal capacity of 35ton per hour should utilize the whole coal ash produced by thermal power plant at Yayu. Beside the cost saving of cement producing at Yayu CIC will take the geographical advantages to the delivery the southern west of Ethiopia. This will increase the market share of Mugher Cement.

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In this study, the suitability and optimum utilization of Yayu coal ash for blended cement production was investigated. The coal sample collected from Yayu was burned and sieved at home to get ash. The chemical analysis of coal ash was done according to ES1176-3:2005 and EN 196.3:1998 testing methods. Using coal ash blended cements were produced in laboratory ball mill with the clinker replacement level of 20, 25, 30, 35, and 40% by mass of cement. Each level of replacement cements were produced for three different fineness of 16-20, 10-16 and ≤10 % residue on 45μm sieve. 4.5% by mass of cement gypsum were used for all cement mixture to reduce the effect of gypsum on cement performance. The chemical and physical properties of cement were evaluated like SO_3, loss on ignition, % residue on 45μm sieve, normal consistency, setting time, expansion and compressive strength. Based on observations and trends determined from the results of this evaluation, the following conclusions were made:

- The chemical and physical properties of the Yayu coal ash was suitable to use as cement extender and based on ASTM C 618, the ash is grouped in F class. But the loss of ignition 10.42% was high, which leads to increase the water requirement above the reference OPC cement. The water requirements were increased with replacement level. But this does not reduce the cement quality.
- The initial and final setting times of all blended cements were greater than the reference OPC. As the replacement level increases both initial and final setting times too. All blended cement meets the minimum requirement set by ES 1177.1:2005 minimum 75 minute and maximum requirement set by ASTM C1157 420 minute.
- The expansions of blended cements were greater than the reference OPC. The replacement level does not have any significant effects. All cements have very small expansion as compared to the maximum requirement level set by ES1177.1:2005 10mm.
- The compressive strength of the blended cements was increased with the cement fineness at all replacement level. The ignition loss of coal ash forces to increase the water to cement ratio during mortar preparation above the standard value of 0.5. As the cement % residue on 45

μm sieve were below 5% all cement produced was satisfy the 2days and 28 days minimum requirements set for 32.5R strength class 10 and 32.5 MPa. But producing cement to this fineness was not economical. The optimum sieve residue used by many cement manufacturers was greater than 10%. For cement % residue greater than 10% only cement mortars of 20 and 25 % replacement level fulfill the minimum requirements set for 32.5R strength class. Therefore the optimum clinker replacement range was between 20- 25% by mass.

- Establishing cement milling and packing at Yayu site by transporting clinker from Mugher have a cost saving advantages of producing cement at Tatek and distribute at southern west of Ethiopia.
- The use of Yayu coal ash as presented is not only beneficial to the cement industry, but also is friendly to the environment. This will increase the culture of green building and technology by a sector that is a major contributor of emissions and reduction of landfills and landfill cost to Chemical industry corporation
- The alternative use of coal ash are for road construction, soil stabilization, as aggregate in concrete production etc,

5.2 RECOMMENDATIONS

- Since the Yayu coal based thermal power plant under establishment, the ash used for this experiment was prepared by burning of the coal at home. But the chemical and physical properties of coal ash mainly depend on the burning conditions. Therefore, coal ash has to be collected and investigated for further clarification when the power plant starts the operation to arrive at the better coal ash blending ratio and other characterization.
- According to the test result stated in chapter four up to 25% by mass coal ash was used for blended cement production without affecting the cement quality, and in the south west of Ethiopia currently there is no cement industry. Therefore, CIC strongly recommend to establish cement mill near power plant for efficient utilization of the opportunity of infrastructure built for fertilizer and power plant, coal ash produced by power plant, clinker from Mugher and the cement market found at south west Ethiopia.
- Due to the time and financial resources limitation this experiment was not cover some aspects. But this does not change the above test results. Therefore, the following test should be recommended in order to have farther constractive information of Yayu coal ash.
    1. The XRD analysis in order to know the mineralogical compositions the ash.
    2. SEM analysis in order to know the particle shapes of the ash
    3. Effect of the Yayu coal ash addition in concrete

REFERENCE

[1] Jozef Junák, & Nadežda Števulová., "Effective utilization of coal fly ash in building material production" Civil Engineering Faculty, Institute of Building and Environmental Engineering, Technical University of Košice, Vysokoškolská 4, 042 00 Košice, Slovakia, August 10, 2011. 1-2.

[2]Ramme-Tharaniyil,"Coal combustion products utilization handbook" 3rd edition, A we energies publication, United state, 2013, 1-3, 6-7, 54-56.

[3]Craig Heidrich, Hans-Jochim Feuerborn, & Anne Weir, "Coal combustion products: a Global Perspective", World of Coal Ash (WOCA) conference-April 22-25, 2013 in Lexington, KY; 2013. 3-4, 7-8.

[4] Tarun R., & Shiw S. Singh., "Fly ash generation and utilization - an overview" Department of Civil Engineering and Mechanics, College of Engineering and Applied Science, The University of Wisconsin-Milwaukee, June 1993, 6-7

[5] Messele Gebre Hiwot" Transformation "National Journal No. 9, June-July 2014, 84-91

[6]J.Alam and M.N Akhtar," Fly ash utilization in different sectors in Indian scenario" International journal of emerging trends in Engineering and Development Issue1, Vol. 1 August 2011, 3-4

[7] H Du Plessis,"the use of gasification ash in cement concrete", University of Pretoria ETD 2006, p26 -27,p 31-32

[8] Bhatty, Javed I.; Miller, F.MacGregor; and Kosmatka, Steven H.; editors, "Innovations in Portland Cement Manufacturing", CD400, Portland Cement Association, Skokie, Illinois, U.S.A., 2004, p1- 40

[9] Peter C.Hewlett,"Lea's chemistry of cement and concrete" 4th edition, Elsevier Science & Technology Books, January 2004, 1-19, 41-43, 241-245

[10] Dr.B. Salah,"Portland cement" concrete technology, seen on November 20/2015 uotechnology.edu.iq/dep.../Chapter%20One-portland%20cement.pdf

[11]Ali Akbar Ramezanianpour;"cement replacement material, Properties, Durability, Sustainability, Springer-Verlag Berlin Heidelberg, 2004, p17 – 20, p65

[12] Rachel J. Detwiler, Javed I. Bhatty,and Sankar Bhattacharja; "supplementary cementing materials for use in blended cements" PCA Research and Development Bulletin RD112T, PCA R&D serial No. 2038,1996, p1-2, p40-45

[13] Mengistu Aregaw;" investigation of calcite and volcanic ash for their utilizations as cement filling and additive materials" AAU faculty of Science, 2010,p 1-2

[14] Rachel J.Detwiler, Javed I. Bhatty, & Sankar Bhattacharja, "Supplementary cementing materials for use in blended cements" ,Portland cement association research and development bulletin RD112T, Serial.No.2038, 1996, 1-2.

[15] Ethiopian Standard (ES 1177-1:2005),"Cement Part 1: composition, specifications and conformity criteria for common cements", 2005

[16] Hendric G. van Oss;"Background facts and issues concerning cement and cement data", U.S geological servey,Open-File Report 2005-1152, p17-20,

[17] World energy resource: Coal world energy council 2013

[18] Mugher Cement Enterprise," Feasibility study coal firing for clinker production", July, 2013, Addis Ababa.

[19] Technical assessment report; "a technical assessment of coal utilization and research trends", Global climate and energy project, Stanford university, 2006

[20] Wolela Ahmed," Fossil fuel energy resource of Ethiopia" Bulletin Chemical society of Ethiopia, ISSN1011-3924, 2008, p67-84

[21] Yoseph Dejene;" the utilization of indigenous coal as energy substitute in cement industry", Addis Ababa university department of chemical engineering, August, 2004, p34-47

[22] Madawala Liyanage Duminda Jayaranjan, Eric D. van Hullebusch,& Ajit P. Annachhatre," Reuse options for coal fired power plant bottom ash and fly ash", Springer Science + Business Media Dordrecht, April 2014, 1-2

[23] Michael Thomas;"Optimizing the use of fly ash in concrete" concrete thinking for sustainable work, Portland Cement Association, p1-24

[24] Rakesh Kumar Behera," Characterization of fly ash for their effective management and utilization", National institute of technology Rourkela, Orissa – 769008,Department of mining engineering, 2009-2010, 2

[25] R. Siddique and M. Iqbal Khan;" Supplementary Cementing Materials", Engineering Materials, DOI: 10.1007/978-3-642-17866-5_1,© Springer-Verlag Berlin Heidelberg 2011, p2-5

[26] R.B. Freeman;"Optimization of physical and compositional characteristics of fly ash cement for the production of sulfate resistant concrete", University of Texas at Austin, August, 1992, p81-82

[27] K. Wesche.,"Fly ash in concrete properties and performance",Technical committee reports 67-FAB Use of Fly Ash in Building, ISBN 0-203-63026-2 (Adobe eReader Format), RILEM, 1991, p57-60

[28] Rafat Siddique," Waste materials and by-products in concrete", Engineering materials, e-ISBN: 978-3-540-74294-4, Springer-Verlag Berlin Heidelberg, 2008, p190-196

[29] Mugher cement enterprise, "Product development and quality assurance service laboratory working manual with basic notes in cement technology" June,2008

[30] Ethiopian Standard (ES 1176-2:2005),"Method of testing cement Part 2: Methods of chemical analysis of cement", 2005

[31] Ethiopian Standard (ES 1176-7:2005),"Method of testing cement Part 7: Methods of taking and preparing samples of cement", 2005

[32] Ethiopian Standard (ES 1176-6:2005),"Method of testing cement Part 6: Designation of fineness", 2005

[33] Ethiopian Standard (ES 1176-3:2005),"Method of testing cement Part 3: Designation of setting time and soundness", 2005

[34] Ethiopian Standard (ES 1176-1:2005),"Method of testing cement Part 1: Determination of strength", 2005

[35] J. Talaber,"Factor influencing the quality of cement", Department of Building Materials,Technical University, Budapest, February 1981, p27-39

[36] Amin A. and Mohamad H.Aboud,"Determination of optimum quantity of raw gypsum addition for Atbara cement clinker" ,Department of mining, faculity of engineering, Khartoum University, www.jeaconf.org/ on October 13/2015, p 1-6

[37] Gleb Gennadievich M.," Improved cement quality and grinding efficiency by means of closed mill circuit modeling",Texas A & M University, December 2007, p11-15

[38] Da-zuo CAO, Eva SELIC, Jan-Dirk HERBELL," Utilization of fly ash from coal-fired power plants in China", Journal of Zhejiang University SCIENCE A,ISSN 1673-565X (Print); ISSN 1862-1775 (Online),March 27,2008, p681-686

Appendix A:

PICTURES OF EQUIPMENTS USED FOR THE EXPERIMENT

Fig.1. Digital balance

Fig.2.Laboratory ball mill

Fig.3.Compressive strength test machine

Fig.4. Blain apparatus

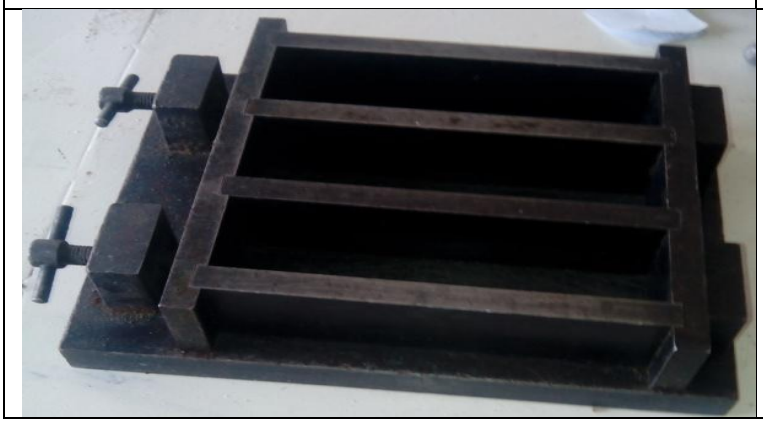

Fig.5. Molding plate	Fig.6. Jolting apparatus
	
Fig.7. Graduated cylinder	Fig.8. Le-chatelier apparatus
	
Fig.9. Sieve machines	Fig.10. Muffle Farnese
	
Fig.11. Stop watch	Fig.12. X ray fluoroscope /XRF/

Fig.13. Mortar mixer

Fig.14. Vicat apparatus

Fig.15. Humidity cabinet

Fig.16. Water bath

Fig.17. Drying oven

Fig.18 Powder mixer

Appendix B:

AVERAGE XRF TEST RESULTS OF LAB CEMENTS

Oxides	Coal ash addition amount [%]					
	0	20	25	30	35	40
CaO	61.52	51.25	48.50	47.60	45.44	43.81
SiO_2	21.85	29.72	31.43	31.56	31.97	32.05
Al_2O_3	6.57	6.84	7.25	7.62	7.85	7.93
Fe_2O_3	3.76	3.45	3.53	3.61	3.75	3.85
MgO	1.03	0.85	0.87	0.90	0.94	0.98
SO_3	2.65	2.67	2.73	2.79	2.85	3.02
LOI	1.65	3.87	4.20	4.38	5.44	6.51

DECLARATION

I, **the undersigned**, declare that this thesis entitled "**Optimum utilization of coal ash as additive for blended cement production**" has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due references to the literature review and discussions.

Information taken from the published and unpublished work of the others has been acknowledged in the text and a list of references was give.

The work was under the guidance of Prof. Whasik Min (Dean, School of Chemical and Bio Engineering) ,and instructor in Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering.

Name

Signature

Place of Submission

Date of Submission

CERTIFICATION

This thesis has been read and approved as meeting the requirement of the School of Chemical and Bio Engineering in the Addis Ababa Institute of Technology for the award of degree of masters of Science in chemical engineering.

Advisor

Signature

Date