

**CEMENT RAW MIX DESIGNING, CLINKERIZATION,
ADDITION OF WASTE BAGGASE FROM SUGAR INDUSTRIES
AND ITS IMPACT ON FUEL CONSUMPTION AND CLINKER
POTENTIAL**

By
NOOR-UL-AMIN



**DOCTOR OF PHILOSOPHY
IN
CHEMISTRY**

**INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR
PAKISTAN**

2005

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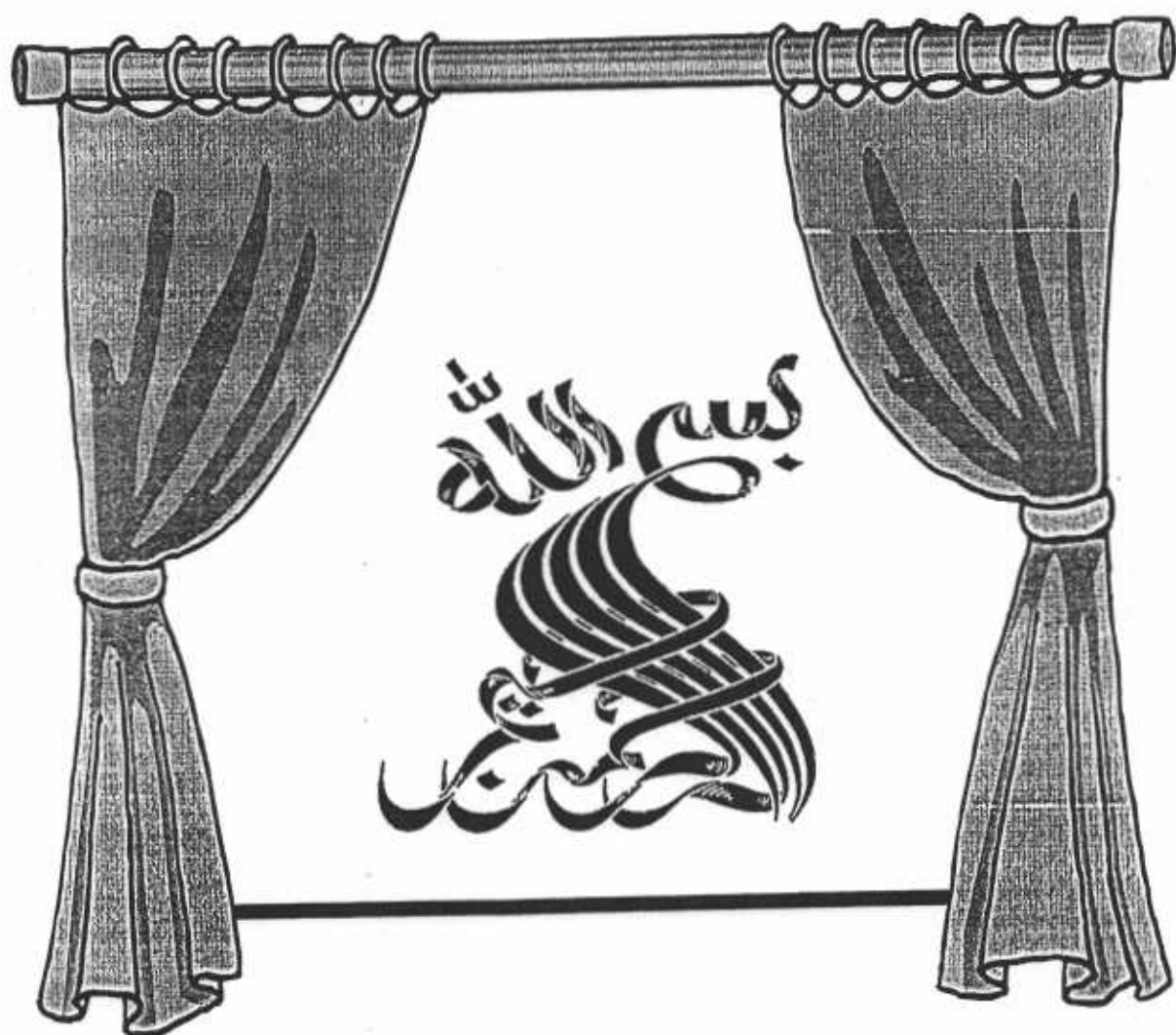
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APPROVAL SHEET

It is recommended that the thesis prepared by Mr. Noor-ul-Amin, entitled
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from Sugar Industries and its Impact on Fuel Consumption and Clinker
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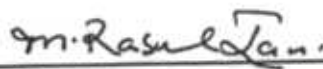
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*Do they not reflect on,
The camels, how they were created?
The heaven, how it was raised up?
The mountains, how they were set down?
The earth, how it was leveled flat?*

*Al- Quran
Al-Ghafiya (17-20)*

Dedicated to my

Late Mother

May Allah keep her soul in peace

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ABSTRACT

This work comprises the study of Darukhula and adjoining areas of Nizampur District Nowshera NWFP Pakistan for the search of Raw Material for cement manufacturing. Secondly, the same raw material has been used to prepare cement and its physical and chemical parameters, have been studied. Thirdly, baggase ash from the sugar industries has been used in cement manufacturing and its effects on different physical and chemical parameters have been studied.

The sampling and analysis of limestone and clay from the study area, have been carried out. These samples were tested for loss on ignition, silica, alumina, iron, calcium, magnesium, sodium, potassium and sulphuric anhydride.

In the second part of the thesis, all the samples were subjected to raw mix designing. Different raw mixes for high strength Portland cement (HSPC), sulphate resisting cement (SRC) and white cement (WC) were designed by mixing the raw material in different proportions. Only those mixes, which match the British Standard Specification and Pakistan Standard Specification, are included in this report. The raw mixes were processed for clinker formation, the clinker thus formed were studied for free lime, liquid phase and all constituents necessary for cement using standard analytical techniques. The clinkers, for high strength Portland cement, sulphate resisting cement and white cement were converted to their respective cements, whose physical parameters like compressive strength, setting time, consistency, expansion and blaine, and chemical parameters like insoluble residue, loss on ignition etc. were determined and compared with British and Pakistan Standard Specifications.

About 40000 tons, annual waste (baggase ash) from local sugar industries produces a number of environmental problems. In this work ways of recycling waste baggase ash in cement manufacturing have been suggested.

The third portion of the thesis, comprises the analysis of baggase ash and its use in the preparation of high strength Portland cement and study of the physical and chemical parameters of the resulting cement

Different parameters of the ash such as moisture, loss on ignition, calorific value, ash content, sulfur content, carbon content and other elements necessary for

cement manufacturing according to British and Pakistan Standard Specifications were determined.

In this study it was found that baggase ash contains some unburned carbon, which acts as alternate fuel in cement manufacturing and reduced the fuel up to 6.46%. Baggase ash, being already a calcimined material, reduced the emission of CO₂ to the environment up to 1.73%.

Baggase ash has also been used in cement mortar, in which different percentages of baggase ash has been mixed with cement, and compressive strength of the resulting cement- ash mixes have been studied. The pozzolanic reactivity of baggase ash in cement has been enhanced by using chemical activator. Aqueous solution of calcium chloride (CaCl₂ .2H₂O) in different percentages has been used instead of water in cement paste formation. 4% aqueous solution of calcium chloride has been found to be the optimum concentration of activator, as it gives maximum compressive strength to the resulting cement mortars. The use of chemical activator has increased the use of baggase ash from 5 to 15%.

The analytical instruments used for these studies were atomic absorption spectrometer, bomb calorimeter, flame emission spectrophotometer, geographic positioning scale, dual range sulfur and carbon analyzer, thermogravimetric analyzer, UV/Visible spectrophotometer and X-Ray fluorescence spectrophotometer.

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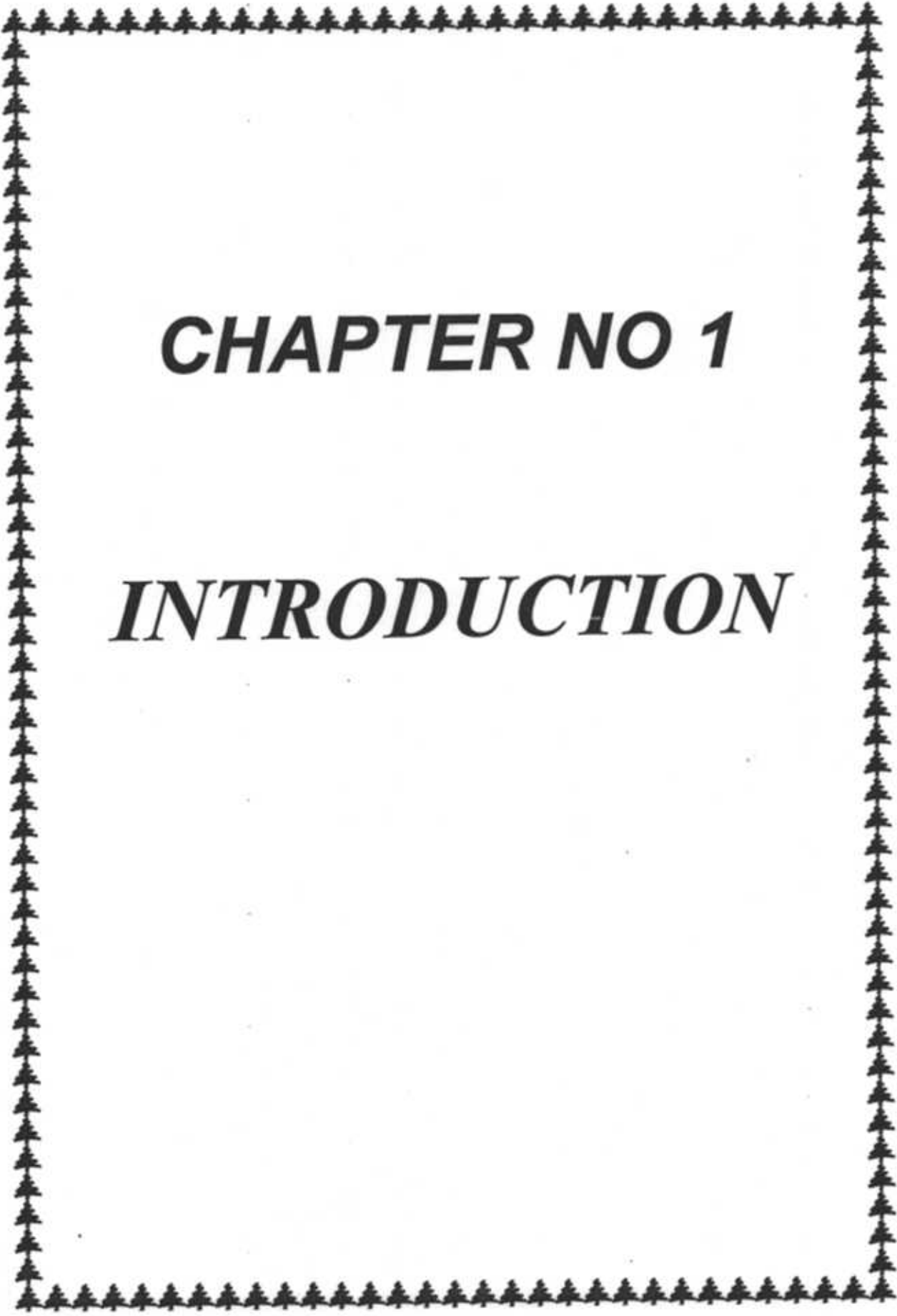
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CHAPTER NO 1

INTRODUCTION

CHAPTER – 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

Now a day, in this rapidly developing world, cement plays an important role in the construction industry of any country. Therefore, the need and use of cement is increasing day by day. New cement factories are being installed with a very rapid speed. The reserves of the raw material for the cement, already explored, are limited. It is therefore, very much necessary to find out new reserves of the raw material for different types of cement.

The economy of a country is mostly depending upon its industrial development. Those countries, which are industrially developed, are considered stable in the world. It is therefore considered that industry is the backbone of the country's development. So it is the need of the time to improve cement industries in Pakistan to make it economically stable.

There are twenty-seven cement plants in Pakistan. Out of which six are in the North West Frontier Province (N.W.F.P) namely Cherat Cement Company Limited Nowshera, Lucky Cement Limited, Kohat Cement Company Limited, Askary Cement Limited Nizampur (Army welfare trust), Bestway Cement Company Limited and Mustehkam Cement.

The annual production of the cement at the North West Frontier Province along with their location is given in Table 1.1

Table 1.1 Annual Production of Cement in N.W.F.P

Name of cement plant	Location	Annual production (Tons)
Army Welfare Trust	Nizampur	660000
Bestway Cement	Haripur	900000
Cherat Cement	Lakarai	759000
Kohat Cement	Babri banda	330000
Lucky Cement	Pezu	1320000
Mustehkam Cement	Hattar	660000
Total production		4629000

The main problem related to the cement industry is the cost of production, which is mainly due to the high cost of the fuel. The scientists are trying to find out new and alternate sources of energy to decrease the fuel consumption in cement manufacturing.

The second important problem in the world relative to cement industry is the environmental pollution. Carbon dioxide is a green house gas and a primary pollutant, which causes global warming. Green house effect has become the global issue; therefore the scientists are working on the remedial measure to reduce the effect of this problem. With the production of cement, a huge quantity of carbon dioxide is produced, which causes a number of environmental problems. Studies are underway to overcome these problems. The present study is a part of these efforts.

There are several sugar industries in Pakistan, especially in N.W.F.P, which use baggase as a fuel. The sugarcane contains 30% baggase and 70% juice. When baggase is burnt, it give only 3% ash. The total production of ash per day in North West Frontier Province (N.W.F.P.) is given in Table 1.2

Table 1.2 Daily Crushing of Sugarcane and Production of Baggase Ash in N. W.F.P.

Name of sugar mill	Sugarcane crushing (Tons)	Baggase produced (Tons)	Baggase ash (Tons)
Cheshma Sugar Mill (CSM)	3800	1140	34.2
Frontier Sugar Mill (FSM)	3800	1140	34.2
Khazana Sugar Mill Peshawar (KSM)	4000	1200	36.0
Premier Sugar Mill Mardan (PSM)	4000	1200	36.0
Total	15600	4680	140.4

About 40000 tons of baggase ash, produced in local sugar industries per year is wasted and presently has no use and being dumped here and there causing a number of environmental problems. The best solution to this problem is its use in cement manufacturing as a part of raw material. It may perform two functions; firstly it can be used as a raw material for cement because it may have pozzolanic properties. Secondly it can be used as additional fuel in the cement manufacturing if it contains unburnt carbon, which will also reduce the cost of fuel for cement manufacturing. Moreover, the use of baggase ash will reduce the carbon dioxide emission to the environment and so can solve the environmental problem to some extent. Moreover, the ash, instead of raw material, can also be used in mortars, which can replace significant amount of cement.

The North West Frontier Province (NWFP) is bestowed with extensive deposits of suitable grade raw material for the manufacture of Portland cement. The raw materials used for the manufacture of Portland cement are mainly composed of calcareous (limestone or chalk) and argillaceous (clay or shale) material. The occurrence of both types of materials in various areas of N.W.F.P. can be evaluated for the cement manufacturing.

The present work is divided in to three parts. The first part deals with the identification and characterization of the types of material (limestone and clay etc.) present in Darukhula and adjoining areas of Nizampur. The second part of this study deals with the raw mix designing for different types of cements, clinkerization and cement formation and with the study of different physical and chemical parameters of the resulting cements according to British and Pakistan Standard Specification while the third part of this study deals with the characterization of baggase ash from sugar industries, its use in cement preparation for the reduction of fuel cost and environmental pollution and study its effects on different parameters of cement.

1.2 INTRODUCTION TO STUDY AREA

1.2.1 Location

The study area covers Darukhula and adjoining areas of Nizampur, District Nowshera, North West Frontier Province of Pakistan. The area is located on survey of Pakistan Topo sheet Nos 43 C/1, 43 C/2, 38 O/13 and 38 O/14 between the Latitudes $33^{\circ}-45'-0''$ to $33^{\circ}-47'-12''$ N" and Longitude $72^{\circ}-0'-0''$ to $72^{\circ}-2'-30''$ E".

Darukhula area is located at a distance of about 5 kilometers in the southwest of Nizampur village. Nizampur village is located at a distance of 32 kilometers in south west direction of Attock Bridge which in turn is located on the main GT road at a distance of about 110 km from Peshawar towards East.

The area is approachable by a metalled road which bifurcates from the G.T road near the old Attock Bridge and runs parallel to the Indus river and leads to Nizampur. The area has no rail link. The nearest railway station is Khairabad, located at a distance of about 32 kilometers.

1.2.2 Topography and Climate

The area is marked by rugged topography. The relief of the mountains ranges between 313 meters to 740 meters. Nizampur village is situated at an elevation of 335 meters.

The Indus is the only river which captures the entire drainage of the area. There are several other major and minor streams traversing the area. However, the majority of the streams are dry. The climate of the area is more or less the same as

that of Peshawar valley. The winters are cold and the minimum temperature reaches as low as 6 °C during the months of December and January. The summers are hot and the temperature ranges from 45 °C to 47 °C during the months of July and August.

The area receives poor rainfall. The maximum rainfall is during the moon soon season and the annual rainfall is usually about 12 inches.

1.2.3 Geology of the Area

The area of study is a part of the Kohat range, which is an extension of the Kalachitta range, west of the Indus river. The rocks of the Kalachitta range, ranging in age from Jurassic to recent are exposed in the study area. This Range has well-established stratigraphy with eighteen lithostratigraphic units. These units are of marine and non-marine origin. Among these eight stratigraphic units (i.e., Samana Suk Formation, Chichali Formation, Lumshiwal Formation, Lockhart Formation; Patala Formation, Kuldana Formation, Kohat Formation and Murree Formation) are exposed in the study area (Figure 1.1). The Patala and Lockhart Formations are the dominant rock units exposed in the study area. The Lockhart Formation is the main focus of this study. Besides these formations, the area of study is extensively covered with the lacustrine quarternary deposits, which are mainly composed of clay and siltstone with intercalated sandstone. The stratigraphic units exposed in the study area are briefly discussed as below:

1. Samana Suk Formation: Samana Suk Formation consists of gray color limestone. The limestone is medium to thick bedded with some marl and ferrogenious sandy beds. Some yellowish dolomitic sandstone bands are also interbedded with limestone together with highly sheared shale. The limestone is extensively fractured and contains calcite veins at some places. The thickness of the formation in the study area is approximately 300 m. In the mapped area the contact is not exposed while the upper contact with Chichali Formation is disconformable.

2. Chichali Formation: The Chichali Formation in the study area is exposed in the northern part opposite to Jhungrai village where it is mixed with Lumshiwal Formation due to intense faulting. The main lithology consists of dark-gray to black and greenish-gray sandstone in the lower part and shale in the upper part. The sandstone is medium-grained, glauconitic and contains reddish-brown and yellowish ferrogenous stainings. The shale is thinly bedded, sandy, silty and glauconitic.

Phosphatic and pyretic nodules are also common. The Chichali Formation has disconformable contact with lower Samana Suk Formation, while the upper contact with the Lumshiwal Formation is normal.

3. Lumshiwal Formation: Lumshiwal Formation is exposed in various places in the study area. The lithology of Formation, west of Nizampur, consists of sandstone and limestone from bottom to top. The sandstone is yellowish – brown to greenish – gray, fine to coarse-grained, medium to thick bedded, feldspathic, silty, calcareous and ferrogenious at places. Limestone is dark-gray and brownish-gray, medium to thick bedded shelly. Both the upper contact with Kawagarh Formation and lower contact with the Chichali Formation are disconformable.

4. Lockhart Formation: Lockhart Formation consists of limestone with marl and shale intercalations. The limestone is dark-gray on weathered surface and is massive. It is bituminous and gives off fetid smell on fresh surface. The marl and shale are also dark-gray on weathered surface and light gray to bluish-gray on fresh surface. It has uncomfortably upper contact with Patala Formation in the study area.

5. Patala Formation: Patala Formation is exposed over most part of the study area. It occupies the middle part of the study area along the Nizampur-Kohat road. It consists of shale, marl and intercalated limestone. The shale is light-brownish-gray and dusty yellowish-green, laminated to thin bedded, fissile and splintery. The marl is light-gray, thin bedded and richly fossiliferous. The limestone is light-gray, medium-bedded, medium-grained, fossiliferous and nodular at places. The formation has some coal showings of low quality. In the study area the Patal Formation lies as a thrust sheet, therefore, the thickness sometime reaches to 2500 m. The Patala Formation has thrust contact with the underlying Kuldana Formation.

6. Murree Formation: The Murree Formation is exposed in the southern part of the study area. It exhibits mixed lithology with Kamli Formation. It mainly comprises sandstone, siltstone, and clay. The sandstone is of reddish-brown and buff color. It is medium to fine-grained, hard, medium to thin-bedded, calcareous and cross stratified. Clay is purple and pink. The Murree Formation lie unconformably over the Kohat Formation.

7. Kuldana Formation: Kuldana Formation is comprised of various colored shale and limestone. The shale is gray, green and purple red, thinly bedded, fissile and at places gypsiferous. Limestone is gray, fine-grained, medium-bedded, argillaceous fossiliferous and intercalated with marl. The average thickness is 140 m in the study area. The formation has thrust contact with the underlying Kohat Formation and overlying Patala Formation

8. Kohat Formation: Kaldana Formation is exposed in the southern part of the study area along the Nizampur-Kohat road. The formation is only a few meters thick and cannot be traced laterally in the area. The formation is mainly comprised of limestone and shale. The shale is greenish-gray in color, thin bedded and fossiliferous. The limestone is gray and thick to medium-bedded. The shale is usually interbedded with limestone. The formation is about 50 m thick in the area. It has conformably lower contact with Kuldana Formation; where as the upper contact with Murree Formation is unconformable.

1.3 OBJECTIVES OF THE WORK

The objectives of this work are given in the following lines

1. To evaluate the raw material of the study area for cement manufacturing. Especially for those cements, which are not being manufactured in N.W.F.P, and also to search for the new sites for cement plants.
2. To investigate ways and means for reducing the cost of production of cement.
3. To search for some alternate fuel sources which can be used in cement as a supplementary source of energy and new raw material for cements.
4. To minimize the environmental pollution caused by the manufacturing of cement and baggase ash discarded by sugar industries.

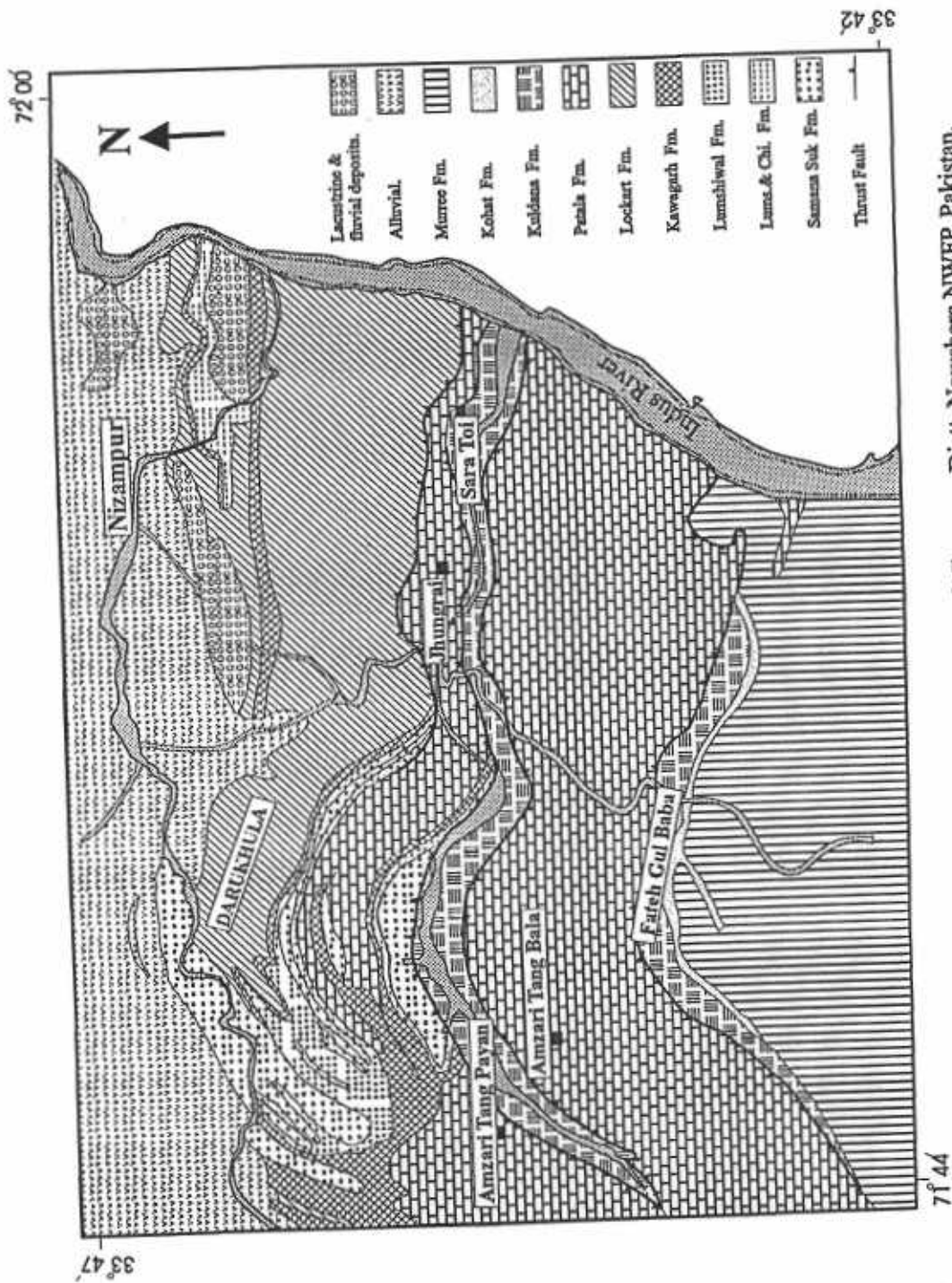


Fig.1.1. Geological Map of Darukhula and adjoining areas of Nizampur, Distt. Nowshera NWFP, Pakistan.

CHAPTER NO 2

INTRODUCTION

TO CEMENT

MANUFACTURING

CHAPTER – 2

INTRODUCTION TO CEMENT MANUFACTURING

2.1 DEFINITIONS AND MEANINGS OF CEMENT

Cement may be defined as the adhesive substance capable of uniting fragments or masses of solid matter to a compact whole. Such a definition embraces a large number of very different substances having little in common with one another but their adhesiveness, and the very unequal technical and scientific importance of different members of the class has tended to bring about a restriction of the designation to one group of adhesive substances, namely, to the plastic materials employed to produce adhesion between stones, bricks, etc. in the construction of buildings and engineering works. Cements of this kind also bear a chemical relationship to each other, consisting as they do of mixtures, which contain compounds of lime as their principal constituents [1]. The term cement in this restricted sense then becomes equivalent to calcareous cements, but it may be allowed to include certain allied compounds of magnesium.

Cement is a material, which binds together solid bodies (aggregate) by hardening from a plastic state [2]. This definition includes organic polymer based cements. Apart from their use as adhesives, some larger scale use of polymers has developed, mainly in the USA, as binders for aggregate in a rapidly hardening patching material for damaged roads and bridge decks, for example, a monomer such as methyl methacrylate is polymerized and hardened in situ. However, the use of materials, as expensive as these, is very limited compared to the use of inorganic cements among which Portland cement is pre-eminent.

An inorganic cement functions by forming a plastic paste when mixed with water, which develops rigidity (sets) and then steadily increases in compressive strength (hardens) by chemical reaction with the water (hydration). Cement, which increases in strength even when stored under water after setting is said to be hydraulic.

Portland cement is defined as hydraulic cement, obtained by burning a mixture of lime and clay to form a clinker, and then pulverizing that clinker into powder. This

greenish gray powder is composed primarily of calcium silicates, calcium aluminates and calcium ferrites. When mixed with water, it solidifies to an artificial rock, similar to Portland stone. A Portland stone is a yellow limestone from the Isle of Portland in Great Britain.

2.2 HISTORY OF CEMENT

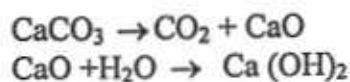
2.2.1 Early History of Portland Cement

Modern day Portland cement was brought into existence only during the early nineteenth century. However, mankind has used burnt lime and clay as cementing material for construction purposes through many centuries. The Assyrians and Babylonians [3] used clay for this purpose, and the Egyptians advanced to the discovery of lime and gypsum mortar as a binding agent for building Pyramids.

The Greeks made further improvements and finally the Romans developed cement that produced structures of remarkable durability.

2.2.2 Roman Formula

The Romans recognized the importance of compaction to produce dense, durable material. Examples of their success are the pantheon in Rome and the pont du Gard aqueduct in southern France, both of which have survived intact. Roman mortar contained hydrated (slaked) lime produced from limestone by calcinations and hydration of the quicklime.



The hydrated lime was intimately mixed with sand and a fine material of volcanic origin. This mortar hardened as a compacted mass in the presence of water by interaction of the volcanic material with lime to form hydrated calcium silicates similar to those found in hardened Portland cement paste [4]

The secret of Roman success in making cement was traced to the mixing of slaked lime with pozzolana, a volcanic ash from Mount Vesuvius. This process produced cement capable of hardening under water. During the Middle Ages this art was lost and it was not until the scientific spirit of inquiry revived that we rediscovered the secret of hydraulic cement that will harden under water.

Other men experimenting in the field of cement during the period from 1756 to 1830 include L. J. Vicat and Lesage in France and Joseph Parker and James Frost in England.

Before Portland cement was discovered and for some years after its discovery, large quantities of natural cement were used. Natural cement was produced by burning a naturally occurring mixture of lime and clay. Because the ingredients of natural cement were mixed by nature, its properties varied as widely as the natural resources from which it was made.

The Romans found out that mixing lime with pozzolana (a rock like material, which shows natural hydraulic properties) produces cementing material, which shows hydraulic properties of pozzolonic material was also found in large areas of Italy, Greece, Germany, and Ireland. In a town called Portland, in England, raw materials for present day cement were naturally present in the limestone. The Portland stone, as it is popularly known as, is burnt to sintering temperature to form Portland cement. This naturally occurring stone consists of all the required oxides of cement in the right proportions.

2.2.3 Aspdin Patent for Cement

In 1824 Joseph Aspdin, a British stonemason, obtained a patent for cement, he produced in his kitchen. He heated a mixture of finely ground limestone and clay in his kitchen stove and ground the mixture into a powder and named the product as Portland cement. Two fundamental developments have improved on the early product, i.e. the introduction of gypsum, added when grinding the clinker, to act as a set retarder and the use of higher burning temperatures to allow the production of higher lime content silicates which are necessary for more rapid strength development in concrete [5]

The use of cement in building is not met with below a relatively advanced stage of civilization. The earlier structures were composed of earth, sometimes raised in the form of walls of domes by ramming successive layers, or of stone blocks, set one above another without the aid of any cementing material as in prehistoric megalithic structures, and in the Cyclopean masonry of Greece. The simplest plan is that found in the brick walls of ancient Egyptian buildings. The bricks are dried in the sun without baking, and each course is covered with a moist layer of the loam (Nile

mud) used for making the bricks, with or without the addition of chopped straw. The drying of this layer makes the wall a solid mass of dry clay; such a mode of construction is only possible in a rainless climate, as the unburnt material possesses little power of resistance to water.

The ancient writers insisted on storing lime in the slaked condition for a long time preferably several years, before use, but in 1765 Lorient, a French engineer engaged on this work, maintained that the passages in question had been misunderstood, and proposed the addition of quicklime to the mortar at the time of mixing, in order to obtain increased strength and impermeability [6]. De la Faye [7] contested this, and recommended that egg-sized lumps of lime should be immersed in water, transferred after a time to a cask, and there allowed to slake, evolving steam. This practice is borrowed from St. Augustine. Faujas de Saint-Fond [8], in the course of a very careful study of pozzolonic materials, favored this latter plan of slaking, and also called attention to an Indian process, employed on the Malabar Coast, of mixing molasses with lime concrete in order to increase the hardness. Finally, Rondelet [9] after a careful examination of Roman buildings and after making many experiments with the methods proposed by Lorient and others came to the conclusion that the excellence of Roman mortars depended, not on any secret in the slaking or composition of the lime, but on the thoroughness of mixing and ramming.

The Romans carried their knowledge of the preparation of mortar with them to the remoter parts of their empire, and the Roman brickwork found in England, for example, is equal to the best of that in Italy. Ground tiles were the most commonly used ingredient, but in a few districts deposits bearing some resemblance to the natural pozzolana of the Bay of Naples were found. The use of Rhenish volcanic tuffs known as Trass was probably introduced at this time, and this material, like pozzolana, is still employed at the present day.

A gradual decline in the quality of the mortar used in buildings set in after Roman times, and continued throughout the middle ages. Saxon and Norman buildings, for instance, show evidence of badly mixed mortars, often prepared from imperfectly burnt lime. The conclusion appears certain, from the examination of French buildings [10], that during the ninth, tenth, and eleventh centuries the art of burning lime was almost completely lost, the lime being used in badly burnt lumps,

without the addition of ground tiles. From the twelfth century onwards the quality improved, the lime being well burnt and well sifted. After the fourteenth century excellent mortar is found, and the precaution was evidently taken of washing the sand free from adhering dirt or clay [11]

The Roman mixture of lime and natural or artificial pozzolana long retained its position as the only suitable material for work under or exposed to water. Thus Belidor, for a long time the principal authority on hydraulic construction, recommends an intimate mixture of tiles, stone chips, and scales from a black smith's forge, carefully ground, washed free from coal and dirt, dried and sifted, and then mixed with freshly slaked lime [12]. The same author mentions the use of pozzolana or trass where such materials are available. A very thorough and illuminating survey of the subject, which will be referred to later, is that in Rondelet's great work on building. It is remarkable that even at this late date most of the authorities quoted are ancient, including Pliny, Vitruvius, and St Augustine.

The investigations of L. J. Vicat [13] on hydraulic lime led him to prepare an artificial hydraulic lime by calcining an intimate mixture of limestone (chalk) and clay, ground together in a wet mill. This process may be regarded as the principal forerunner of the manufacture of Portland cement

James Franks also patented a cement of this kind in 1811, and established works at Swanscomb, the first in the London district. He only calcined his mixture lightly, and the product was evidently inferior to Roman cement as it was sold at a lower price. In 21st Oct. 1824, Joseph Aspdin, a Leeds builder used a limestone as used for the repairing of roads, crushed and calcined it in the furnace and then that material was used for making cement or artificial stone. A higher temperature of firing must have been introduced in Aspdin's works before this, as on the resumption of the construction of the Thames Tunnel in 1838, Brunel employed Portland cement in spite of the fact that its price was double that of Roman cement, and in the face of strong opposition [14-17].

As the demand for Portland cement, especially as an ingredient of concrete, increased, and the requirements of engineers called for a more perfect material it became increasingly desirable that standards of quality should be set up, by which any consignment could be judged after the performance of certain agreed tests. In this way

standard specifications have arisen in most countries, either under official auspices, or as the work of voluntary organizations of engineers and consumers, or of associations of cement manufacturers. Such an association was founded in Germany so far back as 1877, and shortly afterwards established rules for controlling the quality of the product. The first German standard specification was drawn up by this body. The British standard specification was drawn up in 1904 by the engineering standards committee (now the British Standards Institution) and its ninth revision appeared in 1958. A specification for Portland blast furnace cement was issued in 1923 and its fifth revision appeared in 1958. The first ASTM specification was issued in 1904. All such specifications are liable to revision from time to time, the alterations made being almost invariably in the direction of increasing the stringency of the requirements. At the same time, most commercial cements commonly more than fulfill the conditions of the official specifications.

2.2.4 Cement in the 20th Century

Two major discoveries occurred in the early 20th century, by Lafarge Research Laboratory. The first concerned the discovery of the principle of the production of white cement, characterized by the use of kaolin, which has no iron oxide, instead of clay. This different composition, however, did not bring about any change in the intrinsic characteristics of the cement, which continued to provide the same strength capacities as comparable to gray cement.

The year 1908 saw the discovery of Ciment Fondu "the first industrial calcium aluminate, made with limestone and bauxite". This important discovery was made by Jules Bied, director of the Lafarge Research Laboratory, which was founded in 1887 and is the oldest research center in the cement industry in the world. High-alumina cement, which is resistant to aggressive agents and to high temperatures, quickly revealed its multi-purpose possibilities, such as use as a high-performance binder or a chemical reactant in many different applications. Today, calcium aluminates stand at the leading edge of technological progress in the construction field, and have spurred the development of many technical products such as special mortars, refractory concretes and others.

2.2.5 The History of Concrete

Cement has been around for at least 12 million years. When the earth itself was undergoing intense geologic changes, natural cement was being created. It was this natural cement that humans first put to use. Eventually, they discovered how to make cement from other materials. The history of concrete can be given in short as below;

3000 BC	Chinese used cementitious materials to hold bamboo together in their boats and in the Great Wall.
800 BC	Greeks, Crete & Cyprus used lime mortars, which were much harder than later Roman mortars.
1200 - 1500 The Middle Ages	The quality of cementing materials deteriorated. The use of burning lime and pozzolana (admixture) was lost, but reintroduced in the 1300's.
1802	In France, a similar Roman Cement process was used.
1824	Joseph Aspdin of England invented Portland cement by burning finely ground chalk with finely divided clay in a limekiln until carbon dioxide was driven off. The sintered product was then ground and he called it Portland cement named after the high quality building stones quarried at Portland, England.
1830	The first production of lime and hydraulic cement took place in Canada.
1836	The first systematic tests of tensile and compressive strength took place in Germany.
1860	The beginning of the era of Portland cements of modern composition.
1871	David Saylor was issued the first American patent for Portland cement. He showed the importance of true clinkering.
1886	The first rotary kiln was introduced in England to replace the vertical shaft kilns.
1889	The first concrete reinforced bridge is built.
1903	The first concrete high rise was built in Cincinnati, OH.
1936	The first major concrete dams, Hoover Dam and Grand Coulee Dam, were built. They still exist today!
1967	First concrete domed sport structure, the Assembly Hall, was constructed at The University of Illinois, at Urbana-Champaign.
1970's	Fiber reinforcement in concrete was introduced.
1980's	Super plasticizers were introduced as admixtures.
1985	Silica fume was introduced as a pozzolanic additive. The "highest strength" concrete was used in building the Union Plaza constructed in Seattle, Washington.
1992	The tallest reinforced concrete building in the world was constructed at 311 S. Wacker Dr. Chicago, Illinois.

2.3 CLASSIFICATION OF CEMENTS

Cements are classified in the following types:

2.3.1 Natural Cement

Natural cements are materials formed by calcining a naturally occurring mixture of calcareous and argillaceous substances at a temperature below that at which sintering takes place. The British 'Roman' cement which preceded Portland cement but which is still manufactured on a small scale, and the former American rock cements, belongs to this class. The Belgian Natural Portland cements were also similar but burnt at a some what higher temperature. These materials represent a group intermediate between the hydraulic limes and Portland cement.

2.3.2 Portland Cement

Portland cement may be defined as in the British standard as a product obtained by intimately mixing together calcareous and argillaceous or other silica, alumina, and iron oxides bearing materials, burning them at a clinkering temperature, and grinding the resulting clinker.

2.3.3 High Alumina Cement

Aluminous, or high alumina, cement is manufactured by heating until molten, or more rarely by sintering a mixture of limestone and bauxite, the product is cooled and finely ground. High alumina cement is characterized by a very rapid rate of development of strength and approaches closely to its final strength in twenty four hours after gauging. Its setting time is similar to that of Portland cement. Its color is black.

2.3.4 Oil well Cement

These are cements produced for cementing the steel casing of gas and oil wells to the walls of the borehole and to seal porous formations. The cement slurry has to be pumped into position, before it sets, under conditions of high temperature and pressure. Portland cements, more coarsely ground than normal, with the addition of special retarders such as starches, sugars or organic hydroxyl acids, are used; also slow setting Portland cements of a composition between the Ferrari and Erz types and pozzolonic cements.

2.3.5 Masonry Cement

This group of cements consists of materials intended for use in mortar. Their purpose is to provide cement, which gives a more plastic mortar than ordinary Portland cement. They are often produced by grinding more finely, than a usual mixture of Portland cement and limestone together with a plasticizer that entrains air. They are also made by intergrinding mixtures of Portland cement with hydrated lime, granulated slag or inert fillers with the addition of calcium stearate or some other waterproofing agents. Natural cements and cold process slag cements are also found in this group and also materials such as 'grapier' cement in France.

2.3.6 Sorel Cement or Magnesium Oxychloride Cement

Sorel cement is the product obtained when magnesia and a solution of magnesium chloride react together. Magnesite is calcined so as to give a lightly burnt reactive product and the ground material mixed as required with a strong solution of magnesium chloride. Combination of magnesia and magnesium chloride takes place with the development of heat and results in the formation of Sorel cement [18-20]

This product is hard and strong, but is attacked by water. It is used mainly as a flooring material with an inert filler and a pigment to color it and is often known as Magnesite flooring.

2.3.7 Pozzolanas and Pozzolanic Cement

A pozzolana may be defined as a material, which is capable of reacting with lime in the presence of water at ordinary temperature to produce cementitious compounds. Italian pozzolana, trass and Santorin earth are examples of naturally occurring pozzolanas of volcanic origin. Artificial pozzolanas are prepared by burning at suitable temperatures certain clays, shales, and diatomaceous earths containing a proportion of clay. Diatomaceous silica and some natural amorphous silica deposits may also form pozzolanas, either with or without a heat treatment. Pulverized fuel ash (fly ash) is also used as a pozzolana. Pozzolanic cements are produced by grinding together Portland cement clinker and a pozzolana or by mixing together a hydrated lime and a pozzolana.

2.4 PRODUCTION OF CEMENT

2.4.1 The Cement Production Process

Cement kilns are massive cylindrical structures, lined with refractory brick, into which a lime-bearing material and fuel such as coal or gas is fed. There is a range of different kiln designs but all rely on the same basic processes — raw feed passing through the kiln is heated to very high temperatures by the burning of fuel and is transformed chemically and physically into a grey pebble-like material called clinker. Clinker is ground to produce cement.

The three broad processes of cement manufacturing are:

- **Raw milling:** The preparation of the kiln feed.
- **Calcining and burning or clinkering:** The conversion process that takes place within the cement kiln and associated equipment.
- **Finish milling:** The grinding of clinker to produce cement.

2.4.1.1 Raw Material

The raw material for cement manufacturing may be divided into four groups:

- Calcareous material
- Siliceous material
- Argillaceous material
- Ferrieous material

The calcareous material supply lime stone, siliceous material supply silica, argillaceous material supply alumina and ferrieous material supply iron. Gypsum in a very small amount is required to control the setting time of cement. Thirty different rock materials can be used in the manufacture of Portland cement. The calcareous materials include cement rock, limestone, marl, alkali waste, oyster shell, coquina shell, chalk and marble. The argillaceous materials include sand, trap rock, quartzite, calcium silicate, and fuller's earth. The ferriferous material includes iron or iron calcine, iron dust, iron pyrite, iron smelters, iron oxide and blast furnace flue dust. The cement rock is ideal low magnesium bearing argillaceous limestone with such a composition that it may be used for cement manufacturing without addition of other earth materials or with addition of only a relatively small amount of such materials.

Limestone is composed essentially of calcium carbonate with varying percentages of magnesium carbonate and admixed impurities of clay and sand. For the manufacture of Portland cement, the limestone should have above 50% lime (CaO) if the percentage is less than 50%, the rock should be given other names with the appropriate qualifying adjectives [21]

Limestone may be white, grey, dark grey, yellowish blue and some times black in color. Limestone is wide spread in nature. Calcium carbonate of all geological formations qualifies for the production of Portland cement. The purest grades of limestone are calcspar (Calcite) and aragonite. Calcite crystallizes hexagonally, and aragonite is rhombic. The specific gravity of calcite is 2.7 and of aragonite 2.95. A macroscopic granular variety of calcite is marble. It would not be profitable to use marble for cement manufacturing.

The most common forms of calcium carbonate, most similar to marble, are limestone and chalk; limestone is of a predominantly fine-grained crystalline structure. The hardness of limestone depends on its geological age, usually the older the geological formation.

2.4.1.2 Clay

The second important raw material for cement manufacturing is clay, which is formed by the weathering of alkali and alkaline earth containing aluminum silicates and of their chemical conversion products, mainly feldspar and mica. The main component of clays is formed by hydrous aluminum silicates. Clays are divided into the following mineral groups

1. Kaolin group

Kaolin, which consists of kaolinite, dickite, nacrite and halloysite. Minerals of the kaolin group differ in content of SiO_2 as well as by the crystallographic structure and optical properties. The designation kaolinite refers to the pure kaolin mineral. Texturally, clays are fine grained, usually under 2 microns in diameters.

2. Montmorillonite group

This group consists of

- | | |
|--------------------|---|
| a. Montmorillonite | $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$ |
| b. Beidellit | $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ |
| c. Nontronite | $(\text{Al}, \text{Fe})_2 \text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ |
| d. Saponite | $2\text{MgO} \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ |

3. Alkali bearing Clays group ($K_2O-MgO-Al_2O_3-SiO_2-H_2O$)

The chemical composition of clay vary from those close to the pure clay, to that containing a considerable amount of chemical admixtures as iron hydroxide, iron sulfide, sand, calcium carbonate etc. Iron hydroxide is the principal coloring agent in clays, also organic matter may give the clay different colors. Clays with no impurities are white. The major source of alkalis in cement is found in the argillaceous component of the raw mix.

2.4.1.3 Clay and Sand

Clay and sand are not objectionable impurities as they supply alumina, silica and iron oxide, necessary for the formation of the desired silicates in cement. Dolomite cannot be used for the manufacture of Portland cement, because of its high magnesium content. The most important factor controlling the suitability of limestone for the manufacture of Portland cement is its magnesium oxide content. The permissible limit of which is 5% in the finished cement or less than 3% in limestone because during calcinations the magnesium oxide content will increase due to elimination of carbon dioxide [22]. The excess of magnesia may be dangerous to the soundness of concrete, especially at the latter stages. If the contents of silica and alumina are high, pure high calcium, limestone must be added to lower the impurities. Alkalies (Soda and Potash) generally amount up to 1.5%.

2.4.1.4 Marl

Limestone with admixtures of silica, clay substance, and iron oxide are called marls. Marls are earthy friable accumulations of calcareous materials secreted by plants and animals in lakes and marshes over long periods of time to skeletal remains of plants mixed with shells of animals may form some thick beds of marl suitable for cement manufacturing but such deposits are not common.

Geologically marls sedimentary rocks generated by simultaneous sedimentation of calcium carbonate and clay substance, the hardness of marls is lower than limestone, the higher the content of clay substances the lower their hardness some times marls contain also bituminous constituents. The color of marls depends on the clay substance and ranges from yellow to grayish black. Marls are an excellent raw material for cement manufacture, because they contain the lime and the clay component in an already homogenized condition. As to the quantitative proportions of

the lime and clay components in cement raw materials, the following classification is established.

2.4.1.5 Chalk

Chalk is a sedimentary rock, which was formed during the cretaceous period in geological time, geologically it is relatively young. In contrast to limestone, chalk is characterized by a soft earthy texture, this property qualifies chalk as a raw material especially for the wet process of cement manufacture, Since blasting is not required for quarrying of chalk, and the crushing process can also be omitted, this kind of raw material considerably lowers the cement production costs. In some deposits the calcium carbonate content of chalk amounts to 98-99% with small admixtures of SiO_2 , Al_2O_3 , and MgCO_3 . In cement raw materials the lime component is generally represented up to an amount of 76-80%. Therefore, the chemical and physical properties of this component are of decisive influence, when it comes to selecting methods of cement manufacturing as well as the type of production machinery.

2.4.1.6 Clay and Shale

Clay stone and similar rocks are earthy, easily disintegrated mass of colloidal clay or silt size material. Shale is a similar material but it does not disintegrate as easily as clay stones. Where alumina and silica are not present in the limestone in sufficient amounts, it is necessary to add clay or shale. Both clays and shales have wide variations in mineralogical and chemical content from essentially hydrated aluminum silicate to more than 50% free silica along with alumina and iron oxide.

2.4.1.7 Laterite and Bauxite

Residual deposits formed under special climatic condition in tropical regions. Laterite consists essentially of hydrated iron oxides, bauxite of hydrated aluminum oxides, the most common impurity in both being silica, aluminous laterites and ferruginous bauxites are quite common. Occasionally bauxite and laterite are eroded and redeposited, although it is unlikely that they can be transported over great distances. They may become mixed with other sedimentary material, to form such rocks as bauxites and laterites.

The main raw material for the manufacture of clinker is a lime-bearing material. Ideally, this material will be mined from a location near the plant to minimize transport and handling costs. Limestone is the most common material used

although chalk, seashell deposits and other calcareous material (calcium carbonate) can be used. The importance of limestone ore bodies close to the plant is that it makes up around 80 per cent of the approximately 1.65 tons of raw material input needed to make one tone of clinker. Approximately 50 per cent by weight of the lime-bearing material is lost as carbon dioxide in the manufacturing process.

2.4.2 Manufacturing

The process of cement manufacture consists of the incorporation of the raw materials to form a homogeneous mixture, the burning of mix in a kiln to form a clinker and the grinding of the clinker with the addition of a small proportion of gypsum to a fine powder. The brief detail of the process is given below,

2.4.2.1 Proportioning, Mixing and Raw Milling

Proportioning involves determining the correct proportions of materials to be combined to form the raw mix. The proportions are governed by the chemical properties of the materials to be used and the desired properties of the clinker that is produced. After proportioning, the raw materials for a dry process kiln are mixed to produce an aerated dry raw mix. Mixing is an important step in the process to ensure an even distribution of the properly proportioned components of the raw mix so that the clinker will be of a uniform quality.

Raw materials with high moisture content are more likely to be slurried then dewatered to a filter cake before being introduced into the kiln. This is known as the semi-wet process. Another process, the semi-dry process is used where there is a requirement for the raw materials to be in the form of nodules or pellets. For example, the Lepol kiln requires water to be added to the raw mix to form pellets that can be preheated by the hot kiln exhaust gases in a pre heater.

2.4.2.2 Formation of Clinker

There are four stages to this process as follow:

- Evaporation and preheating,
- Calcination
- Clinkerization
- Cooling.

Evaporation and preheating remove moisture and raise the temperature of the raw mix preparatory to calcining. Calcination takes place at 800-900 °C and breaks the

calcium carbonate down into calcium oxide and carbon dioxide, which is evolved in the process. Clinkering completes the calcination stage and fuses the calcined raw mix into hard nodules resembling small grey pebbles. Kiln temperatures in the burning zone range from 1350-1450 °C, and retention times in this zone are four to six seconds.

Clinkering is critical to the quality of cement and requires accurate control of the energy input. Insufficient heat will cause the clinker to be underburnt, containing unconverted lime, and reducing the hydration (setting and hardening) properties of the resulting cement. Excess heat will shorten the life of the refractory bricks lining the kiln, may damage the kiln shell and diminish product reactivity.

The high temperatures required for burning of the raw mix mean that the process is energy intensive. Electrical energy is required for the raw milling and mixing, burning and finish milling. The largest energy demand is for fuel for burning of the raw mix. This has been the focus of technological developments.

2.4.2.3 Finish Milling of Clinker

Finish milling is the grinding of clinker to produce a fine-grey powder. Gypsum (CaSO_4) is blended with the ground clinker to produce finished cement. The gypsum controls the rate of hydration of the cement in the cement-setting process.

Significant amounts of electrical energy are required for milling. The total power demand depends on the fineness of the grind, the distribution of particle size, and the efficiency of separation of the finely ground particles. The finer the grind, the more reactive is the finished cement. Rapid-setting cements have smaller particle size than the less reactive low heat of hydration cements. Cement is more reactive than clinker and can absorb moisture from the environment leading to some degree of pre-hydration.

The large power demands of finish milling mean that improving the efficiency of grinding and separation of the ground clinker can yield significant energy efficiency improvements and cost savings.

2.5 TYPES OF PROCESSES IN CLINKER FORMATION

Two distinct processes are employed in the production of clinker. In the wet process slurry of the finely divided raw materials is made and pumped into a long

rotary kiln. In the dry process the raw materials are prepared for pyroprocessing as a blend of finely ground powders and initial heating is usually carried out in a preheater using the hot gases from a relatively short kiln. However, in those parts of the world where the raw materials are relatively dry and fuel costs are not prohibitive, drying, calcining and clinkering may be carried out in a long dry kiln. The wet process was at one time predominant but a rapid increase in fuel costs in the 1970s accelerated the final stages of its replacement, since it involves the evaporation of a substantial quantity of water, typically 30-35% of the mass of the kiln feed [23].

2.5.1 Wet process

In this process soft materials are converted in to slurry with water in a wash mill. The slurry produced, controlled by measurement of its density and the addition rates of the materials, and should contain the highest concentration of solids at which it is pumpable. Reduction of water content necessary for pumping can often be achieved by adding a deflocculant, such as sodium carbonate or silicate at a cost, which is less than that of the kiln fuel saved.

Either clay or chalk may be slurried first and the second component blended with it in a second wash mill. When chalk contains flints it may be added to the clay slurry in the form of tube mill, called a wash drum, in which the flints act as grinding media and are then 'scalped off'. Remaining coarse material is removed from the slurry by fine screens or by hydro cyclones.

Further adjustment using minor components such as ground sand, pulverized fuel ash or iron oxide, may be necessary to optimize chemical composition. The refined slurry is monitored by determination of residues, when a sample is washed through standard sieves. Chemical composition is checked by sampling at different stages. The slurry is then held on tanks in which it is agitated both mechanically and by compressed air to prevent segregation.

2.5.2 Dry process

In this process raw materials are crushed and put into stockpile. A considerable degree of homogenization is obtained by laying them sown in strips or layers and systematically reclaiming from the stockpiles produced. Passing the hot gases coming from the kiln dries the material. The raw material is grinded usually in the ball mill. The milled raw meal is transferred in to the blinding silo where the

material is stored and blended. The homogenized material is then processed further for clinker formation [24].

2.6 PYROPROCESSING

The physical and chemical processes occurring as the temperature of the raw material is raised to the maximum is called pyroprocessing [25]. It involve the following steps:

2.6.1 Preheating

The decomposition of the clay minerals takes place in the temperature range of 350-650 °C. The almost amorphous intermediates formed initially by dehydroxylation do not subsequently recrystallize because they react with calcite before high enough temperatures are reached. Any magnesite present will also decompose in this part of the system, its equilibrium decomposition pressure P_{CO_2} , reaching 1 atmosphere at about 400°C.

2.6.2 Calcining

The decarbonation of calcite is strongly endothermic. Specific rather than molar enthalpies are usually quoted because they are used in calculating the theoretical energy needed to produce 1kg of clinker. Values of the equilibrium partial pressure of calcite have been determined as a function of temperature by a number of workers with significant discrepancies. The relationship between the equilibrium constant K_p for decarbonation and temperature is given by the Van't Hoff equation which, in the integrated form, is

$$\ln \frac{K_{p2}}{K_{p1}} = - \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Where ΔH is the molar enthalpy for the reaction and R is the gas constant. The above equation is only applicable over a range temperature in which ΔH is sensible constant to within the error in equilibrium pressure measurement. Over large temperature interval ΔH changes significantly because the difference between the specific heats of reactants and products changes.

The factors determining the overall rate of decarbonation are:

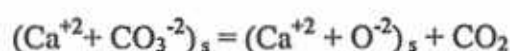
- a. The material temperature which determines P_{CO_2}
- b. The gas temperature which determines heat transfer rate

- c. The external partial pressure of CO₂, which is the sum of the partial pressure derived from the calcite decomposed and from the combustion of the fuel.
- d. The size and purity of the calcite particles.

In the wet or long dry kilns the strongly endothermic nature of the reaction and the depth of the bed resulting heat transfer being rate controlling. If the individual calcite particles are suspended in the combustion gas stream then possible rate controlling factors are:

The rate of heat through any already decarbonated material to the undecomposed core of a particle.

The reversible process of breaking a chemical bond in the carbonate ion and rearrangement of ions to form CaO crystals.



The diffusion of CO₂ through the product layer of lime crystals.

The slowest of these steps will determine the overall rate of decarbonation. For large crystals, high gas temperatures and low CO₂ partial pressures, heat transfer will be the rate limiting factor, while at lower temperatures with high external CO₂ pressures, diffusion of CO₂ will be rate controlling.

Khraisha and Dugwell determined rates of calcinations of a natural limestone with particle sizes in the range 40-90 μm using a reactor simulating the conditions in a commercial precalciner. They monitored exit gas composition with an on-line mass spectrometer, measurements of calcinations rate were made over the temperature range 1076-1156K in air, and in a mixture of 15% CO₂ with O₂ and N₂. The results were in accord with the shrinking sphere model and suggested that, under the conditions employed, chemical reaction was rate controlling with an activation energy of 196 kJ/mol. Simultaneous injection of coal and limestone into the reactor was found to enhance combustion of the coal but inhibit calcinations by increasing the partial pressure of CO₂.

Direct chemical interactions between calcite and the decomposition products of clay minerals also occur in this zone of the kiln, their importance depending on the fineness and intermixing of the original minerals. These endothermic reactions, which occur at slightly lower temperatures than normal calcite decomposition are detected

by different thermal analysis as a shoulder on the low temperature side of the decarbonation endotherm. Solid-solid reactions increase in extent throughout the calcination zone and fluorides, sulfates, and alkalis may produce melts, which, although small in amount, promote reaction. At the contact between two reacting particles, such as lime and silica, a range of compositions would be expected to develop, corresponding to the subsolidus of the binary system at the temperature involved. C_2S (dicalcium silicate) is formed from about 800 °C upwards. Some product phases are likely to be form in very small bands, only revealed by determination of atomic ratios using x-ray microanalysis. Intermediate products, which have been found in amounts revealed by conventional x-ray diffraction, in samples taken through ports in a kiln shell, are $2C_2S$, $CaCO_3$, $C_{12}A_7$ and C_2F .

2.6.3 Clinkering

Clinkering is the sintering in the presence of a liquid phase. After the completion of decarbonation, material temperature rises rapidly and all but the coarsest siliceous material is quickly converted to C_2S (dicalcium silicate). Acidic melts form in silica-rich regions where interactions with lime, alumina and /or iron oxide can occur. For example, melting occurs from 1170 °C in the C-A-S system. In the first stage of clinkering the melt formed exerts significant capillary forces as a result of its high surface tension. Producing rapid shrinkage and nodule formation, if this has not already occurred. Both Russian and Japanese researchers have shown that in a slower, second stage of clinkering the fractional shrinkage $\Delta L/L_0$ with time t , can be fitted to an equation proposed by Kingery (1959) for the sintering of a solid in the presence of a reactive liquid

$$\frac{\Delta L}{L_0} = \left[\frac{6k_2\partial DC_0\gamma V_0}{k_1RT} \right]^{\frac{1}{3r} - \frac{4}{3\gamma}}$$

Where k_1 and k_2 are constants

∂ is the thickness of the liquid film between the interfaces

D is the diffusion coefficient in the liquid

C_0 is the solubility of the solid

V_0 molar volume

r initial particle size

γ liquid vapor interfacial tension

$\frac{\Delta L}{L_0}$ is the fractional shrinkage

The processes finally bringing the clinker closer to equilibrium involve the dissolution of lime and C_2S in the melt, diffusion of ions and crystallization of C_3S (tricalcium silicate). Identification of the rate controlling step or steps therefore requires independent measurement of these processes.

The activation energy for viscous flow was found to be 364 kJ/mol and the similarity to E_A Si indicates the dominance of the silicate ion on melt viscosity. Rates of solution of CaO and C_2S increase with increasing temperature and because dissolution involves diffusion of ions away from the liquid immediately adjacent to the solid surface. They also increase with decreasing melt viscosity at constant temperature. The influence of alkali and sulphate ions added simultaneously was found to be complicated, by their forming immiscible liquids

In rotary kiln three additional processes complicate the simple dissolution-diffusion- crystallization module. These are:

1. Movement of material involving shear and compaction within nodules, which aids chemical combination.
2. Volatilization of alkalis and sulfur oxides.
3. The existence of low partial pressures of oxygen with some reduction of Fe^{3+} to Fe^{2+} . Reduction, if excessive, may destabilize C_3S and hence adversely influence cement quality but is minimized by proper flame control.

Potassium and sodium sulfates and chlorides are volatile at kiln burning zone temperatures. At 1400 °C the vapor pressures of the chlorides are more than 1 atm, while those of the sulfates are approximately 0.5 and 0.2 atm for sodium and potassium respectively. A cycle is set up involving evaporation of these minor constituents of the raw materials in the burning zone and their return to the kiln after condensation on the cooler material entering the system. Condensation of sulfates on the cooler walls of the system can lead to a build up of raw feed adhering to the deposits and a serious restriction in material flow. The levels entering the clinkering zone increase until a steady state is reached, in which is a balance between what is entering this zone and what is leaving it by evaporation and in the clinker.

2.6.4 Cooling

Once the material has passed the flame, it enters a short cooling zone in which the melt solidifies with the crystallization of C_3A ferrite phase and dissolved silicates. Clinker leaves the kiln with a surface temperature of about $1100^{\circ}C$ and the rate of cooling between the burning zone and kiln exit has a considerable influence on its microstructure. A major objective in cooling the clinker is the rapid recovery of heat in the air subsequently used for combustion of the fuel and the resulting relatively rapid cooling prevents significant cooling of C_3S , which is metastable below $1250^{\circ}C$. The rate of decomposition of C_3S reaches a maximum of $1175^{\circ}C$ and the critical temperature interval is usually regarded as $1150^{\circ}C - 1250^{\circ}C$ although solid solution effects may modify this somewhat. The final phases to solidify are the alkali sulfates which are formed from a melt immiscible with the major aluminosilicates melt. Alkali sulfates may also be formed on the surface of a clinker by condensation from the vapor phase.

2.7 CHEMICAL REACTIONS IN CLINKER FORMATION

The raw material fed to the kiln contains carbonate, a little magnesium carbonate, clay or shale, and water. The reactions that occur during burning may be classed as follow:

- Evaporation of free water
- Release of the combined water from the clay
- Dissociation of magnesium carbonate.
- Dissociation of calcium carbonate
- Combination of lime and clay

Evaporation of free water takes place at, or below, $100^{\circ}C$, but release of combined water from the clay only become appreciable above about $500^{\circ}C$. Clays are composed of a number of different hydrated aluminosilicates with ratios of $SiO_2:Al_2O_3$ varying from 2:1 to 4-5:1; some clays also contain ferric oxide as an essential constituent, but attention may be restricted here to one of the simplest of the clay compounds, kaolinite, $2SiO_2 \cdot Al_2O_3 \cdot H_2O$. There has been much controversy about the changes that kaolinite undergoes when it loses water at about $500-600^{\circ}C$. The main two alternative theories are that an anhydrous aluminosilicates $2SiO_2 \cdot Al_2O_3$ known as metakolin is produced or that the kaolin splits into an intimate mixture of amorphous

silica and alumina. On further heating an exothermic reaction occurs at about 970 °C. Various attributed to the formation of a silicon spinal phase approximating to $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$, which converts to mullite above 1000 °C. By splitting off silica, or to the crystallization of $\gamma \text{Al}_2\text{O}_3$ from amorphous alumina [26]. On either theory mullite is formed at higher temperatures, but in cement burning the reaction with lime takes place before this stage is reached and indeed commences before the exothermic reaction of kaolinite at 970 °C. Magnesium carbonate decomposes at about 600-700 °C but the temperature reported vary considerably with the source of the material used. The decomposition pressure of calcium carbonate, when heated alone, reaches atmospheric pressure at 894 atm.

In mixes of calcium carbonate and finely divided quartz reaction occurs very slowly at as low a temperature as 600 °C, proceeds very slowly at 800 °C, at an appreciable speed at 1100 °C and rapidly at 1400 °C. Dicalcium silicate probably as the α form is first formed whatever the ratio of lime to silica in the mix for the formation of the monosilicate is normally slow and is generally a secondary reaction between the disilicate and silica [27-31]. In masses of sufficient lime content all the combined silica is present as C_2S by 1200 °C. Though the formation of tricalcium silicate commences at about 1300-1400 °C it proceeds only very slowly even at 1500 °C, but the addition of alumina and particularly to the lime silica mix increases markedly the rate of its production.

When mixes of lime, alumina and silica are heated the first compounds formed are monocalcium aluminates and α dicalcium silicate. Products obtained from burning at 1150-1350 °C, dust down on cooling owing to the formation of $\gamma \text{C}_2\text{S}$. Initial melting commences at about 1400 °C and at higher temperatures dusting ceases to occur unless the cooling is slow. This may be due to the formation of the relatively more stable $\alpha \text{C}_2\text{S}$ or to the formation of solid solutions in the C_2S . Formation of tricalcium aluminates does not occur readily, nor that of tricalcium silicate commence, until a temperature of 1300 °C, is reached. In mixes of CaO , Al_2O_3 and Fe_2O_3 the first iron compound to form at about 800 °C, is C_2F followed by a transient appearance of CF between 900 °C, and 1100 °C. Formation of tetracalcium aluminum ferrite (C_4AF) spreads over a temperature range of 1100 °C to 1250 °C. Mixes of CaO , Al_2O_3 , Fe_2O_3 and SiO_2 show some evidence of a transient appearance of C_2AS

between 1000 °C and 1100 °C and formation of C_3A and C_4AF beginning at somewhat lower temperatures than in the ternary mixes [32-36]. The free CaO rapidly decreases above 1330 °C as C_3S is formed.

A somewhat similar progress of reactions is found when mixes of kaolin and calcium carbonate are heated [37-39], but at corresponding temperatures the reactions proceed more vigorously than in the oxide mixes. Gehlenite (C_2AS) starts to form at about 900 °C and then decomposes again by 1100 °C. A double salt, spurrite, $2C_2S \cdot CaCO_3$ may form as a transient phase and it has also been observed in clinker rings in rotary kilns. The compound $C_{12}A_7$ is observed between 900 °C and 1100 °C and converts to C_3A at 1100 °C upwards. Tricalcium silicate starts to form between 1200 °C and 1300 °C and by 1400 °C the reaction products are C_3S , C_2S , C_3A , C_4AF and any remaining uncombined lime.

First formation of liquid occurs at about 1250 °C -1280 °C when the heated mass undergoes a pronounced shrinkage, some times known as the Nachen shrinkage. Montmorillonite and illite are less reactive than kaolinite and higher temperatures are needed for comparable extents of reaction [40].

The course of the reactions can be summarized as follows:

Below 800 °C	Formation of CaO , Al_2O_3 , $2CaO \cdot Fe_2O_3$ and $2CaO \cdot SiO_2$ begins
800 – 900 °C	Formation of $12CaO \cdot 7Al_2O_3$ begins
900 -1100 °C	$2CaO \cdot Al_2O_3 \cdot SiO_2$ forms and decomposes again. Formation of $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ starts. All $CaCO_3$ decomposed and free CaO reaches a maximum
1100 -1200 °C	Formation of major part of $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. Content of $2CaO \cdot SiO_2$ reaches a maximum
1260 °C	First liquid formation starts
1200 -1450 °C	Formation of $3CaO \cdot SiO_2$ with progressive disappearance of free lime

The above table can only be regarded as approximate, but it indicates broadly the mode of cement compound formation. Formation of $3CaO \cdot SiO_2$ (C_3S) does not occur to any appreciable extent until liquid is present in mix at 1260 °C and above. No formation of this compound, even by solid reaction, is needed to be anticipated much below this temperature in view of its stability at lower temperature. The formation of

tricalcium silicate complete about 1350 °C -1450 °C, when the free lime remaining is reduced to a small quantity. When the clinkering temperature is reached most, if not all, of the alumina, ferric oxide and minor components will have passed into the liquid and the only solids present are C_3S , C_2S and, often, a little free calcium oxide.

The crystallization of this liquid on cooling produces again the compounds C_3A and C_4AF as well as the various compounds that arise from the minor compounds

2.8 THERMOCHEMISTRY OF CLINKER FORMATION

During the formation of cement clinker, heat is absorbed in some processes while in the other; heat is evolved as given below:

Temperature	Process	Heat change
100 °C	Evaporation of free water	Endothermic
500 °C and above	Evolution of combined water from clay	Endothermic
900 °C and above	Crystallization of amorphous dehydration products of clay	Exothermic
900 °C and above	Evolution of carbon dioxide from calcium carbonate	Endothermic
900 °C to 1200 °C	Reaction between lime and clay	Exothermic
1250 °C to 1280 °C	Commencement of liquid formation	Endothermic
Above 1280 °C	Further formation of liquid and completion of formation of cement compounds	Probably endothermic on balance

Evaporation of free water at 100 °C requires 538 cal/g or 968 Btu /lb. The heat absorbed in the dehydration of kaolin at 20 °C is 168cal/g or 335 Btu/lb. In the case of montmorillonite the corresponding values are 58.5 and 94.6 cal/g. and for illite 43 and 84.5. The product of dehydration shows an exothermic reaction at about 900-950 °C arising from the crystallization of the amorphous material and amounting in the case of kaolin to 72±10 cal/g dehydrated kaolin. The heat absorbed in dissociation of calcium carbonate is 422 cal/g or 760 Btu/lb at 20 °C and 393 cal/ g or 708 Btu /lb at 890 °C. For magnesium carbonate the values found by different investigations vary from 284–324 cal/g at 20 °C and 250 - 290 at 590 °C.

The reaction of the dehydrated clay products with lime is associated with a considerable evolution of heat, which varies with the cement composition and raw

materials, but only about 50-70 cal/g when slag and limestone are used. A heat evolution of 100 cal/g or 180 Btu /lb, is sufficient theoretically to raise the temperature of the reacting masses by over 300 °C

The relative order of the theoretical heat quantities involved in the various stages of cement burning may be illustrated by the following example in which 1.55 kg dry calcium carbonate and clay are used to form 1kg clinker [41-45].

Heat absorbed	kcal/kg
Heating raw material from 20 °C to 450 °C	170
Dehydration of clay at 450°C	40
Heating materials from 450°C to 900 °C	195
Dissociation of calcium carbonate at 900 °C	475
Heating the decarbonated material from 900 °C to 1400 °C	125
Net heat of melting	25
Total	1030
Heat Evolved	kcal/kg
Exothermic crystallization of dehydration clay	10
Exothermic heat of formation of cement compound	100
Cooling clinker from 1400 °C to 20 °C	360
Cooling Carbon dioxide (CO ₂) from 900 °C to 20 °C	120
Cooling steam from 450 °C to 20 °C including condensation to water	20
Total	610
Net theoretical heat required to form 1kg of clinker	1030 - 610 = 420 kcal

For different raw mixes, and for slightly different data, different authors have calculated values from 400 to 430 kcal/kg clinkers. The net heat of melting arises from the failure of all the glass to crystallize on cooling and is obviously a variable factor. The value to be used for the exothermic heat of crystallization of the dehydrated clay at about 900 °C is also as we have seen in some doubt and may be greater by about one half than that used in the above example; it is also based on kaolinite and not on other clay minerals that may be present.

The heat required in practice is, of course considerably greater than this theoretical value on account of the heat lost in the exit gases, in the clinker discharged

from the cooler, in radiation and convection losses from the kiln, and, in the wet process, in the evaporation of water from the slurry. With a modern wet process kiln thermal efficiencies are not much above 30 percent, but with special heat recuperators values approaching 50 percent are obtained in the semi dry and dry processes and rather more with shaft kilns.

2.9 MODULI IN CLINKERIZATION

Moduli are the relationship among different oxides present in cement raw mix or clinker. These moduli are used to control the percentage of oxide of elements in raw mix during raw mix designing. Different cements have different ranges of moduli which have to be controlled during clinkerization. Therefore clinker moduli are very much important in quality control during cement manufacturing. The moduli of raw mix and clinker are almost the same. The moduli are classified as follow,

Alumina modulus (MA)

Alumina modulus is the relationship between the oxide of aluminum and iron and is given as

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

Silicon modulus (MS)

Silica modulus is the relationship of the oxide of silica with aluminum and iron and is given as

$$MS = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

Lime saturation factor (LSF)

Lime saturation factor is the relationship of the oxide of calcium with silicon, aluminum and iron and is given as

$$LSF = \frac{CaO}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3}$$

2.10 SOLID SOLUTION OF CLINKER OR CLINKER POTENTIALS

All the major phases in commercial Portland cement exist as multi-component solid solutions. Examples are numerous, and both major and minor constituent elements are involved. In addition, polymorphism (that is the existence of different crystalline forms or phases with the same nominal chemical composition) is exhibited by the silicates. For example, the stability of polymorphs is influenced by relatively low levels of solid solution

The term solid solution does not encompass inclusions, which are observed in clinker by optical microscopy. It involves a distribution of the solute ions either by substitution of them for ions of the host crystal or by their location in normally unoccupied interstitial sites. These processes may produce vacancies at normally occupied sites to maintain electro-neutrality. When substitution of a cation M^{2+} by M^{3+} occurs. For example, a charge balance in substitution may also be maintained by the creation of free electrons or positive holes in the conduction or valence bands of the solid, respectively. These may significantly increase chemical reactivity and also produce a deep color.

Solid solutions often produce a change in the unit cell size of a crystal lattice which depends on the concentration of solute ions and which can be determined by X-ray diffraction. Above a critical concentration there may be a change in unit cell type. Solid solution may stabilize a high temperature polymorph so that on cooling it does not invert to the form stable at room temperature. This effect frequently depends on the rate of cooling: Rapid cooling favors the retention of larger amounts in solid solution, while slow cooling favors ex-solution of foreign ions and phase inversion. At room temperature, the thermal energy available may not be sufficient for the nucleation of the stable phase, although this may sometimes be induced by mechanical shock. A metastable form may also persist, if the crystallite size is small because the probability of nucleation of the stable phase is then low.

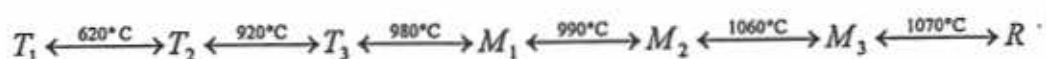
Solid solution compositions in cement clinker are usually expressed in chemical analyses as if oxides rather than elemental ions had gone into solution. This is acceptable because the crystal structures of the cement minerals are based on a framework of O^{2-} ions into which cations are packed, for electro-neutrality each

cation is accompanied by the number of O^{2-} ions in its oxide formula. Elements such as silicon and sulphur are treated as hypothetical cations (Si^{4+} ; S^{6+}) in describing structures.

In characterizing the interaction of a particular phase and related solid solutions with water it is necessary to distinguish between the rate of the chemical reaction in hydration and the development of strength in a mortar or paste hardening under water. The term hydraulicity is usually reserved for the latter and the two evaluations may differ significantly. For example, C_3A is the most reactive constituent of clinker but paste of it, develops little strength.

2.10.1 Tricalcium Silicate (alite)

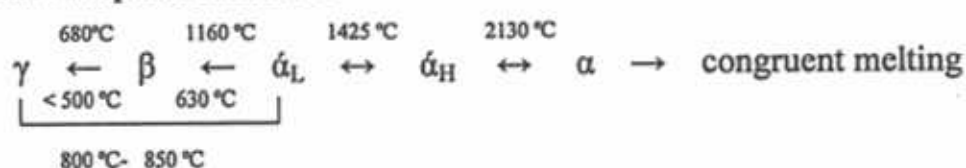
This is an orthosilicate containing discrete SiO_4^{4-} tetrahedral and O^{2-} ions as anions, so that its formula may be written as $Ca_3 (SiO_4) O$. Three triclinic (T), three monoclinic (M) and rhombohedral (R) forms exist, symmetry increasing with increasing temperature as expected. Phase-inversion temperatures have been established both by X-ray diffraction and differential thermal analysis. Structure changes are small and so therefore are the thermal effects.



C_3S is stable (with respect to C_2S) between about $1250^\circ C$ and $1800^\circ C$ and melts incongruently at $2150^\circ C$. The high temperature forms can be stabilized at room temperature by solid solution of the impurities present in the raw materials used in cement manufacture and the impure C_3S present in commercial clinkers is referred to as alite. Alite is usually monoclinic (M1 or M3). Occasionally rhombohedral, or Triclinic. The most frequently found foreign ions are Mg^{2+} , Al^{3+} and Fe^{3+} with smaller amounts of K^{1+} , Na^{1+} and SO_3 . Transition metals such as chromium and manganese are also usually present at low levels and have significant effects on color in white cement. The different forms of alite do not differ greatly in hydraulicity. The formation of solid solutions increases the percentage of alite significantly above that calculated for C_3S by the Bogue method. For example, Mg^{2+} can replace Ca^{2+} in alite, which increases the apparent C_3S level but decreases that of C_2S .

2.10.2 Di calcium Silicate (Belite)

Dicalcium silicate is also an orthosilicate and, as with the alite, differences between polymorphs principally involve the orientation of the SiO_4 tetrahedra. Some transformations occur over a temperature range, which is different for rising and falling temperature. There are four principal polymorphs, which have been designated α , $\acute{\alpha}$, β and γ . Of these $\acute{\alpha}$ has two very similar forms distinguished as $\acute{\alpha}_H$ and $\acute{\alpha}_L$. There are discrepancies in the published literature on the transformation that occur, partly as a result of the more recent findings that time at higher temperature can affect the lower temperature transformation and that transformations are crystallite size dependent. A simplified scheme is



Differences in hydraulicity are considerable. The γ form has an orthorhombic, olivine structure and is essentially non hydraulic although a paste does hydrate slowly. The common form in commercial clinker is the monoclinic β C_2S . This has a strongly distorted low temperature K_2SO_4 structure, while α_H C_2S has a high temperature K_2SO_4 structure.

The impure form of C_2S in commercial clinker is referred to as belite, usually β but occasionally α is found. Belite is stabilized with respect to γ C_2S by foreign ions in solid solution. If the β - γ phase inversion occurs in commercial cement clinker during cooling then the large specific volume change leads to disintegration of the clinker with serious consequences for the efficiency of the cooler and, since γ C_2S is non hydraulic, for the quality of the product. Fortunately this occurrence is very rare because alkalis, in particular K^{1+} , are usually available in sufficient quantity to stabilize β C_2S .

α C_2S is said to be more hydraulic than β C_2S but solid solution of phosphate ions reverses this. α C_2S stabilized at ambient temperature by large amounts of $Ca_3(PO_4)_2$ was found to be non-hydraulic. In general the proportions of foreign ions taken into solid solution are higher than in alite. Cations include Al^{3+} , Fe^{3+} , Mg^{2+} , K^{1+} and anions include SO_4^{2-} and PO_4^{3-} . Those ions which excessively stabilize C_2S at high temperatures during clinkering, e.g. phosphate inhibits the formation of C_3S and

amounts greater than about 0.3% must be avoided. No link between impurity content, dislocation density and reactivity was found from the different forms of C_2S .

2.10.3 Tricalcium Aluminate

Tricalcium aluminate is cubic and does not exhibit polymorphism when pure. It contains six memberd-linked rings of AlO_4 tetrahedra ($Al_6O_{18}^{18-}$). It reacts vigorously with water but pastes develop little strength. In cement clinker Fe^{3+} , Mg^{2+} , Na^{1+} , K^{1+} and Si^{4+} are found in solid solution, but only the alkalis change the symmetry of the structure. The solid solution containing sodium is that most commonly encountered and its reaction with water is less vigorous than that of pure C_3A .

Solid solution involves the substitution of Ca^{2+} by Na^{1+} with a second Na^{1+} going into a vacant site at the centre of a six membered ring of AlO_4 tetrahedra. The effect of the new charge distribution is an expansion of the Ca-O polyhedra whiles the ring contracts. The net effect is a very small decrease in cubic cell size; from 1.5263 nm in C_3A itself to 1.5248nm at 2.4% Na_2O . Site occupation by sodium is affected by the presence of silica in solid solution which extends the range for sodium above 5.7 towards the compound NaC_8A_3 , which is not, however a specific compound.

2.10.4 Calcium Aluminoferrite (the Ferrite Phase)

In the C-A-F system C_2F is stable under ambient conditions but C_2A is stable only at high pressures. In the solid solution series $C_2A_xF_{1-x}$ the limit to x at normal pressures is ca. 0.7. C_2F is orthorhombic, layers of FeO_6 octahedra alternating with layers of FeO_6 tetrahedra with Ca^{2+} ions packed between them. With the values of x up to 0.33, Al^{3+} replaces Fe^{3+} in tetrahedral sites. While at higher levels of replacement the additional Al^{3+} goes increasingly into octahedral sites.

For the aluminoferrite phase in Portland cement, the formula C_4AF ($x = 0.5$) is often assumed, in the Bogue calculation for example. In fact the A/F ratio of the ferrite phase in commercial clinker varies and it contains significant proportions of other elements in solid solution. The most usual are Mg^{2+} , Si^{4+} and Ti^{4+} and Tayler [46] gave a typical composition as $Ca_2AlFe_{0.6}Mg_{0.2}Si_{0.15}Ti_{0.05}O_5$. Variability in composition is found not only between different clinkers but also within a single sample. This phase is the only strongly colored compound in the quaternary system. In thin section it is yellow brown in transmitted light. The black color and associated semi

conductivity of the ferrite in Portland cement are said to result from the combined effects of solid solution and cooling in an oxidizing atmosphere after firing, suggesting the formation of some Fe^{4+} ion. Reactivity with water is moderate and increases with increasing A/F ratio, but hydraulicity is slight. However, if this compound is formed by sintering at lower temperatures than those needed for partial melting (clinkering) then it is more reactive and its hydraulicity is enhanced.

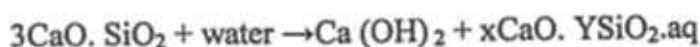
2.10.5 Minor Cement Compounds

In addition to four principal compounds, commercial Portland Cements may also contain several minor constituents as distinct phases. Magnesia may be retained in solid solution or, if present at a level of above about 1.5%, be present as periclase, a substantial proportion of the sodium present goes into solid solution in the main phases, while the remainder and over 90% of the potassium combine with the sulfur in the raw materials and fuel. Some sulfate goes into the silicates but it is largely present as alkali or alkali calcium sulfates. Depending on the relative proportions of sulfate and alkali in the clinker, various combinations of arcanite (K_2SO_4), aphthitalite [$\text{K}_3\text{Na}(\text{SO}_4)_2$], calcium langbeinite [$\text{Ca}_2\text{K}_2(\text{SO}_4)_3$] and rarely, anhydrite (CaSO_4) can be formed.

2.11 THE HYDRATION OF CEMENT

Portland cement is composed of a number of compounds, the reaction of which with water leads to the setting and hardening of the cement. All the compounds present in Portland cement clinker are anhydrous but when brought into contact with water they are all attacked or decomposed, forming hydrated compounds. Supersaturated and unstable solutions are formed temporarily, but these gradually deposit their excess solids and tend to come into equilibrium with the hydrate compounds produced. The rate of attack and the degree of temporary super saturation of the solution is determined by the physical state of the cement compounds as well as by their chemical nature. Since the original anhydrous compounds cannot exist in equilibrium with aqueous solutions, the ultimate result of the action of water must be complete hydration. The hydrated compounds can exist permanently in contact with certain solutions, though in many cases they form what are known as incongruent solutions. This will be seen later to be the cause of the complete decomposition of the hydration products of cement when they are continually extracted with water, and to

be one of the important factors in deterioration, under certain conditions, of concrete structures. The hydration of $3\text{CaO} \cdot \text{SiO}_2$ (C_3S) may be represented as



This action does not stop when the solution is saturated with calcium hydroxide, but hydration continues and the further lime liberated by the reaction, is deposited as crystals of calcium hydroxide. The hydrated silicate formed remains stable in contact with the saturated lime solution, but if it is placed in water, it undergoes hydrolysis, liberating lime into solution until the concentration is raised to the value required to stabilize it. Continued extraction with water of the hydrated calcium silicate eventually leaves a solid composed only of hydrated silica, all the lime having been dissolved and removed whilst very little of the silica is dissolved. The hydrated calcium silicate is an example of a hydrated compound, which forms an incongruent solution; the compound is partially decomposed when it passes into solution, the quantity of lime dissolved being in excess of that of silica. Equilibrium is only attained when a less basic hydrated calcium silicate is also present in the solid and the concentration of lime in solution has attained the value required to render the remaining more basic silicate stable. The two solids and the solution form, at constant temperature, an invariant point in the ternary system lime- silica- water. If more lime is added to the solution, it combines with the less basic silicate, while if more water is added further decomposition of the more basic silicate occurs. In both cases the lime concentration in solution eventually returns to the original value though, owing to the slowness with which equilibrium is reached, this may require a long time. On continued addition of water all the more basic silicate is eventually decomposed and the less basic silicate remains. This in turn decomposes if more water is added, liberating lime, and hydrated silica is formed.

Two extreme mechanisms of cement hydration can be visualized, in the first 'through solution' mechanism, the cement compounds may dissolve to produce ions in solution and these then combine to precipitate the hydrated products. On the other hand, in view of the very low concentrations of alumina and silica observed in the liquid phase very shortly after mixing cement with water. Hansen considered that this mechanism would operate too slowly to account for the observed rates of reaction and he, therefore, suggested that the hydration reactions may take place without the

cement compounds going into solution and by a direct 'topochemical' or 'solid state' reaction.

A definite relationship between the structures and crystallographic orientation of the hydrated and anhydrous compounds may be expected from a solid-state reaction. Such relationship has been observed in the hydration of C_3S and βC_2S and also in the hydration the mineral larnite (βC_2S) and bredigite (αC_2S) in nature. However, in other cases, a 'through solution' mechanism is indicated by the observations, such a mechanism seems also to be clearly involved in many other hydration reactions, despite the extremely low concentrations of alumina and silica that prevail in saturated or supersaturated lime solutions. Such reactions include the formation of hydrated products containing both silica and alumina during the reaction C_3S and C_3A mixtures in water, the production of high sulphate sulphoaluminate from alumina containing C_3S , the conversion of hexagonal plate calcium aluminate hydrates into the cubic C_3AH_6 , and the transformation of initially formed high sulphate sulphoaluminate into the low sulphate sulphoaluminate or its related solid solution. It seems probable, therefore, that both through-solution and solid state types of mechanism occur during the course of the reaction between cement and water and while the former mechanism may predominate in the early stages of hydration the latter mechanism may also operate and perhaps more especially during the later stages when diffusion has become more difficult [47-51]

2.12 HYDRATION OF CEMENT COMPOUNDS

During the course of the reaction of tri- or di-calcium silicate with water, calcium hydroxide is split off and a calcium silicate hydrate gel of lower basicity is formed.

2.12.1 Tricalcium silicate (C_3S)

When finely ground C_3S is mixed with water, hydration commences quickly and both lime and silica pass into solution initially in the same molecular ration 3:1 as in the anhydrous compounds. The concentration of lime in solution increases steadily while that of silica rapidly decreases. Crystals of calcium hydroxide soon appear together with a gelatinous or nearly amorphous hydrated calcium silicate. Complete hydration cannot be obtained under periods of year or more unless the tricalcium silicate is very finely divided and the mix reground at intervals to expose fresh

surfaces to the water. Otherwise the product obtained shows unattached cores of tricalcium silicate surrounded by a layer of hydrated silicate which, being relatively impervious to water, render further attack slow. At complete hydration the reaction can approximately be represented by the equation:



This simple equation does not bring out the complexities of the reaction. The immediate product formed in pastes on mixing has a CaO: SiO₂ ratio near to 3. This forms as a coating on the C₃S surfaces and retards the reaction. After a few hours, dissolution or splitting off of this initial product results in an acceleration of the hydration and the formation as the second product of a C-S-H gel of lower CaO: SiO₂ ratio, 1.5 or less. This is followed by the formation of a third stable product. Evidence obtained by electron microscopy suggests that the second product may be a poorly crystallized CSH (I) and the third CSH (II) or a closely related product. The completely hydrated silicate, which may well be a heterogeneous material containing both these latter products, has a CaO: SiO₂ ratio of about 1.4-1.6. This ratio increases somewhat as the water: solid ratio of the mix is decreased.

2.12.2 Dicalcium silicate (C₂S)

There are four main polymorphic forms of the dicalcium silicate γ , β , $\acute{\alpha}$ and α , of which only the β form or occasionally the $\acute{\alpha}$ or γ form occurs in cement. The β form is only slowly attacked by water and even after some weeks the original crystals show under the microscope only a surface coating of an amorphous hydrated silicate, the thickness of which slowly increases with the passage of time. A hardened paste more than four years old has been found still to contain about 15% unhydrated C₂S. Although the reaction is considerably slower than with C₃S and substantially less calcium hydroxide is produced, and is not detectable microscopically until after many weeks, C-H-S gels produced are of the same type as those from C₃S.

When dicalcium silicate is hydrated in excess water in a ball mill, complete hydration has been obtained in a period of 46 days. In contrast to C₃S, this under these conditions gives afwillite, the C₂S: SiO₂ ratio of 1.5. The reaction equation for this completely hydrated ball mill product can, therefore, be represented by the equation



This equation has to be modified to apply to hydration in pastes where the CaO: SiO₂ ratio varies with age and other factors. For the later stages of hydration in a paste with water: solid ratio of about 0.7 at 25°C which gives a C-S-H gel with a CaO: SiO₂ ratio of about 1.65, the equation becomes



2.12.3 Tricalcium Aluminate (C₃A)

Finely ground C₃A reacts very rapidly with water, though apparently less so in a saturated lime solution. In the presence of excess water a plentiful formation of hexagonal plate crystals is observed, and these when seen on edge appear as small birefringent 'needles' which often form clusters radiating from a centre.

The hydration of C₃A under steam pressure, or even in water at 50 °C, probably results in the direct formation of C₃AH₆ without the intermediate formation of the hexagonal plate hydrates. Similarly, C₃AH₆ can also be formed very rapidly when C₃A is mixed with a limited amount of water at normal temperatures to form a plastic mass, since there is considerable heat evolution and the temperature of the material rises, favoring the formation of C₃AH₆. Complete hydration in such a mass is only reached slowly owing to the protection afforded to the unhydrated cores by the cubic hydrate surrounding them. With larger amounts water the hexagonal plate hydrates produced initially can also form on the C₃A grains and moderate the reaction by limiting the supply of water to the C₃A. At a later stage, perhaps after only a few hours, the transformation to the cubic C₃AH₆ occurs and the reaction then accelerates owing to the removal of the hexagonal hydrates from the surface of the C₃A grains [52-53].

2.12.4 Tetra calcium Aluminoferrite (C₄AF)

Although the ferrite phase in Portland cement is not necessarily C₄AF as such, but a solid solution of composition lying between C₆AF₂ and C₆A₂F, the hydration behavior of the ferrite phase is typified by that of the C₄AF composition. The rate of reaction of the calcium aluminoferrites with water increases with the proportion of alumina in the aluminoferrite and C₄AF, therefore though reacting quickly does so less rapidly than C₃A. When mixed with water, hexagonal plate crystals are rapidly formed. The hexagonal plate crystals occur mostly as foliated masses. The residual

unhydrated C_4AF and a probable hydrated iron oxide or amorphous αFe_2O_3 (hematite) deposited around it form the dark mass.

In saturated limewater or in the presence of excess lime, the reaction of C_4AF is less rapid and rather different in that hydrated iron oxide or αFe_2O_3 is not produced and the reaction products are white [54-55]. Moreover the hexagonal plate phase formed is now a solid solution of the tetra calcium compounds $C_4A.aq$ and $C_4F.aq$. This is metastable with respect to the cubic C_3AH_6 - C_3FH_6 solid solution and transformation to the latter occurs more and more rapidly with increasing temperature above about $15^\circ C$, with liberation of calcium hydroxide.

2.13 EFFECT OF GYPSUM ON THE HYDROLYSIS

In the presence of gypsum, the hydration products of C_3S and βC_2S are slightly modified in that some sulphate enter the structure of the calcium silicate hydrate gel and change its morphology. The manner of hydration of C_3A is, however, altered considerably, and if this compound is placed in a calcium sulphate solution on a microscope slide the rapid formation of extremely fine needles is observed. These are needles of a calcium sulphoaluminate hydrate ($C_3A \cdot 3CaSO_4 \cdot 31H_2O$), and are characterized by a negative elongation in contrast to the positive elongation of the hydrated calcium aluminates 'needle'. In case of C_4AF , hydration in the presence of gypsum and lime yield a solid solution of the sulphoaluminate with an analogous sulphoferrite hydrate. There is some evidence that with smaller amounts of gypsum the trisulphate solid solutions formed first, later convert to the monosulphate solid solution.

2.14 POZZOLANAS AND POZZOLONIC REACTIONS

Pozzolanas are usually defined as materials, which, though not cementitious in themselves, contain constituents, which will combine with lime at ordinary temperatures in the presence of water to form stable insoluble compounds possessing cementing properties. The pozzolanas can be divided into two groups (i.e. natural and artificial).

The natural pozzolanas are for the most part material of volcanic origin, but include certain diatomaceous earths. The artificial pozzolanas are mainly products

obtained by the heat treatment of natural materials such as clays and shale and certain siliceous rocks, and pulverized fuel ash (fly ash).

2.14.1 Natural Pozzolanas

The pozzolanas of volcanic origin consist of glassy incoherent materials or compacted tuffs arising from the deposition of volcanic dust and ash. They may occur, as does for example the Rhenish trass, in a consolidated rock like form underlying material deposited subsequently, or in a more fragmentary and unconsolidated state like some of the Italian pozzolanas. In Europe the materials, which have been the most exploited, are the Italian pozzolanas, Santorin Earth obtained from the Grecian Isle of Santorin, and the German trass which is found in the neighborhood of Coblenz on the Rhine and Bavari sl trass deposits are also worked in Rumania and the U.S.S.R. There are no volcanic ash deposits suitable for use as pozzolanas in Great Britain. A volcanic ash pozzolana known as toska is obtained from Teneriffe in the Canary Islands and a material known as tetin from Azores. Deposits are numerous in United States and Canada and some of the former have been used in pozzolonic cements. As might be anticipated, there are numerous deposits in Japan and New Zealand.

The volcanic pozzolanas are composed of a mixture of silicates and contain both glass and crystalline particles. The volcanic ash and dust from which they were formed has undergone rapid cooling, and in some cases has subsequently suffered considerable chemical alteration leading to the formation of zeolitic compounds [56]. The alteration is generally attributed to the action of superheated steam and carbon dioxide below the earth's surface. The effect of this action has been to convert much of the original material into a more chemically reactive modification, whilst the basic constituents have been partially removed under the combined influence of the carbon dioxide and water. This conversion has proceeded further in trass and some of the older Italian pozzolanas than in Santorin earth. Pozzolonic activity is shown in some degree even by massive lavas and to a feeble extent by some of the products of the decay of igneous rocks such as arenas and psammities.

The effect of heating on natural volcanic pozzolanas seems variable. At temperatures up to 500-600 °C the materials may be dehydrated without any collapse of the atomic or physical structure on which their activity depends, but at a red heat

the activity is much decreased or lost. Thus trass is not adversely affected at 500 °C and tests on American rhyolitic materials showed a tendency for the activity to increase after treatment at 500-800 °C. Santorin Earth loses most of its activity at 750 °C, while the Italian pozzolanas benefit by short heat treatment at 300-700 °C but prolonged heating at 600 °C or above decreases their activity. Though the elimination of combined water, provided no collapse of the structure occurs, may improve reactivity by increasing the porosity, it seems that the main effect of heat treatment may often be to calcine any clay impurities present, changing them from deleterious constituents to inert or pozzolonic ones. A heat treatment at 500 °C is used in processing some roman pozzolanas to be used in pozzolonic cements.

2.14.2 Artificial Pozzolanas

The chief artificial pozzolanas are burnt clays and shale, spent oil shale, burnt gaize, burnt moler and pulverized fuel ash (fly ash)

2.14.2.1 Burnt Clay and Shale

The pozzolonic properties of burnt clays were well known to the Romans, who utilized ground clay bricks and tiles as a substitute for the natural volcanic ash pozzolanas. The value of burnt clay as an addition to fat lime mortars to obtain hydraulic properties has also long been known in India and Egypt, where it passes under the names Surkhi and Homra. Experiments on burnt clay lime mortar were carried out a century ago in connection with the rebuilding of London Bridge, while still earlier smeaon had tried them, without success, as a mortar ingredient for the eddystone lighthouse.

The use of burnt clay in lime mortars was also common at one time in Great Britain. A pozzolonic cement consisting of ground burnt clay and Portland cement was described by potter [57], who stated that over 5000 tons of it, known as potter red cement, were used in fresh water and seawater construction about that time.

For a period of many years up to about 1915 the Lafarge Company in France manufactured and 'undecomposable' cement composed of a mixture of burnt clay and the French grappiers cement. The pozzolonic cement was produced for use in the gypsiferous territories of France. Its manufacture was discontinued following on the production of high alumina cement by the same firm.

The use of a lime surkhi mortar, prepared by grinding lime and crushed bricks or burnt clay together in a mortar mill, has long been a common practice in India, where it has formed the cementing material in dams and structures under water. In Egypt a lime burnt clay mortar was used initially for the hearting of the Assuan dam and found to yield a more watertight mortar than a 1:4 Portland cement and sand mix. Its use was however, given up owing to difficulties in producing the material at the required rate. The slow rate of setting of the material also hindered the progress of construction.

Burnt clays have in the past been used in mortar and concrete mainly when Portland cement was not available, or when a saving in cost has resulted [58-59]. The materials used were, however, produced under crude and uncontrolled conditions of burning and as it has since been shown that a degree of care in burning similar to that required in the manufacture of Portland cement is required to produce the best products, it seems probable that only relatively inferior materials were obtained.

Burning suitable clays or shales at a temperature, which varies from 600 °C to over 900 °C, produces burnt clay pozzolanas, depending on the nature of the clay and the conditions of burning; the product is ground to cement fineness. Certain spent oil shales, which have undergone burning subsequent to distillation also, yield, when selected with due care, a pozzolana of similar type and quality.

Raw clays consist essentially of a group of hydrated aluminum silicates, though alumina may be replaced to varying extents by ferric oxide and to a lesser extent by bases such as MgO, Na₂O and CaO. The water content can also vary considerably. Kaolinite, Al₂O₃ · 2SiO₂ · H₂O is a well-defined mineral and the kaolinite group also includes other minerals of the same composition such as nactite, dickite and metahalloysite. The montmorillonite group covers a variety of minerals with Al₂O₃ : SiO₂ ratios varying from 1:3 to 1:6 and their isomorphous solid solutions. They can be typified by 'ideal' formulac such as montmorillonite Al₂O₃ · 4SiO₂ · aq. The hydro micas and illite form yet another group.

2.14.2.2 Burnt Gaize

Gaize is a soft, porous, highly siliceous, sedimentary rock containing a proportion of clay, which is found distributed over a considerable area in the Ardennes and Meuse valley in France. It contains silica in a gelatinous condition and

has a density of only about 1.4 after drying. The rock has been used in the raw state as a pozzolana, but usually it is burnt at a temperature of 900 °C.

Pozzolonic cement composed of burnt gaize and Portland cement has been manufactured in France and was used at Boulogne, Havre, St. Malo, Dieppe and other French ports for concrete work in sea water.

2.14.2.3 Pulverized Fuel Ash (Fly Ash)

When pulverized coal is burnt in boilers the ash is carried forward in the gases as used particles, which solidify into a roughly spherical shape. The properties of this material as a pozzolana was first reported by Davis and his coworkers [60-62] and its use in concrete started to develop in the U.S.A in the following decade particularly for mass concrete form dams.. Later its use became wider and spread to many other countries. The ash is very finely divided with a specific surface area commonly falling between about 2000 to 5000 cm²/g. though higher values are sometimes found. Its specific surface is thus of the same order as that of cement. The composition and properties of pulverized fuel ash depend both on the coal burnt and the efficiency of the combustion process so that the value of the material from different power stations can vary widely. The product from a modern power station when working on base load will normally be more consistent. In composition the ash approximates to that of burnt clay high in alumina and iron oxide but can vary widely.

Though one of the major uses of pulverized fuel ash has been in dam construction, partly on economic grounds and partly on account of its influence on workability and heat evolution, it is also used in other concrete work. Thus it is used in some countries in ready mixed concrete, while in France up to 20 percent is permitted in one class of Portland cements. Pulverized fuel ash can has a depressing effect on air content increasing with the carbon content of the ash. There has been considerable controversy as to the effect of grinding the ash either with, or separately from, the Portland cement. The effect must depend on the original fineness of the ash but it seems that grinding has some favorable effect on early strength development.

2.14.2.4 The use of Pozzolanas

Pozzolanas are used in lime pozzolana mortars, in blended pozzolonic cements, and as direct additions to a concrete mix. In the traditional use of Pozzolanas in lime mortars the material was used in a relatively coarse state, as indeed it still is

for example, in Italy, where the specification for natural Pozzolanas used in building mortars only requires that the maximum size of grains shall not exceed 5mm. With the development of the use of Pozzolanas with Portland cement the practice has become common of grinding them to cement fineness. Thus the Italian pozzolanic cements, the German trass cement, and the Pozzolanic cements used in the U.S.A., are interground mixtures of pozzolana and Portland cement clinker. In case of pulverized fuel ash, which may be added as a separate ingredient at the concrete mixer, the material is already finer than Portland cement.

2.15 USE OF CARBON FLY ASH IN THE CEMENT MANUFACTURING

Carbon fly ash has pozzolanic property. It can be used in the manufacturing of cement. The use of carbon fly ash requires no processing. It replaces costly raw materials such as shale and clay normally used in as raw materials in cement manufacturing.

The carbon fly ash contains high carbon content, so it can conserves energy by serving as a partial fuel substitute in the energy intensive cement manufacturing operation. Nearly 65 million tons fly ash is annually produced in the U.S., of which only one third is used in commercial products. The majority of the fly ash that is generated is land filled. With the impending regulatory pressure to reduce emission at coal-fired power plants, production of more fly ash with significantly higher carbon contents is imminent. Since high carbon fly ashes are undesirable for use in concrete, the urgency for alternate reuse applications is growing

The utilization of fly ash in the construction industry is growing fast not only as blended cements but also to minimize the pollution of the environment Due to its pozzolanic properties, there is great potential for its use in the construction industry. Fly ash can be incorporated into nearly every stage of the production and use of cement. It can be used as a raw material in some cases because it contains some of the essential components needed for cement like lime, silica, and alumina Javed et al [63-65] used carbon fly ash in cement manufacturing as a raw material. The chemical composition of the fly ash and other raw materials (limestone and shale) limited the fly ash addition in the kiln feed to approximately 6%, which saved the fuel up to

approximately 3.9%, and increased the production up to 9.7% and other parameters were also improved.

Fly ash can also be added during the grinding process [66-67] so that it becomes mixed with the cement and doesn't have to be added and mixed later. If it is not mixed during this stage it can be added as a partial replacement for cement when concrete is mixed. Many researchers have used the fly ash as a pozzolanic admixture in concrete formation [68-78]. Earlier work reported that fly ashes accelerate reinforcement corrosion due to the presence of unburnt carbon and sulphur.[79-81], since the usage of fly ashes in reinforcements are still questionable. In order to produce fly ashes with stable properties and adequate quality, many power plants have implemented its own sophisticated quality control measures. The property improvement of fly ash blended cements were extensively studied and reported that, the physical and mechanical properties were matched to that of ordinary Portland cement [82-85].

Fly ash can also be used as lightweight aggregate. After mixing the ash with different materials including other byproducts, pellets are formed that can be used in concrete as aggregate. Fly ash is ideal for use in mass concrete projects like large pipes because it reduces the heat of hydration. It also reduces cost, since less cement is needed. Concrete piping is more watertight when made with ash because the resulting concrete has a higher density. Coal fly ash is also beneficial for pipes because it increases resistance to weak acids and sulfates.

One product that has been developed using fly ash that has been very successful is controlled low strength material (CLSM), or flowable fill. Flowable fill contains many of the same materials as typical concrete and the same equipment and mixing trucks are used but the proportions of the components are much different. Flowable fill can be used for backfilling in trenches, around pipes, and under roadways because it is self-leveling and leaves no air spaces. Flowable fill also serves as a less expensive alternative to the removal of old, underground storage tanks. The tank can easily be filled in with flowable fill instead of being removed, saving both time and money [86]

The use of coal fly ash conserves energy by reducing the demand for typical construction materials such as lime, cement and crushed stone, which take energy to

produce. Each ton of fly ash used to replace a ton of cement and saves the equivalent for nearly one barrel of oil. The production of cement results in the release of approximately one ton of CO₂ the replacement of cement with fly ash reduces greenhouse gas and lowers the cost and improves some properties of the concrete.

However, the replacement of Portland cement with fly ash, especially in high volume, decreases the early strength of concrete. Several methods, such as elevated temperature curing of fly ash cement concrete, grinding of fly ash and the addition of chemical activators can be used to activate the pozzolonic reactivity of fly ash and to improve the early properties of fly ash cement and concrete. Elevated curing of concrete containing fly ash accelerates the strength development but decreases ultimate strength of the concrete [87]. Also elevated temperature curing is most likely suitable for prefabrication of concrete products. The grinding of fly ash can increase the strength development and ultimate strength of the concrete containing fly ash [88] but decreases the workability of the concrete. Particularly, grinding is an energy intensive process. It is reported that energy cost will increase 10% for an increase of Blaine surface area of every 10m²/kg after it reaches certain Blaine surface area.

Shi and his colleagues [89-92] have published a series of researches on the chemical activation or reactivity of natural pozzolanas and fly ashes. It has been found that that Na₂SO₄ and CaCl₂ are the most effective activators to activate the potential activity of pozzolonic materials, and the use of chemical activator is much more effective than the prolonged grinding of natural pozzolanas or elevated curing temperature.

One of the major environmental challenges facing municipalities around the world is the disposal of worn out automobile tires. To address this global problem, several studies have been conducted to examine various applications of recycled tire rubber (fine crumb rubber and coarse tire chips). Nehdi and Khan [93] used the ground tire rubber as fuel in the production of cement and used recycled rubber chips in asphalt concrete. The metal in the tires is incorporated into the final product and in fact can reduce the amount of iron ore needed in cement manufacturing [94]. Municipal waste incinerator ash and sewage waste have also been used as a raw material for the production of Eco cement [95-96]

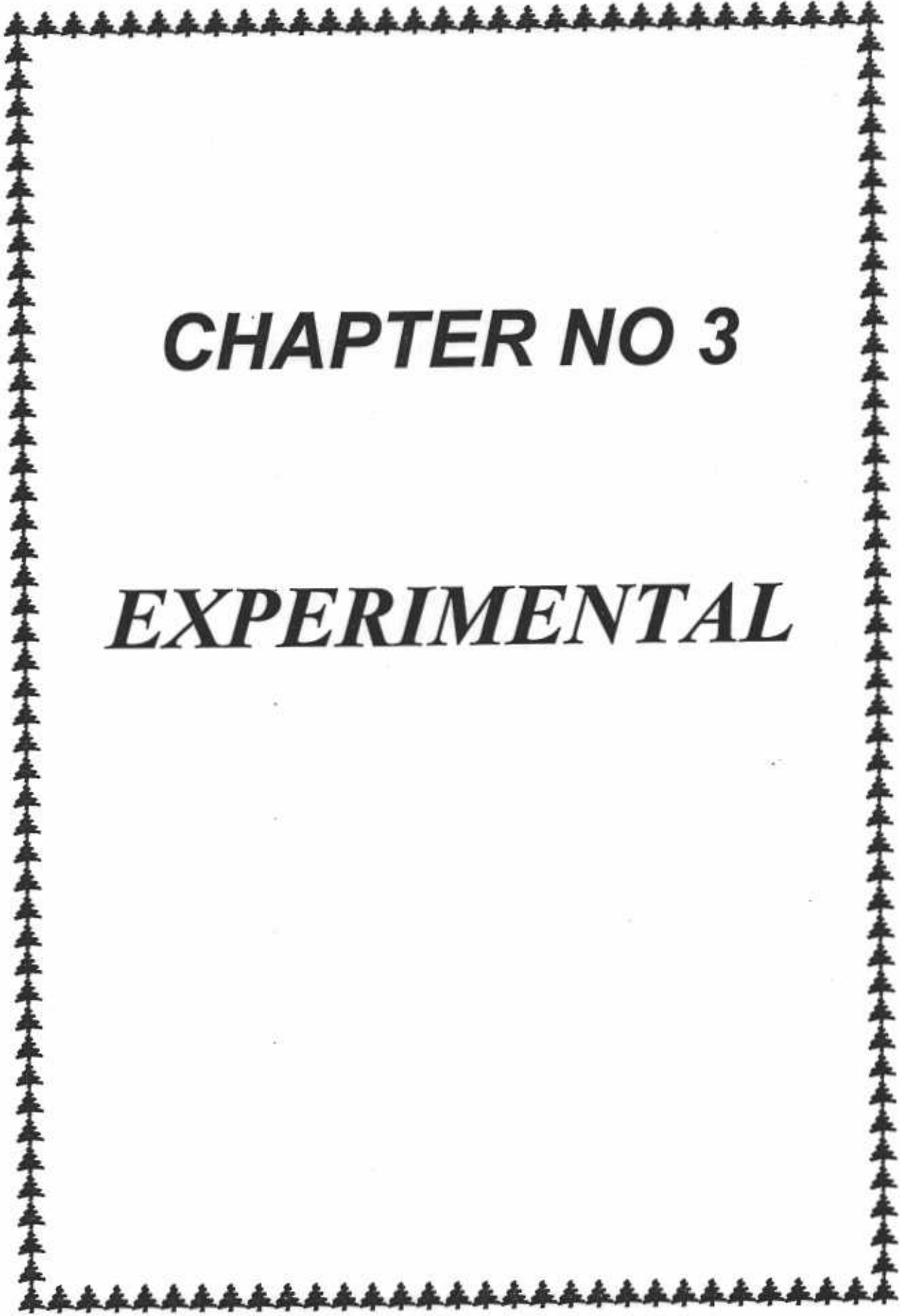
Miller FM and Conway T [97-98] used ground granulated blast furnace slag for reduction of Expansion due to delayed Ettringite formation. Liu Z et al [99] studied the expansion of cement containing crystalline Magnesia with and without fly ash and slag.

Taiheiyo cement [100] is developing a new recycling technology to neutralize the alkali in glass and the chloride in plastics. This allows for waste plastics and used glass to be simultaneously employed as a recycled raw material form cement production. This technology is being used in a NEDO (New Energy and Industrial Technology Development) research project.

Chen. et al [101] has used glass pieces in the production of cement. The alkali content of glass, a major concern for cement production varies from 0-22%. For the glass bottles mainly found in Hong Kong waste glasses, the alkali content (Na_2O) ranges from 10-19% with an average around 15%.

In addition to the increasingly difficulty of guaranteeing proper waste disposal and handling processes carried by waste management, the trend towards a natural resource recycling society demands waste disposal processes that both reduce volume and recycle [102]. As the cement technology for which primary raw materials are municipal waste such as incinerator ash and sewage waste, Eco-cement brings this to reality. Eco-cement is made from the burnt ash, fly ash from municipal waste incinerator and limestone [103]. As 50% of raw materials for Eco-cement are the burnt clay and fly ash from municipal waste incinerator, Eco-cement is one of the most effective utilization methods of municipal waste. By using this process, the landfill space for waste material treatment can be saved.

Calcined clay mixed with lime and water has been used as a cementing material for a long time in Oman [104], this was called Sarooj in the local Omani terminology. It has been used widely in hydraulic structures due to its good hydraulic properties and in military defensive installations due to its durability.



CHAPTER NO 3

EXPERIMENTAL

CHAPTER – 3

EXPERIMENTAL

3.1 SUMMARY OF EXPERIMENTAL WORK

Samples of carbonaceous and siliceous materials were collected from the study area (Darukhula and the adjoining of Nizampur) and transferred to the laboratory. The samples were dried, crushed, ground and analyzed for major and minor elements required for cement manufacturing. The samples were classified as different groups depending upon their composition and location. Different raw mixes were designed including four for high strength Portland cement, three for sulfate resisting cement and three for white cement.

The raw mixes were analyzed and processed for clinkerization. The clinker obtained was processed for cement preparation. The clinker and cement was analyzed according to the British and Pakistan Standard Specifications.

Baggase ash was collected from different sugar mills of N.W.F.P and studied for different physical and chemical parameters. The ash was mixed with different raw mixes in different ratios and processed for clinker and cement formation. The clinker and cement was studied for different parameters and the quantity of the baggase ash was optimized in clinkerization. The impact of baggase ash on the fuel consumption during clinkerization, quality of cement, raw material etc. was studied. The brief summary of the experimental work is given in the following sketch.

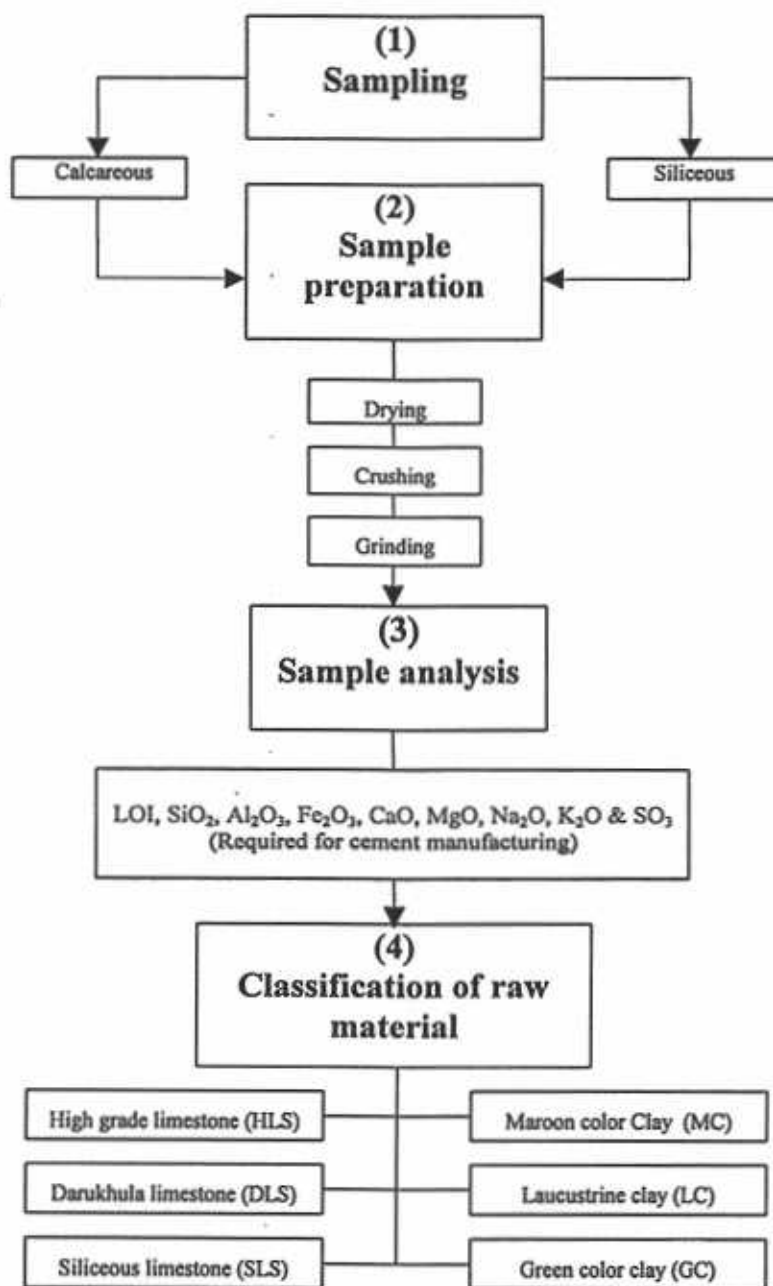


Figure 3.1 Chemical analysis and classification of raw material from the study area.

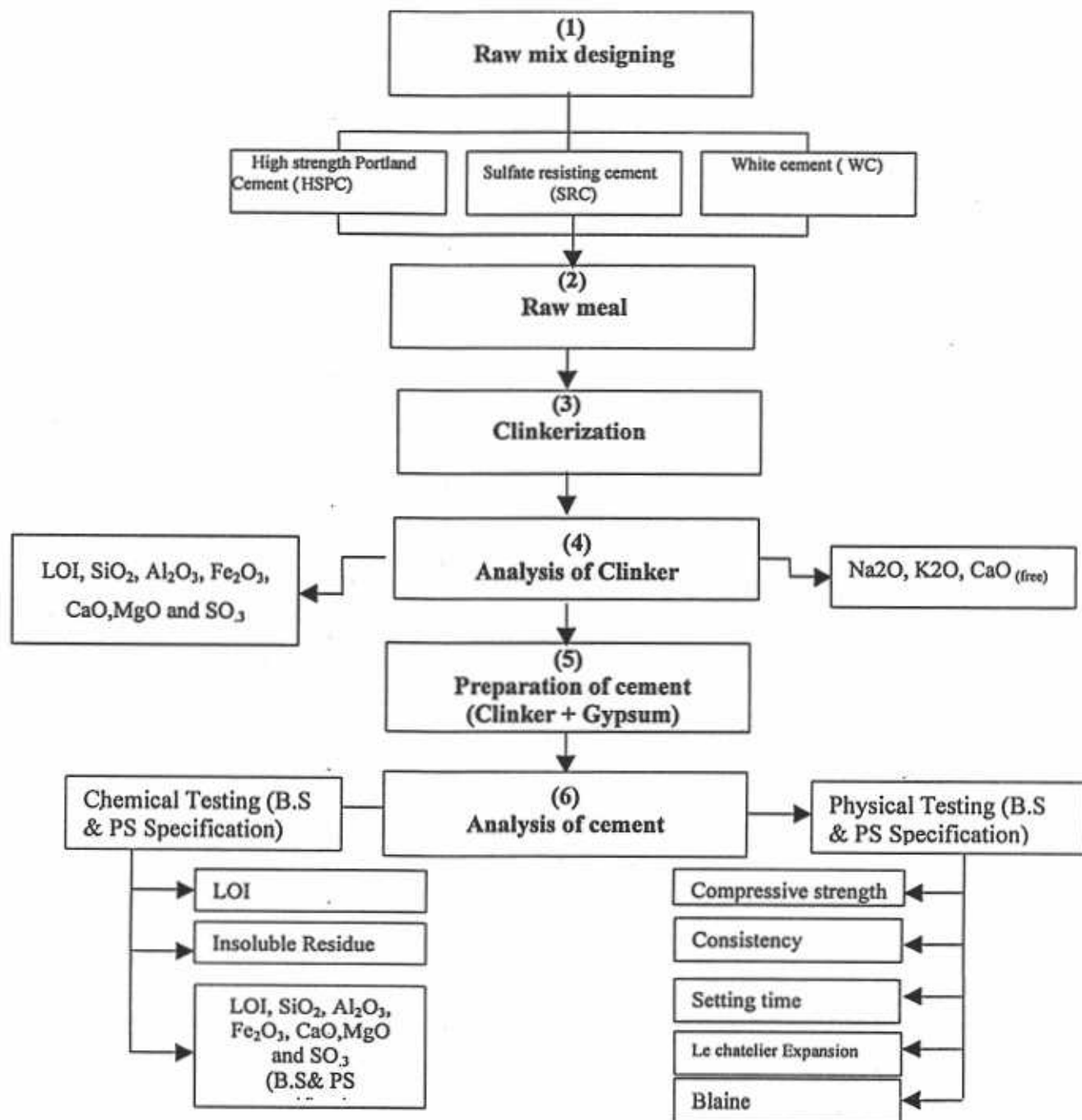


Figure 3.2 Raw mix designing and clinkerization.

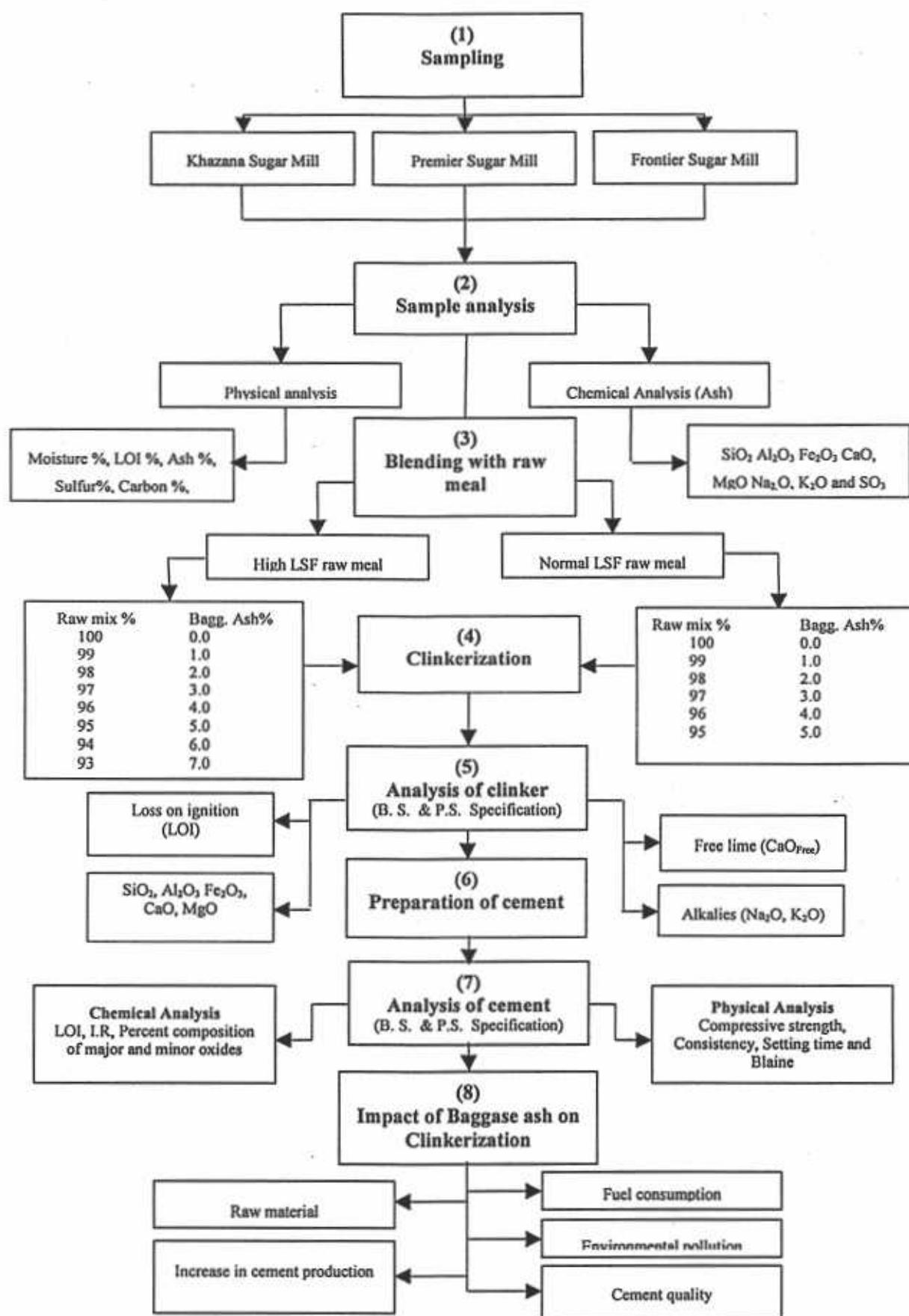


Figure 3.3 Analysis of baggase ash, addition with raw meal and clinkerization.

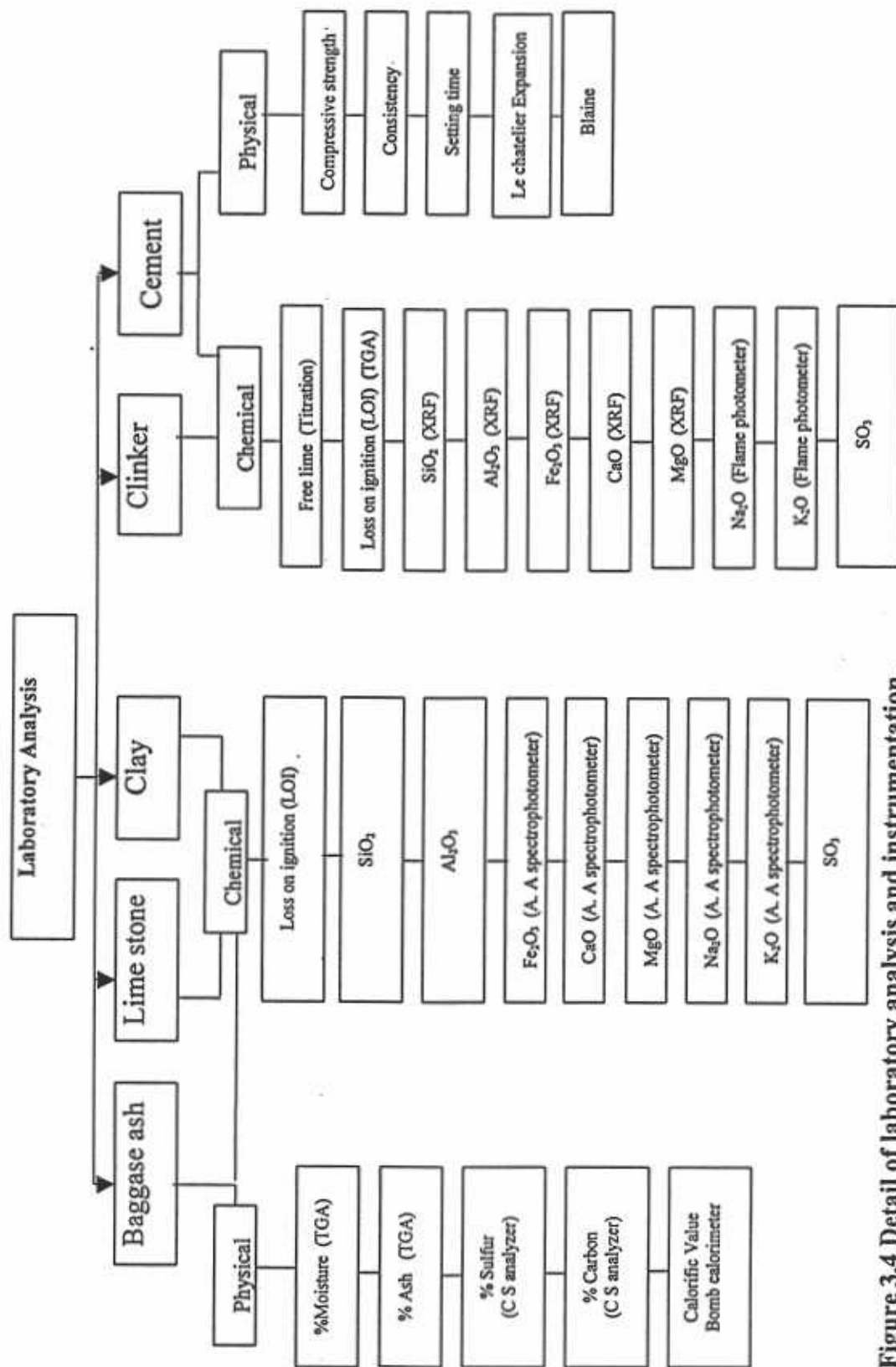


Figure 3.4 Detail of laboratory analysis and instrumentation.

Abbreviation Used TGA = thermogravimetric analyzer, CS = carbon sulfur detector
 XRF = X-Ray flourometer spectrophotometer, AA =atomic absorption

3.2 INSTRUMENTS, CHEMICALS AND GLASS WARES USED

3.2.1 Instruments with their Specifications

The following instruments were used in the experimental work. The detail of instruments along with their specifications are given as follow,

1. Atomic Absorption spectrometer (3300 Perkin Elmer)
2. Bomb calorimeter (AC- 350 LECO Corporation)
3. Flame Emission Spectrophotometer(PFP7/C)
4. Geographic positioning sytem (GPS)
5. Muffle furnace temperature range (0-2000 °C)
6. Oven temperature range (0-250 °C)
7. SC-144 DR Dual Range Sulfur and Carbon Analyzer 2001 LECO Corporation
8. Thermogravimetric Analyzer (TGA701 LECO Corporation)
9. UV/VISIBLE Spectrophotometer (SP8-PYE UNICAME)
10. X-Ray fluorescence spectrophotometer (XRF) PW 2582/00 (Philips)

3.2.2 Chemicals

All the chemicals used were analytical grade and moisture free. The chemicals used were either Merck or BDH. The detail of chemicals is given before the respective experiment.

3.2.3 Glass Wares

The glass wares used were mostly Pyrex. All of them were used after thorough cleaning with distilled water and drying in the oven. The detail of glassware is given before the respective experiment.

3.3 SAMPLING

3.3.1 Sample Collection

Samples from the study area were hammered and collected in the bags. About 3-4 kg of each sample was collected. The position of each sample was noted on the Geographic Positioning system (GPS). All samples were properly numbered and carried to the laboratory for further treatment and analysis.

3.3.2 Field Data Recording

The following observations were recorded for each sample site during the fieldwork

1. **Sample number:** The number of each sample was written on the sample bag.
2. **Sampling interval:** The distance between two successive samples was noted.
3. **Sample location:** The location of samples Latitude / Longitude was recorded with the help of GPS.

3.3.3 Sample Preparation

Sample preparation is a coherent series of procedure applied to a gross sample with a purpose of obtaining test sample for analysis. Samples were prepared by the following process:

1. The rock and clay samples were dried in the sun and crushed into pieces of approximately 2 mm diameter using the jaw crusher.
2. The crushed samples were pulverized in the ball mill in disk grinder using vibrating machine.
3. A portion of the pulverized samples in open glass bottles, were placed in the oven for two hours at 110 °C till constant weight. The bottles after cooling in desiccator were properly stopperd. These moisture free samples were used for further analysis.

3.4 ANALYSIS OF RAW MATERIAL

3.4.1 Preparation of Stock Solutions

The moisture free powders of the samples were converted into stock solutions of known volume by different methods. These stock solutions were used for the determination of major and minor elements by instrumental methods. Two different types of stock solutions were prepared by the following methods.

3.4.1.1 Stock Solution A (for Atomic Absorption Spectrometric Analysis)

0.500 g of the moisture free sample was accurately weighed in a Teflon beaker. 10 mL of the concentrated hydrofluoric acid (HF) and 4 mL of perchloric acid was added to the beaker. The sample in the Teflon beaker was heated on the hot plat for half an hour. 2 mL of the perchloric acid was further added and heated again till the formation of paste. Again 4 mL of perchloric acid and little amount of distilled water was added and the beaker was heated for 5 minutes. The contents of the beaker were diluted to 250 mL. In case of turbidity the solution was transferred to 250 mL glass beaker, adding 2 mL of hydrochloric acid. It was heated till it became clear. All

the samples were treated by the same procedure. The solutions were stored in the plastic bottles. These solutions were used for the determination of iron, calcium, magnesium sodium and potassium. The reference standards of AGV-1, G-2, CM-7 and W₂ were prepared in the same way.

Blank solution was prepared in duplicate in same way except the addition of sample.

3.4.1.2 Stock Solution B (for UV/ Visible Spectrophotometer)

Sodium hydroxide (NaOH) solution was prepared by dissolving 30 g of NaOH pellets in 100 mL of distilled water and stored in a polythene bottle. 5 mL of the solution was added to a cleaned nickel crucible. The crucible was heated on sand bath for complete dryness of the contents and then cooled in a desiccator.

Accurately 0.05 g in case of clay and 0.20 g in case of rock was added to the nickel crucibles separately. The crucible was covered with lid and heated to dull redness over a gas burner for a period of 5 minutes. The crucible was swirled while hot. Distilled water (5-10mL) was added to crucible after it became mildly cool, in order to avoid splashing. The contents of the crucible were washed into an 800 mL glass beaker, already containing 400 mL of the distilled water and 10 mL of concentrated HCl. In most cases clear solutions were obtained. In case the solution was not clear, it was heated until transparent solution was obtained. The resulting solution was diluted up to 1000 mL in a volumetric flask. All the samples were treated by the same procedure. The reference standards of AGV-1, G-2, CM-7 and W₂ were prepared in the same way.

The blank solution was prepared in the same way except the addition of the sample. All the solutions were used for the determination of silica and aluminum.

3.4.2 Determination of Silica in the form of Silicon Dioxide (SiO₂) using Spectrophotometric method

From Solution 'B' Silica was determined by reducing the yellow color of silico molybdate to blue color [105]

Reagents: Ammonium molybdate, distilled water, H₂SO₄ (Conc.), tartaric acid, sodium sulfite (Na₂SO₃), 1-ammino-2-naphthol-4-sulphonic acid (C₁₀H₇NO₄S) and sodium metabisulfite (Na₂S₂O₅)

Preparation of solutions

1. **Ammonium molybdate solution:** 7.50 g of ammonium molybdate was dissolved in 70 mL distilled water having 20 mL of H_2SO_4 and diluted up to 100 mL and was kept in a polythene bottle.
2. **Tartaric acid solution:** 25 g of the tartaric acid was dissolved in 250 mL of distilled water.
3. **Reducing solution:** 0.70 g of sodium sulfite (Na_2SO_3), 0.15 g of 1-ammino-2-naphthol-4-sulphonic acid ($\text{C}_{10}\text{H}_7\text{NO}_4\text{S}$) and 9.00 g of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) was dissolved in distilled water and refrigerated to avoid deterioration after few days.

Procedure

10 mL of the stock solution B of the sample was taken in a 100 mL volumetric flask. About 50 mL of distilled water and 2 mL ammonium molybdate solution were added to the flask and swirled to mix well. After exactly 10 minutes, 4 mL of tartaric acid solution was added, the flask was swirled and mixed well. 1 mL of the reducing solution was then added and swirled and the volume was made to 100 mL with distilled water. The same procedure was followed for all the samples. Blank solution was prepared in the same way except the addition of sample. The solutions were equilibrated for 30 minutes, and used for the determination of silica by using UV/Visible spectrophotometer at a wave length of 630 nm relative to the reference rock standards.

3.4.3 Determination of Aluminum Oxide Al_2O_3 using Spectrophotometric method

Reagents: 8-Hydroxyquinoline, chloroform, hydroxyl amine hydrochloride (HONH_2HCl), sodium acetate trihydrate, beryllium sulfate tetrahydrate, distilled water, 2,2-dipyridyl and HCl (Conc.)

Preparation of Solutions

1. **8-Hydroxyquinoline Solution:** 1.25 g of the 8-hydroxyquinoline was dissolved in 250 mL of chloroform and stored in a refrigerator.
2. **Complexing Reagent:** 1 g of hydroxylamine hydrochloride (HONH_2HCl), 3.6 g of sodium acetate trihydrate and 0.4 g of beryllium sulfate tetra hydrate were

dissolved in 50 mL of distilled water. 0.04 g of 2,2-dipyridyl was also dissolved in 20 mL of 0.2 N HCl. Both of these solutions were mixed and diluted up to 100mL with distilled water.

Procedure

5-10 mL of stock solution B was taken into a 100 mL separatory funnel. 5 mL of distilled water and 10 mL of complexing reagent solution was added to the funnel and mixed well. After a few minutes 20 mL of 8- hydroxyquinoline solution was added to each funnel. This solution was then shaken for about 8 minutes by an automatic flask shaker. The organic layer at the bottom of the separatory funnel was separated into 25 mL volumetric flask by washing the funnel with chloroform for several times and the volume was made up to the mark with chloroform. The yellow color extract obtained through this process was suitable for spectrophotometric determination. Al_2O_3 was determined at wavelength of 381 nm relative to the reference rock standards. Blank solution was prepared in duplicate in the same way except the addition of rock sample.

3.4.4 Determination of total Iron (Fe_2O_3)

The total iron as Fe_2O_3 in the rock samples of the study area was determined by atomic absorption spectrophotometer by using the stock solution A.

Instrument conditions

Mode	Absorption
Wavelength	248.3 nm
Slit width	0.2 nm
Fuel flow rate	1 liter / minute
Air flow rate	5-liter/ minute
Burner height	10 mm

Reagents: Mohr salt ($\text{FeSO}_4 (\text{NH}_4) \text{SO}_4$), distilled water, reference rock standards

Preparation of Solutions

1. **Stock Solution of 1000 ppm:** Stock solution of 1000 ppm in Fe was prepared from Mohr salt in a 1000 mL flask with distilled water.
2. **Stock Solution of 100 ppm:** From 1000ppm stock solution, 100 ppm was prepared by diluting 10 mL to 100mL.

3. **Working Standards:** working standards of 2.5, 5.0, 10.0 and 20.0 ppm were prepared from 100 ppm by diluting 2.5, 5.0, 10.0 and 20.0 ml respectively to 100 mL using 100 mL volumetric flasks.

Procedure

The atomic absorption spectrophotometer was turned on and set according to the above conditions. The cathode lamp for iron was set at the wavelength of 248.3 nm and calibrated with the iron working standard solutions of 2.5, 5.0, 10.0 and 20.0 ppm. The same solutions were then aspirated as unknown samples for verification. The certified reference standard solutions were run on the machine. The results were compared with certified values and found within the confidence limits. The unknown samples were then run on the machine and the results recorded. The samples, which were out of range of standards, were diluted and again run in the same way. The atomic absorption reading for Fe were converted into Fe_2O_3 by the following conversion formula,

$$\% \text{Fe}_2\text{O}_3 = \frac{AA \times 1.429 \times 100 \times D}{2000}$$

Where AA = Atomic Absorption reading in ppm

1.43 = Conversion factor of Fe to Fe_2O_3

D = Dilution factor

3.4.5 Determination of Calcium Oxide (CaO)

Calcium oxide (CaO) in the rock samples of the study area was determined by atomic absorption spectrophotometer by using the stock solution A.

Instrument Conditions

Mode	Absorption
Wavelength	422 nm
Slit width	0.4 nm
Fuel flow rate	5-liter / minute
Air flow rate	5-liter / minute
Burner height	10 mm

Reagents: CaCO_3 , HCl (conc.) distilled water, reference rock standards

Preparation of Solutions

1. **Stock Solution of 1000 ppm:** Stock solution of 1000 ppm of Ca was prepared in a 1000 mL flask by dissolving 2.497 g of CaCO_3 in 1 N HCl and diluted up to 1000 mL with distilled water.
2. **Stock Solution of 100 ppm:** 100 ppm Ca solution was prepared by diluting 10 mL of 1000 ppm stock solution to 100 mL with distilled water.
3. **Working Standards:** working standards of 2.5, 5.0, 10.0 and 20.0 ppm were prepared by diluting 2.5, 5.0, 10.0 and 20.0 mL of 100 ppm solution respectively to 100 mL with distilled water.
4. **Lanthanum Solution (5%):** 5% Lanthanum solution was prepared from La_2O_3 by dissolving 58.64 g in 200 mL distilled water to which 150 mL of 60% HClO_4 was added. It was heated until completely dissolved. The solution was then filtered through ordinary filter paper into 1000 mL volumetric flask and the volume was made up to the mark with distilled water.

Dilution of the Samples: Dilution of the samples was made depending upon the concentration of Ca in different samples. Only samples without of range signals, were diluted. Before diluting the concentrated sample, 6 mL per 50 mL lanthanum solution was added.

Procedure

Atomic absorption spectrophotometer was adjusted for Ca at a wave length of 422 nm by using Ca cathode lamp. Then different working standards (2.5, 5.0, 10.0 and 20.0 ppm) were run and their calibration curve was drawn. The curve was verified by running a couple of certified reference standard solution.

The unknown samples were run on the atomic absorption and the concentrations of Ca in ppm were noted. The more concentrated solutions were further diluted depending upon their concentrations. The atomic absorption readings of Ca in ppm were converted into % CaO by the following conversion formula

$$\% \text{ CaO} = \frac{\text{AA} \times 1.399 \times 100 \times \text{D}}{2000}$$

Where AA = Atomic Absorption reading in ppm

1.40 = Conversion factor of Ca to CaO

D = Dilution factor

3.4.6 Determination of MgO

Magnesium oxide (MgO) in the rock samples of the study area was determined by atomic absorption spectrophotometer by using the stock solution A.

Instrument conditions

Mode	Absorption
Wavelength	285.2 nm
Slit width	0.4 nm
Fuel flow rate	5-liter / minute
Airflow rate	5-liter / minute
Burner height	10 mm

Reagents: MgCO_3 , HCl (conc.), distilled water, reference rock standards

Preparation of Solutions

- 1. Stock Solution of 1000 ppm:** Stock solution of 1000 ppm in Mg was prepared using MgCO_3 in a 1000 mL flask by dissolving 3.057 g in 1N HCl and diluting up to 1000 mL with distilled water.
- 2. Stock Solution of 100 ppm:** 100 ppm Mg solution was prepared by diluting 10 mL of 1000 ppm to 100 mL with distilled water.
- 3. Working Standards:** working standards of 2.5, 5.0, 10.0 and 20.0 ppm were prepared by diluting 2.5, 5.0, 10.0 and 20.0 mL of 100 ppm solution respectively to 100 mL with distilled water.
- 4. Lanthanum Solution (5%):** 5% Lanthanum solution was prepared from La_2O_3 by dissolving 58.64 g in 200 mL distilled water to which 150 mL of 60 % HClO_4 was added. It was heated until completely dissolved. The solution was filtered through ordinary filter paper into 1000 mL volumetric flask and the volume was made up to the mark with distilled water.

Dilution of the Samples: Dilution of the samples was made depending upon the concentration of Mg in different samples. Only sample, without of range signals, were diluted. Before diluting the concentrated sample, 6mL per 50 mL lanthanum solution was added.

Procedure

Atomic absorption spectrophotometer was calibrated for Mg at a wavelength of 422 nm by using Mg cathode lamp. The instrument was calibrated and standardized with the working standards of 2.5, 5.0, 10.0 and 20.0 ppm Mg solutions. All the working standards and the certified reference standards were checked and their actual concentration verified.

The unknown samples were run on the atomic absorption and the concentrations of Mg in ppm were recorded. The more concentrated solutions were further diluted depending upon their concentrations. The atomic absorption readings of Mg in ppm were converted into % MgO by the following conversion formula

$$\% \text{ MgO} = \frac{\text{AA} \times 1.658 \times 100 \times D}{2000}$$

Where AA = Atomic Absorption reading in ppm

1.65 = Conversion factor of Mg to MgO

D = Dilution factor

3.4.7 Determination of Na₂O

The Na₂O was determined by atomic absorption spectrophotometer by using the stock solution A.

Instrument Conditions

Mode	Emission
Wavelength	589 nm
Slit width	0.2 nm
Fuel flow rate	1 litre / minute
Airflow rate	5 liter / minute
Burner height	20 mm

Reagents: NaCl, distilled water, reference rock standards

Preparation of Solutions

1. **Stock Solution of 1000 ppm:** 1000 ppm stock solution of Na was prepared in a 1000 mL flask by dissolving 2.54 g NaCl in distilled water and diluting up to the mark.
2. **Stock Solution of 100 ppm:** 100 ppm stock solution was prepared from 1000 ppm by diluting 10 mL of it up to 100 mL with distilled water.

3. **Working Standards:** Working standards of 2.5, 5.0, 10.0 and 20.0 ppm were prepared by diluting 2.5, 5.0, 10.0 and 20 mL of 100 ppm solution respectively up to 100 mL with distilled water.

Procedure

Atomic absorption spectrophotometer was calibrated for Na at a wavelength of 589 nm, by using Na cathode lamp. The instrument was calibrated and standardized with the working standards of 2.5, 5.0, 10.0 and 20.0 ppm in Na solutions. All the working standards and the certified reference standards were checked and their actual concentration was verified. The unknown samples were run on the atomic absorption spectrophotometer and concentrations of Na were noted. The more concentrated solutions were further diluted depending upon their concentrations. The atomic absorption readings of Na in ppm were converted into % Na₂O by the following conversion formula,

$$\% \text{Na}_2\text{O} = \frac{\text{AA} \times 1.348 \times 100 \times D}{2000}$$

Where AA = Atomic Absorption reading in ppm

1.35 = Conversion factor of Na to Na₂O

D = Dilution factor

3.4.8 Determination of K₂O

The K₂O was determined by atomic absorption spectrophotometer by using the stock solution A.

Instrument Conditions

Mode	Emission
Wavelength	766 nm
Slit width	0.4 nm
Fuel flow rate	1 litre / minute
Airflow rate	5 liter / minute
Burner height	20 mm

Reagents: KCl, distilled water, reference rock standards

Preparation of Solutions

1. **Stock Solution of 1000 ppm:** 1000 ppm stock solution in K was prepared in a 1000 mL flask by dissolving 1.91g KCl in distilled water and diluting up to the mark.

2. **Stock Solution of 100 ppm:** 100 ppm stock solution was prepared from 1000 ppm by diluting 10 mL of it up to 100 mL with distilled water.
3. **Working Standards:** working standards of 2.5, 5.0, 10.0 and 20.0 ppm were prepared from 100 ppm solution by diluting 2.5, 5.0, 10.0 and 20 mL of 100 ppm respectively up to 100 mL with distilled water.

Procedure

Atomic absorption spectrophotometer was calibrated for K according to the above instrumental conditions. The instrument was then calibrated and standardized with the working standards of 2.5, 5.0, 10.0 and 20.0 ppm in K solutions. All the working standards and certified reference standards were checked and their actual concentration was verified. The unknown samples were then run on the atomic absorption spectrophotometer, and the concentrations of K in ppm were noted. The more concentrated solutions were further diluted depending upon their concentrations. The reading of atomic absorption spectrophotometer of K in ppm were converted into % K₂O by the following conversion formula

$$\% K_2O = \frac{AA \times 1.205 \times 100 \times D}{2000}$$

Where AA = Atomic Absorption reading in ppm

1.2046 = Conversion factor of K to K₂O

D = Dilution factor

3.4.9 Determination of Sulfuric Anhydride (SO₃)

Method: Gravimetric

Reagents and Apparatus: Fusion mixture, deionized water, hydrochloric acid barium chloride, nickel crucible, muffle furnace and filter paper.

Preparation of solutions

Barium chloride solution: 100 g of barium chloride was dissolved in some distilled water and diluted up to 1000 mL.

Procedure

One gram of sample was mixed with six gram of the fusion mixture (Na₂CO₃+K₂CO₃) in nickel crucible and heated in the muffle furnace for one hour at

1000 °C, the contents of crucible was dissolved in dilute hydrochloric acid and evaporated to dryness in a fume box.

The contents were again dissolved in dilute hydrochloric acid and filtered through Wattman filter paper 41. The precipitate was thoroughly washed with distilled water till the filtrate gave no ppt with silver nitrate solution, showing that the ppt became free from chlorides.

The filtrate was boiled and 10 mL of barium chloride solution in hot condition was added with constant stirring. The ppt was digested for about 12-24 hours. The ppt was filtered through filter paper 42 and washed thoroughly with hot water. The ppt was dried, charred and ignited in the muffle furnace at 900 °C for 45 minutes. The ppt was cooled in the desiccator and weighed again. The % age SO₃ was calculated by the following formula,

$$\% \text{SO}_3 = \frac{A \times 0.343 \times 100}{W}$$

Where A = wt of BaSO₄

W = wt of the sample

0.343 = Molecular weight ratio of SO₃ to BaSO₄

3.4.10 Determination of Loss on Ignition (LOI)

Apparatus: porcelain crucible, analytical balance, muffle furnace

Procedure

One gram of the sample was taken in already weighed porcelain crucible. This was ignited in the muffle furnace at 400 °C for 30 minutes and then the temperature was increased to 1000 °C and maintained at this temperature for two hour. The sample was cooled in desiccator and weighed again. The percent Loss on Ignition (LOI) was calculated by the following formula,

$$\% \text{LOI} = \frac{\text{Weight of the sample after ignition}}{\text{Weight of the sample before ignition}} \times 100$$

3.5 CLINKERIZATION

3.5.1 Raw Mix Designing

The analyses of limestone and clay of the study area were classified into different groups based on the location and chemical composition, and were assigned names depending on the analysis and location as follow:

1. High grade limestone (HLS)
2. Darukhula limestone (DLS)
3. Siliceous limestone (SLS)
4. Green color clay (GC)
5. Maroon color clay (MC)
6. Lacustrine clay (LC)

The samples of each group were mixed and thoroughly blended to get a homogeneous material, which represent certain location of the study area.

This material was analyzed through atomic absorption and X-ray spectrophotometric techniques. The analyses of all the groups were fed into the computer for raw mixes designing. Different raw mixes were made by mixing the material in different proportions, and given different numbers. The raw mixes were thoroughly mixed and blended to get a homogeneous material

Each raw mix was analyzed through different analytical techniques. All the raw mixes were stored in plastic bags. In some raw mix preparation some additional material like laterite, silica sand and high alumina clay were used in a smaller quantity, which are not present in the study area. In most of the cement factories these substances are procured from other sources.

3.5.2 Preparation of Clinker

The raw mix was converted into paste by adding water. Small granules in the range of 5-10 mm were made manually, which were dried in the oven at 110 °C. These granules were ignited in the muffle furnace at 1450 °C for one hour in nickel crucible for complete clinkerization. All the raw mixes were converted into clinker using the same procedure. The black color clinker was cooled in desiccator and stored in polythene bags.

3.6 ANALYSIS OF CLINKER

The clinker was analyzed in laboratory using different analytical techniques

3.6.1 Loss on Ignition (LOI)

Apparatus: Porcelain crucible, analytical balance, muffle furnace

Procedure

1 g of the clinker sample was taken in already weighed porcelain crucible. This was ignited in the muffle furnace at 400 °C for 30 minutes and then the temperature was increased to 1000 °C and maintained at this temperature for one hour. The sample was cooled in desiccator and weighed again. The percent loss on ignition (LOI) was calculated by the following formula,

$$\% \text{ LOI} = \frac{\text{Weight of the sample after ignition}}{\text{Weight of the sample before ignition}} \times 100$$

3.6.2 Determination of Free Lime ($\text{CaO}_{(\text{free})}$) in Clinker

Method: Titration

Apparatus: Titration flask, magnetic stirrer, air condenser and micro burette

Reagents: Strontium nitrate, glycerin, ethyl alcohol, ammonium acetate and phenolphthalein.

Preparation of Solutions

1. **Ammonium Acetate Solution:** 16 g desiccated ammonium acetate was dissolved in one liter of ethanol and stored in a dry clean stoppered bottle.
2. **Phenolphthalein:** 0.1 g of dry phenolphthalein was dissolved in 100 mL ethanol and stored in a dry plastic dropper bottle.

Determination of Factor

Pure analytical grade CaCO_3 was ignited to CaO in a muffle furnace at 1000 °C. 0.05 g of the CaO was taken in a titration flask. 60 mL solvent (glycerin + ethanol) was added to the flask. 2 g strontium nitrate was also added to the flask and mixed completely. The solution was boiled on a hot plate for 20 minutes with mild stirring in the presence of air condenser at the mouth of the flask. The condenser was removed

and the content of the flask was filtered through small polypropylene Buckner funnel under vacuum.

The filtrate was brought to boiling immediately titrated in a hot condition against standard ammonium acetate solution using phenolphthalein as indicator. The factor was calculated as under,

$$\text{Factor} = \frac{\text{Weight of CaO taken}}{\text{Volume of ammonium acetate used}}$$

Determination of CaO_(free) in Clinker

The clinker was grinded into fine powder using disk grinder. 0.05 g of the powdered clinker was taken in a titration flask. 60 mL solvent (glycerin + ethanol) was added to the flask. 2 g strontium nitrate was also added to the flask and mixed completely. The solution was boiled on a hot plate for 20 minutes with mild stirring in the presence of air condenser at the mouth of the flask. The condenser was removed and the contents of the flask were filtered through small polypropylene Buckner funnel under vacuum. The filtrate was brought to boiling and immediately titrated in hot condition against standard ammonium acetate solution using phenolphthalein as indicator. The percent free lime in the clinker was calculated as under,

$$\text{CaO}_{(\text{free})} (\text{percentage}) \text{ in clinker} = \text{Vol. of ammonium acetate used} \times \text{Factor}$$

3.6.3 Analysis of Major Elements in Clinker

The major elements in the clinker present in form of oxide i.e. SiO₂, Al₂O₃, Fe₂O₃, CaO and MgO were determined by XRF

Instrument conditions

Voltage	50 kV
Current	40 mA
Sample status	Glass bead

Apparatus: Platinum crucible, analytical balance, muffle furnace

Reagents: Lithium bromide, dilithium tetra borate (Spectromelt)

Preparation of Glass Bead

1 g powdered clinker was mixed with 6 grams of dilithium tetra borate (spectromelt) and taken in a platinum crucible. 0.001 g of lithium bromide was also

added to the crucible and mixed thoroughly. The crucible was heated in a muffle furnace at 1150 °C for exactly fifteen minutes.

The content after fifteen minutes was transferred to a platinum mould inside the furnace and shaken to acquire the shape of the mould. The mould was cooled and the glass bead was obtained. The glass beads of the certified standards were prepared in the same way.

Calibration of the Instrument

The instrument was turned on and allowed for 20 minutes to warm up. The instrument conditions were set before starting the analysis. Certified reference standards of clinker were run on the machine for calibration and the calibration plot was drawn. The same reference standards were fed as unknown samples into the machine for analysis. The results were compared with certified results.

Analysis of the Clinker Sample

The clinker beads were made to run into the machine for analysis. The calibration curve was used to find out the composition of all the sample of clinker.

3.6.4 Determination of Alkalies through Flame Emission Spectrophotometer

3.6.4.1 Determination of Sodium Oxide (Na₂O)

The Na₂O was determined by flame emission spectrophotometer.

Analytical grade sodium chloride and potassium chloride were used for the preparation of working standard. As all elements in the clinker and cement are present in oxide form, so the calculation of working standards for calibration curve was made in such a way as to represent sodium as sodium oxide and potassium as potassium oxide.

Instrument Conditions

Voltage	190-250V @50 Hz
Fuel	propane or butane regulated to 10-15 inches water gauge
Limit of detection	Na ≤ 0.2 ppm K ≤ 0.2 ppm Li ≤ 0.25 ppm Ca ≤ 15 ppm Ba ≤ 30 ppm

Sample requirement	2.0- 6.0mL /minute
Warm up time	15 minutes

Apparatus: Glassware, balance, hot plate

Reagents: NaCl, distilled water, hydrochloric acid (analytical grade)

Preparation of Solutions

1. **Primary Stock Solution of 1000 ppm Na₂O:** 1000 ppm stock solution of Na₂O was prepared from NaCl in a 1000 mL flask by dissolving 1.8859 g NaCl in distilled water and diluted up to the mark.
2. **Secondary Stock Solution of 100 ppm Na₂O:** 100 ppm stock solution was prepared from 1000 ppm by diluting 10 mL to 100 mL with distilled water.
3. **Working Standards:** working standards of 2.0, 4.0, 8.0, 12.0, 16.0 and 20 ppm were prepared from the secondary stock solution with distilled water in 100 ml volumetric flasks.
4. **Preparation of Clinker Solution:** 1 g powdered clinker was taken in 100 mL beaker. 10 mL of HCl and 25 mL of distilled water was added to it. The solution was heated to boiling on hot plate and digested for 15 minutes and filtered through Whatman filter paper 41 to separate silica. The ppt was washed with hot water and the filtrate was diluted up to 1000 mL.
 1. High grade limestone (HLS)
 2. Darukhula limestone (DLS)
 3. Siliceous limestone (SLS)
 4. Green color clay (GC)
 5. Maroon color clay (MC)
 6. Lacustrine clay (LC)

The samples of each group were mixed and thoroughly blended to get a homogeneous material, which represent certain location of the study area.

This material was analyzed through atomic absorption and X-ray spectrophotometric techniques. The analyses of all the groups were fed into the computer for raw mixes designing. Different raw mixes were made by mixing the material in different proportions, and given different numbers. The raw mixes were thoroughly mixed and blended to get a homogeneous material

Each raw mix was analyzed through different analytical techniques. All the raw mixes were stored in plastic bags. In some raw mix preparation some additional material like laterite, silica sand and high alumina clay were used in a smaller quantity, which are not present in the study area. In most of the cement factories these substances are procured from other sources.

3.6.4.2 Determination of K_2O

The K_2O was determined by Flame emission spectrophotometer

Instrument Conditions:	(same as in section 2.6.4.1)
Apparatus:	Glassware, balance, hot plate
Reagents:	KCl, Distilled water, hydrochloric acid (analytical grade)

Preparation of Solutions

1. **Primary Stock Solution of 1000 ppm K_2O :** 1000 ppm stock solution of K_2O was prepared from KCl in a 1000 mL flask by dissolving 1.5828 g KCl in distilled water and diluting up to the mark.
2. **Secondary Stock Solution of 100 ppm K_2O :** 100 ppm stock solution was prepared from 1000 ppm by diluting 10 mL to 100 mL with distilled water.
3. **Working Standards:** working standards of 2.0, 4.0, 8.0, 12.0, 16.0 and 20 ppm were prepared from the secondary stock solution with distilled water in 100 mL volumetric flasks.
4. **Preparation of Clinker Solution:** One gram of the powdered clinker was taken and 10 mL of HCl and 25 mL distilled water was added to it. The solution was heated to boiling on hot plate and digested for 15 minutes and filtered through Whatman filter paper 41 to separate silica. The ppt was washed with hot water and the filtrate diluted up to 1000 mL.

Procedure

Flame emission spectrophotometer was turned on and warmed up for 15 minutes for accurate performance. During this period distilled water was aspirated. The read out was set to zero by adjusting the blank control during the aspiration of

distilled water. The hundred of the instrument was adjusted with the most concentrated working standard (20 ppm)

All the working standards were aspirated and their intensities recorded. The intensities were plotted against their concentrations. The working standards were also run as unknown samples during the analysis, to verify the accuracy of the instrument. The clinker solutions were also aspirated and the intensities noted. The concentration of K_2O in the clinker solution was noted from the calibration plot.

The concentration of K_2O was converted from ppm to percentage using the following formula

$$\% \text{ age } K_2O = ppm \times 1000$$

3.6.5 Determination of Sulphuric Anhydride (SO_3)

Method: Gravimetric

Reagents and Apparatus: Distilled water, hydrochloric acid, barium chloride, muffle furnace and filter paper

Preparation of Solutions

Barium Chloride Solution: 100 g of barium chloride was dissolved in some distilled water and diluted to 1000 mL.

Procedure

1 g of the powdered clinker sample was taken in a glass beaker. 5 mL of hydrochloric acid and 25 mL distilled water was added to it. The material was heated to boiling and digested for 15 minutes. The silica was separated through Whatman filter paper 41. The ppt was washed with hot water till the filtrate gave no ppt with $AgNO_3$ solution showing that the ppt in funnel became free from chloride.

The filtrate was boiled and 10 mL of barium chloride solution in hot condition was added with constant stirring. The ppt was digested for about 12-24 hours. The ppt was filtered through Whatman filter paper 42, and washed thoroughly with hot water. The ppt was dried; charred and ignited in the muffle furnace at $900^\circ C$ for 45 minutes. The ppt was cooled in the desiccator and weighed again. The % age SO_3 was calculated by the following formula,

$$\% \text{SO}_3 = \frac{A \times 0.343 \times 100}{W}$$

Where A = wt of BaSO₄

W = wt of the sample

0.343 = Molecular weight ratio of SO₃ to BaSO₄

3.6.6 Determination of Burnability Factor (BF)

Burnability factor is used as a guideline for the kiln operator to show if a given clinker is easier or harder to burn. Higher burnability factors yield a clinker that is harder to burn. Conversely, lower factors make the clinker easier to burn.

The burnability factor of the resulting clinker was calculated from the chemical data obtained by, using different analytical techniques, as follow:

$$\text{BF} = \text{LSF} + 10 \text{ SR} - 3 (\text{MgO} + \text{Alkalies})$$

Where LSF = lime saturation factor of the clinker and is given as

$$\text{LSF} = \frac{\text{CaO}}{(2.8\text{SiO}_2 + 1.18\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3)}$$

SR = silica ratio and is given as

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

3.7 PREPARATION OF CEMENT

Cement is the clinker mixed with small quantity of gypsum. Gypsum controls the setting time of cement. The usual SO₃ content of the cement is 2.55% for which 95% clinker and 5% gypsum is mixed and pulverized. The percentage of gypsum can be increased or decreased depending upon the purity of gypsum (percentage of CaSO₄ in gypsum).

3.8 ANALYSIS OF CEMENT

3.8.1 Determination of Sulphuric Anhydride (SO₃)

The determination of sulphuric anhydride (SO₃) was carried out by gravimetric method as that of clinker (section 3.6.5).

3.8.2 Determination of Major and Minor Elements

Major and minor elements in the cement were determined in the cement using X-ray fluorescence spectrophotometer like that of clinker (3.6.3 -3.6.4).

3.8.3 Determination of Insoluble Residues

Apparatus: Glassware, balance, hot plate, furnace, nickel crucible

Reagents: Distilled water, hydrochloric acid, sodium hydroxide, ammonium nitrate, methyl red indicator

Preparation of Solutions

1. **Sodium hydroxide solution:** 10 g sodium hydroxide pellets were dissolved in a small amount of water and diluted up to 1000 mL with distilled water.
2. **Ammonium nitrate solution:** 20 g ammonium nitrate was dissolved in a small amount of water and diluted up to 1000 mL with distilled water.

Procedure

1 g of cement was taken in a 100 mL beaker. 10 mL of distilled water and 5 mL of concentrated hydrochloric acid was added into it. The mixture was swirled and diluted up to 50 mL with water. The solution was warmed and digested for 15 minutes. The residue was filtered on Whatman filter paper 41 and washed six times with hot water. The ppt along with the filter paper was transferred back to the reaction beaker.

100 mL of sodium hydroxide solution was added to the beaker and heated just below the boiling for 15 minutes. The solution was acidified with hydrochloric acid in the presence of methyl red indicator. The ppt was filtered through whatman filter paper 41 and washed with hot solution of ammonium nitrate.

The ppt was dried, charred and ignited at 1000 °C for 45 minutes in a nickel crucible, the residue was cooled, weighed and the results were recorded.

3.9 PHYSICAL TESTING OF CEMENT

3.9.1 Determination of Fineness of Cement (Blaine)

Apparatus with specifications

Permeability cell, filter paper, manometer, timer

1. Permeability cell

Physical nature	metallic
Internal diameter of upper of cylinder	12.7 ± 0.1 mm
Depth of the bed space when plunger in fully inserted	10.00 ± 0.03 mm
Thickness of the perforated disk	1.60 ± 0.03 mm
No. of holes	30-40
Filter paper	12.7 mm Whatman

2. Manometer

Outer diameter	9 mm
Manometer liquid	Dibutyle phthalate

3. Timer

Min limit	0.5 second
Max limit	300 second

Procedure

2.8970 g of cement was accurately weighed and carefully into the permeability cell. The cement was pressed in the cell by using plunger and pushing down, so that the shoulder of the plunger was in contact with the top of the permeability cell. The cell was inserted in the air chamber of the manometer slowly so that the air in manometer was not disturbed. The air was allowed to pass through the cement till the level of liquid in the manometer reached its position.

The process was repeated three times and the time interval was noted each time. The fineness of the cement was calculated as under.

$$S_w = \frac{K}{e} \sqrt{\frac{h_1}{h_2}}$$

Where K is the constant of apparatus

e is the density (kg/m^3) of the cement

$\frac{h_1}{h_2}$ is the average ratio of the manometer readings

3.9.2 Compressive Strength

Apparatus: Glass graduated cylinder, specimen moulds, trawls, balance, scales for weighing, vibration machine, compression testing machine, humidity condition chamber.

The specifications for apparatus were noted as below

1. **Mould**

Size	70.7 ± 0.1 mm
Area of the face	5000 mm ²
2. **Sieves**

square mesh size	300 μ m
------------------	---------
3. **Graduated cylinder**

500 mL

4. **Trawls**

cast steel 150 mm with straight edges

5. **Graded Standard Sand**

Grain size	100 % pass from 850 μ m
	10 % pass and 90 % retain from 600 μ m
Moisture	0.2 % on 105 °C
6. **Vibrating Machine**

Normal running speed	1200 ± 400 r/min.
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7. Temperature and Humidity Conditions

The temperature was recorded as below

Testing place	Temperature	Relative humidity
Mixing room	$20 \pm 2^{\circ}\text{C}$	65 %
Moist curing chamber	$20 \pm 1^{\circ}\text{C}$	90 %
Water curing tank	$20 \pm 1^{\circ}\text{C}$	100 %
Compression testing room	$20 \pm 2^{\circ}\text{C}$	50 %

Preparation of Specimen Mortar

Mixes for mortar cubes

The following proportion of water, cement and sand was used for mortar preparation

Material used	Proportion by mass	Weight taken (gram)
Cement	1.0	185
Sand	3.0	555
Water	0.4	74

Procedure

The cement and sand in the above ratio was mixed in dry form for one second with the help of two trowels. Water was added and mixed the whole for 4 minutes with the two trowels. The mortar was placed in the hopper of the mould and compacted with the help of vibration machine for 120 seconds.

After vibration the moulds were placed in the moist curing chamber. The upper surfaces of the cubes were covered with a plastic cover to avoid evaporation. After 24 hours the cubes were removed from the moulds and placed in the water tank.

Testing of the Specimens

The compressive strength of the mortar cubes after the specified period i.e. 3days, 7days and 28days was determined under the temperature and relative humidity conditions using the compression machine and the results were recorded.

3.9.3 Determination of Standard Consistence

The standard consistence of cement was determined by vicat apparatus.

Apparatus: mould, frame, plunger, trawls and top loading balance

The specifications for the apparatus were noted as below

1. Mould

Internal diameter	80.0 ± 0.5 mm
External diameter	89.0 ± 0.1 mm
Height	40.0 ± 0.5 mm

2. Plunger of Polished Brass

Diameter	10.00 mm
Length	50 mm

3. Humidity condition chamber

Temperature of the mixing room	20 °C
Relative humidity	65 %

Procedure

400 g cement and a measured quantity of water were mixed vigorously on non-porous surface by means of two trawls for 240 seconds. The mould was filled immediately with the cement paste and the surface of cement was smoothed in the mould. The plunger was lowered to touch the surface the cement paste and allowed to sink in the surface.

The same procedure was performed with different paste containing different amounts of water and the amount of water was noted for which the plunger remained about 5 mm above from the bottom of the mould.

3.9.4 Determination of Setting Time

The initial and final setting time was determined by using vicat apparatus

Apparatus: mould, frame, initial setting time needle, final setting time needle, trawls and balance

The specifications for apparatus were noted as below

1. Initial Setting Time Needle

Diameter	1.14 mm
Length	50 mm

2. Final Setting Time Needle

Diameter	5.0 mm
Length	30 mm

3. Temperature and Humidity Conditions

Temperature of the mixing room	20 °C
Relative humidity	65 %

Procedure

The cement paste, which was already used for standard consistence, was used for the study of setting time.

3.9.4.1 Determination of Initial Setting Time

The initial setting time needle was slowly lowered to contact the surface of the cement paste in the mould and slowly allowed to sink into the paste. The process was repeated on the undisturbed places till it stopped 10 mm above the bottom of the mould. The time interval between this condition and the adding water to the cement was recorded.

3.9.4.2 Determination of Final Setting Time

The initial setting time needle was replaced by the final setting time needle. The needle was carefully lowered and brought into contact with the surface of the cement paste, and quickly released to sink into the surface. This process was repeated till the condition, when only impression on an undisturbed part of the surface of the cement paste was made. The time interval from the addition of water till only the impression formation on the surface of cement paste was recorded.

3.9.5 Determination of Lechatlier Expansion (soundness)

Apparatus: small split cylinder, glass plates

The following specifications were observed

Split Cylinder

Thickness	0.5 mm
Internal diameter	30 mm

Procedure

100 g of the cement was mixed with sufficient quantity of water to give a standard consistence. The mould was placed on a glass plate and filled with cement paste, keeping the split closed. The second glass plate was placed on the mould and a small weight was placed on it. The whole apparatus was immersed in water at a temperature of 20 °C and left for 24 hours. The mould was removed from the water and measured the distance separating (expansion) the indicator points.

3.10 BAGGASE ASH

Sugar industries use baggase of sugarcane as a fuel in the preparation of sugar. The ash, which is produced as a result of burning is of no use and is wasted. This waste baggase ash is usually dumped sporadically here and there on the roadsides or some other places, which causes many environmental problems. One can find baggase ash in the vicinity of sugar mills, for some kilometers all around.

Sampling

Samples of baggase and baggase ash were collected from the sugar mills of N.W.F.P. on different dates. The samples were collected in the plastic bags and properly numbered. Baggase was in the form of crushed pieces ranging in size from 0.5-10 mm, which was ready for burning in the sugar mill. The sampling dates, time and sizes were noted. The samples were carried to the laboratory for analysis and further process. Both baggase and baggase ash were separately studied for further treatment and analysis.

3.11 ANALYSIS OF BAGGASE AND BAGGASE ASH

Baggase ash collected from the sugar mills of N.W.F.P was analyzed for different physical and chemical parameters using standard analytical techniques. Thermogravimetric analyzer was used for the determination of moisture, loss on

ignition and ash contents, carbon-sulphur detector for carbon and sulphur and Bomb calorimeter for calorific value was used respectively.

3.11.1 Determination of Moisture in Baggase and Baggase Ash

Instrument: Thermogravimetric Analyzer

Instrument Conditions

Crucible	Ceramic
Lower temperature	25 °C
Upper temperature	105 °C
Method	ASTM D-5142

Apparatus and Reagents

Ceramic crucible, scoop, oven, baggase and baggase ash samples collected from sugar mills

Procedure

The scoop and the crucibles were properly washed with distilled water and dried in the oven at 105 °C for two hours. The crucibles were placed in the instrument. One scoop (5 mm²) of the unknown baggase sample was taken in each of the crucible. The moisture of all the samples was determined. The same procedure was repeated for baggase

The whole analysis was repeated three times by the instrument automatically to get consistent results.

The results of the samples, instrument conditions etc. were displayed on the computer. All the samples were analyzed in triplicate.

3.11.2 Determination of Loss on Ignition of Baggase Ash

Instrument: Thermogravimetric Analyzer

Instrument Conditions

Crucible	Ceramic
Lower temperature	25 °C
Upper temperature	850 °C
Method	ASTM D-5142

Apparatus and Reagents

Ceramic crucible, scoop, oven, baggase and baggase ash samples from sugar mills

Procedure

The sample scoop and the crucibles were properly washed with the distilled water and dried in the oven at 105 °C for two hours. All the crucibles were placed properly in the carousel of the instrument while the reference crucible was placed at the zero position.

The instrument was standardized with the moisture free oxalic acid and then one scoop of the unknown baggase sample was taken in each of the crucible. The loss on ignition of all the samples was determined. All the samples were taken in triplicate.

The results were displayed on the computer. The whole analysis was repeated three times by the instrument automatically to get consistent results.

3.11.3 Determination of Ash Content in Baggase and Baggase Ash

Instrument: Thermogravimetric Analyzer

Instrument Conditions

Crucible	Ceramic
Lower temperature	25 °C
Upper temperature	850 °C
Method	ASTM D-5142

Apparatus and Reagents

Ceramic crucible, scoop, oven, baggase and baggase ash samples

Procedure

The sample scoop and the crucibles were properly washed with the distilled water and dried in the oven at 105 °C for two hours. All the crucibles, along with the reference one at the zero crucible location, were placed in the carousel of the instrument.

The instrument was standardized with the moisture free oxalic acid and then one scoop of the unknown baggase sample was taken in each of the crucible. The ash

content of all the baggase samples was determined. All the samples were taken in triplicate. The same procedure was followed for all samples of the baggase ash.

The whole analysis was repeated three times by the instrument automatically till the results were consistent. The results of the samples, instrument conditions etc. were displayed on the computer.

3.11.4 Determination of Carbon and Sulfur in the Baggase Ash

Instrument: Dual Range Sulfur and Carbon Analyzer

Apparatus: Boats for samples. Analytical balance, steel tongs,

Temperature of the furnace	1350 °C
Weight of sample taken	0.350 g
Flow of sample gas	3.5L / minute

Procedure

The boats were properly washed with distilled water and dried in the oven. After complete setup when the analyzer reached to the set temperature, analysis was started. The certified standards and their analysis were entered to the software of the machine. The certified standards were run and their results used to compensate for differences between the total carbon and sulfur measured and the actual carbon and sulfur. When the calibration analysis was completed, calibration plot was drawn by the instrument. To get more consistent results the samples and certified standard were taken evenly distributed in the boat.

The unknown samples were analyzed in the same way as that of the certified standards. The weight and moisture value of the samples were fed to the instrument. Some of the certified standards were also run as the unknown samples in order to check the reliability of the results.

3.11.5 Determination of Calorific Value of the Baggase Ash by using Bomb Calorimeter

Instrument: Bomb calorimeter

Instrument Conditions

Equilibrate time	3.0 minutes
Pre-fire time	2.0 minutes
Post fire time	3.0 minutes
Main time	5.0 minutes
Analysis time	13.0 minutes
Fuse wire length	6.00 centimeters

Procedure

The combustion vessel bucket was filled with 2000 mL water. The water was allowed to stream from the peppet tank to hit the inside wall of the combustion vessel bucket to help the water swirled and reduce the bubbles in the bucket.

The combustion vessel bucket was placed inside the combustion vessel bucket well, making sure that the indent in the bottom of the combustion vessel bucket is positioned towards the front of the analyzer. The carrying handle was attached to the combustion vessel by inserting the pins on the end of the handle into the holes around the top of the combustion vessel.

The sample was placed in the crucible which was fitted in the sample holder. A fuse wire of 6 cm long was fitted in such a way that the wire does not touch the sample crucible. The sample holding assembly was fitted in the combustion chamber and lowered into the combustion vessel bucket with a great care so as the sample remain undisturbed. The combustion vessel valve was closed.

The carrying handle was removed from the combustion vessel and shoke the excess water from the handle back into the combustion vessel bucket. The amount of water in the bucket should remain the same for accurate results. The combustion vessel bucket lid was closed and pressed down on the front of the lid to latch it, and then the analysis was triggered.

After the analysis was complete, the combustion vessel bucket lid was lifted to the complete vertical position. The combustion vessel fuse leads were removed and dried with cloth.

The combustion vessel was removed from the combustion vessel bucket, using the combustion vessel carrying handle, and poured the combustion vessel bucket water back into the reservoir tank from the combustion chamber. The sample holder assembly was removed from the combustion chamber. The same procedure was adopted for reference standards and unknown samples. The results were recorded from the display as the calorific value.

3.11.6 Determination of Various Elements in Baggase Ash

Instrument: X-Ray fluorescence spectrophotometer

Instrument Conditions

Voltage	50 kv
Current	40 mA
Sample status	Glass Bead

Apparatus: Platinum crucible, analytical balance, muffle furnace

Reagents: Lithium bromide, dilithium tetra borate (Spectromelt)

Procedure

Baggase ash was treated in the furnace for loss on ignition and used for x-ray analysis. Rest of the procedure was followed as that for clinker (section 3.6.3 - 3.6.5)

3.12 DESIGNING OF RAW MIX WITH BAGGASE ASH AND ITS CLINKERIZATION

Apparatus

Nickel crucible, muffle furnace, analytical balance, raw material for cement, baggase ash

Procedure

After complete analysis of the baggase ash, it was interground with the other raw materials like lime stone and clay etc. which are normally used for cement production, and was processed in a normal manner for clinker production. The resulting clinker was ground with gypsum for cement formation. The clinker and cement were studied and compared with standards.

Different raw mixes were prepared with baggase ash for optimization:

1. First baggase ash was mixed with normal raw mix for high strength Portland cement in different percentages. The effect of baggase ash on the percent composition of all elements and parameters in the raw mix was studied.
2. Baggase ash was added to high lime saturation factor (LSF) raw mix in different percentages and the effect on the percentage composition of elements and parameters of the resulting clinker and cement was studied. In this way the optimum quantity of baggase ash was determined for the raw mix designing.

3. The clinkerization, cement formation and study of the physical and chemical parameters were carried out in the same way as that of the normal cement.

3.13 REPLACEMENT OF CEMENT WITH BAGGASE ASH

Baggase ash was added with ordinary Portland cement in different proportions, the cubes were prepared and the compressive strength was determined after three days, seven days and twenty-eight days using distilled water. The impact of Baggase ash on the cement compressive strength was studied.

3.14 USE OF CHEMICAL ACTIVATOR ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) FOR THE ENHANCEMENT OF POZZOLONIC ACTIVITY OF BAGGASE ASH

Preparation of Calcium Chloride Solutions

Different concentrations of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (1, 2, 3, 4, 5 and 6 %) were prepared using distilled water.

Optimization of Activators

The cement pastes were prepared with different percentages of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ activators. The cubes were prepared and tested for compressive strength after three days, seven days and twenty eight days. The optimum quantity of the activator was determined from the sample cubes with the maximum compressive strength and the results were compared with Pakistan Standard Specification.

CHAPTER NO 4

RESULTS

AND

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RESULTS AND DISCUSSIONS

PART-1

4.1 CHEMICAL COMPOSITION OF LIMESTONE AND CLAY COLLECTED FROM THE STUDY AREA

The samples collected from the study area were analyzed in the laboratory using standard analytical techniques like atomic absorption spectrophotometer, UV/visible spectrophotometer, thermogravimetric analyzer, flame photometer, and x-ray spectrometer (see chapter 3).

The results of analysis of limestone and clay are reported in Table 4.1, 4.2, 4.3, 4.4, 4.5 and 4.6.

The material collected from the study area, are classified on the basis of physical and chemical characteristics as under:

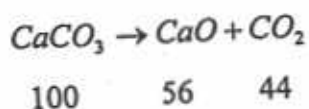
1. High grade limestone (HLS)
2. Darukhula limestone (DLS)
3. Siliceous limestone (SLS)
4. Maroon color clay (MC)
5. Lacustrine clay (LC)
6. Green color clay (GB)

4.1.1 High Grade Limestone (HLS)

High grade limestone (HLS) varies from white to greenish white in color. It is present in the Darukhula and other adjoining areas of Nizampur. Chemically greater variation in all the oxides has been noticed in the limestone (Table 4.1; Figure. 4.1). SiO_2 is ranging from 0.43 to 0.81 wt%, Al_2O_3 from 0.49 to 0.86 wt %, Fe_2O_3 from 0.11 to 0.34 wt %, CaO from 51.97 to 53.66 wt %, MgO from 0.21 to 1.52 wt %, Na_2O from 0.04 to 0.24 wt %, K_2O from 0.11 to 0.34 wt % and sulphuric anhydrous (SO_3) is ranging from 0.05 to 0.12 wt %. The average composition of the studied limestone suggest that this limestone on average contain $\text{SiO}_2 = 0.61$ wt%, $\text{Al}_2\text{O}_3 = 0.66$, $\text{Fe}_2\text{O}_3 = 0.23$ wt%, $\text{CaO} = 53.00$ wt%, $\text{MgO} = 0.58$ wt%, $\text{Na}_2\text{O} = 0.13$ %, $\text{K}_2\text{O} =$

0.24 % and $\text{SO}_3 = 0.08$ %. The alumina modulus (MA), silica modulus (MS) and lime saturation factor (LSF) of the studied limestone are 2.87, 0.69 and 20.10 respectively.

From the results it is clear that high grade limestone, as the name indicates, has high amount of calcium oxide. The maximum percentage of CaO is 56 % present in 100% pure calcium carbonate (CaCO_3). The purity of limestone is directly related with loss on ignition (LOI). Table 4.1 shows that the loss on ignition of high grade limestone (HLS) varies from 42.27% to 43.25 %. The highest possible loss on ignition of limestone is 44 % which can be observed in 100 % pure calcium carbonate as given below,



So from the percentage of CaO and LOI of the studied high grade limestone, it is concluded that this limestone contains roughly 94 % calcium carbonate.

Table 4.1 Chemical Analyses of High Grade Limestone (HLS)

Analyte	Wt. %																	Average
	HLS-10	HLS-11	HLS-13	HLS-14	HLS-15	HLS-16	HLS-17	HLS-18	HLS-20	HLS-21	HLS-37	HLS-38	HLS-39	HLS-40	HLS-54	HLS-55		
SiO ₂	0.58	0.79	0.55	0.43	0.61	0.47	0.81	0.67	0.77	0.38	0.69	0.66	0.58	0.61	0.61	0.61		
Al ₂ O ₃	0.86	0.69	0.58	0.62	0.49	0.69	0.68	0.73	0.66	0.54	0.81	0.73	0.64	0.55	0.66	0.66		
Fe ₂ O ₃	0.17	0.20	0.24	0.22	0.18	0.18	0.34	0.11	0.24	0.17	0.28	0.28	0.24	0.34	0.23	0.25		
CaO	53.66	52.88	53.41	52.64	51.97	53.44	53.42	53.17	52.04	53.27	52.75	53.31	52.88	53.21	52.98	53.01		
MgO	0.65	0.68	0.85	0.54	1.52	0.58	0.88	0.98	0.69	0.24	0.25	0.52	0.21	0.24	0.25	0.23		
Na ₂ O	0.10	0.07	0.20	0.11	0.04	0.14	0.13	0.14	0.11	0.17	0.11	0.24	0.17	0.11	0.13	0.14		
K ₂ O	0.24	0.18	0.14	0.27	0.16	0.11	0.24	0.23	0.31	0.24	0.28	0.34	0.26	0.34	0.24	0.25		
SO ₃	0.09	0.08	0.08	0.09	0.08	0.07	0.10	0.05	0.07	0.07	0.06	0.10	0.07	0.07	0.05	0.12		
LOI	42.66	42.84	42.27	43.25	42.98	42.71	42.6	42.53	43.21	43.21	43.21	42.99	43.21	42.29	42.35	42.48		
Total	99.01	98.41	98.32	98.17	98.26	98.39	99.2	98.56	98.43	98.29	98.44	99.17	98.26	99.01	98.41	98.32		

Calculated on average basis: MA = 2.87; MS = 0.69; LSF = 20.10

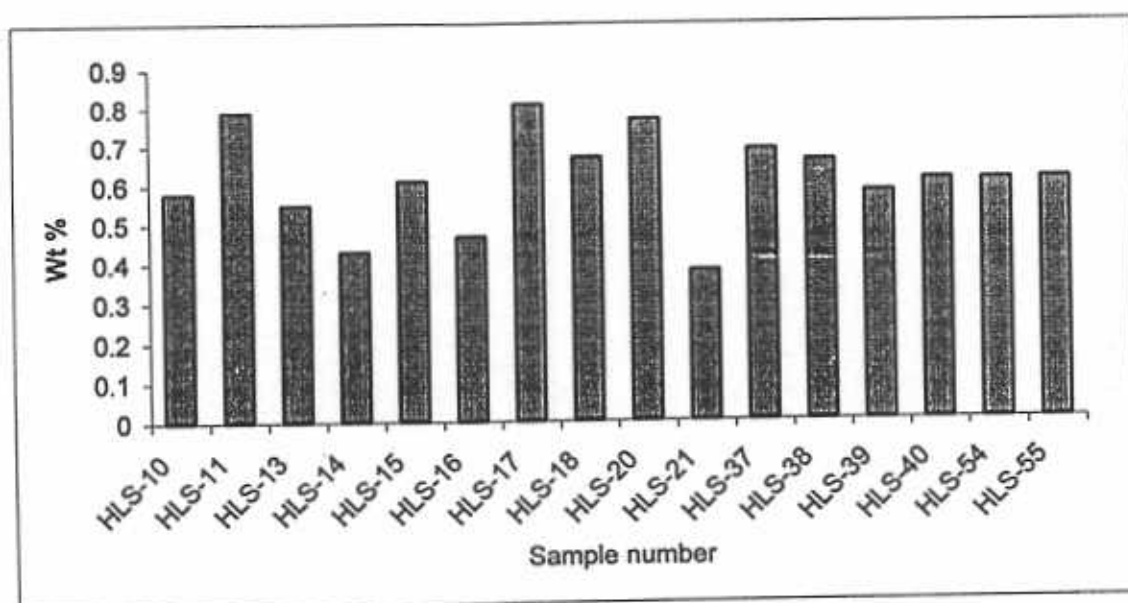


Figure 4.1 (a) Variation of silicon dioxide (SiO_2) in the high-grade limestone samples.

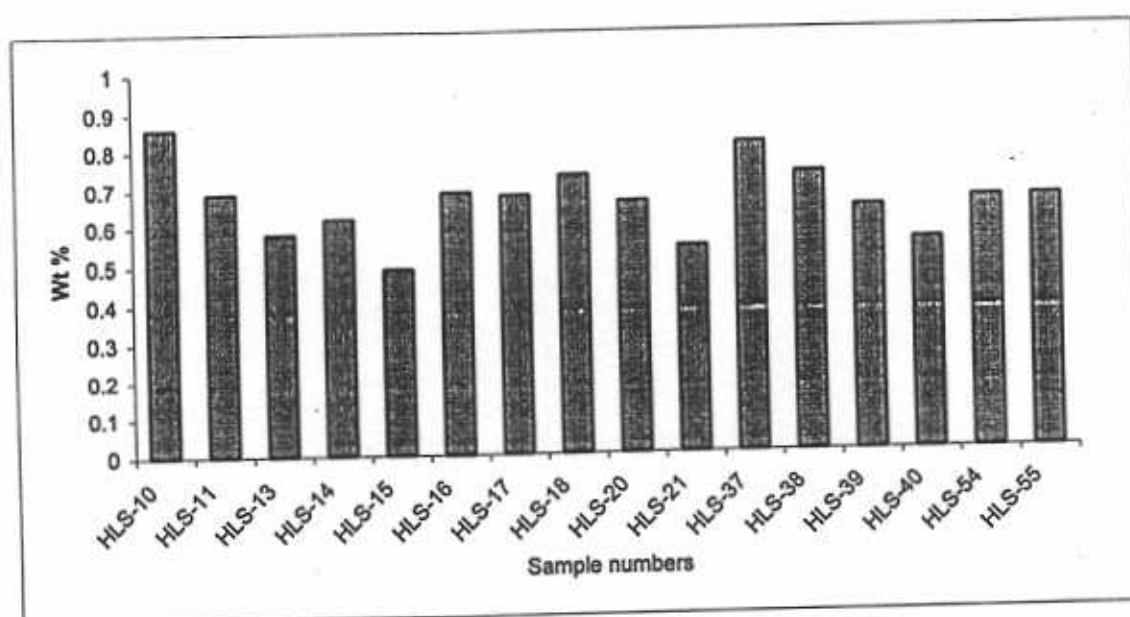


Figure 4.1 (b) Variation of aluminum oxide (Al_2O_3) in high-grade limestone samples.

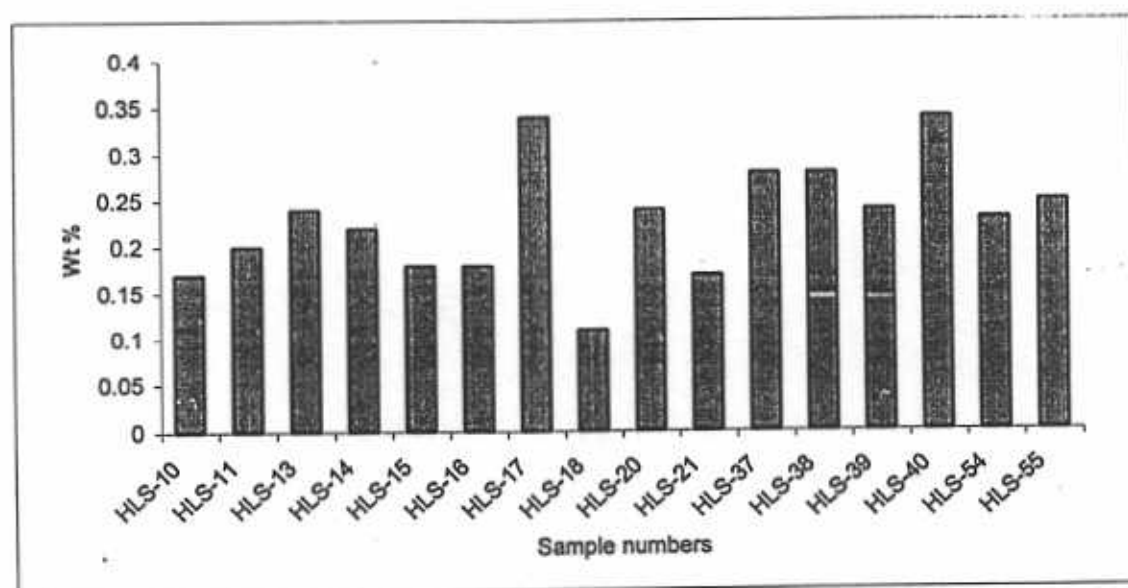


Figure 4.1 (c) Variation of iron oxide (Fe_2O_3) in high grade limestone samples.

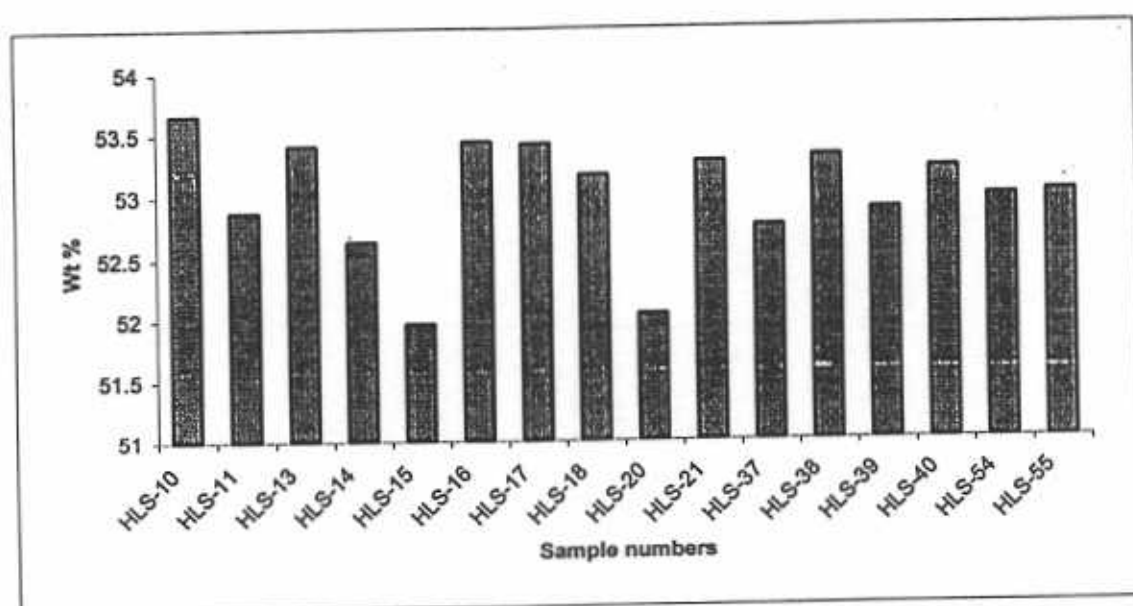


Figure 4.1 (d) Variation of calcium oxide (CaO) in high grade limestone samples.

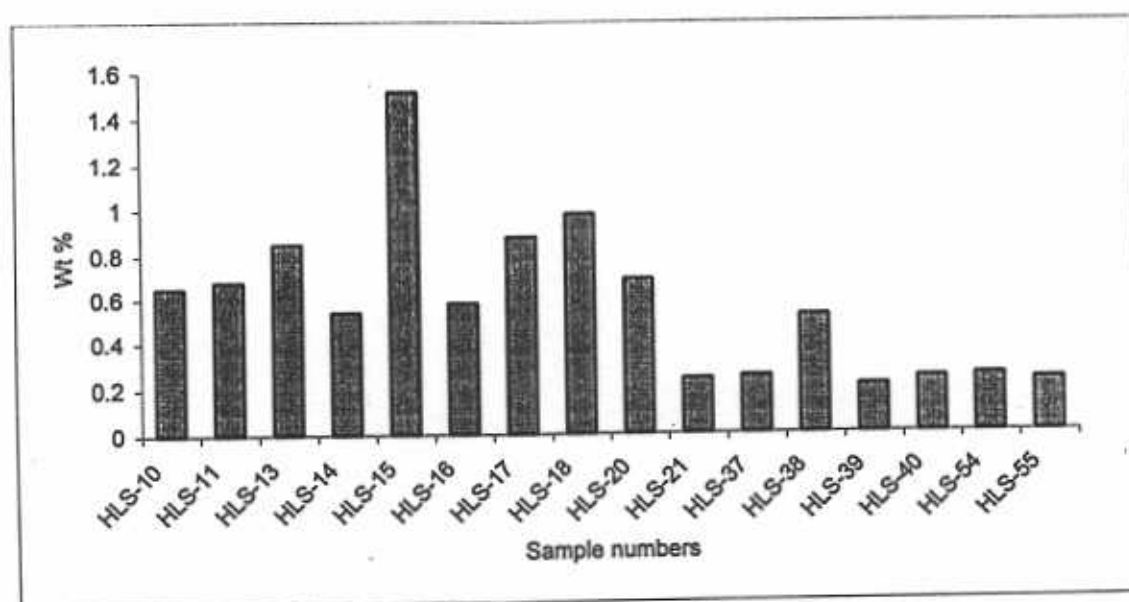


Figure 4.1 (e) Variation of magnesium oxide (MgO) in high-grade limestone samples.

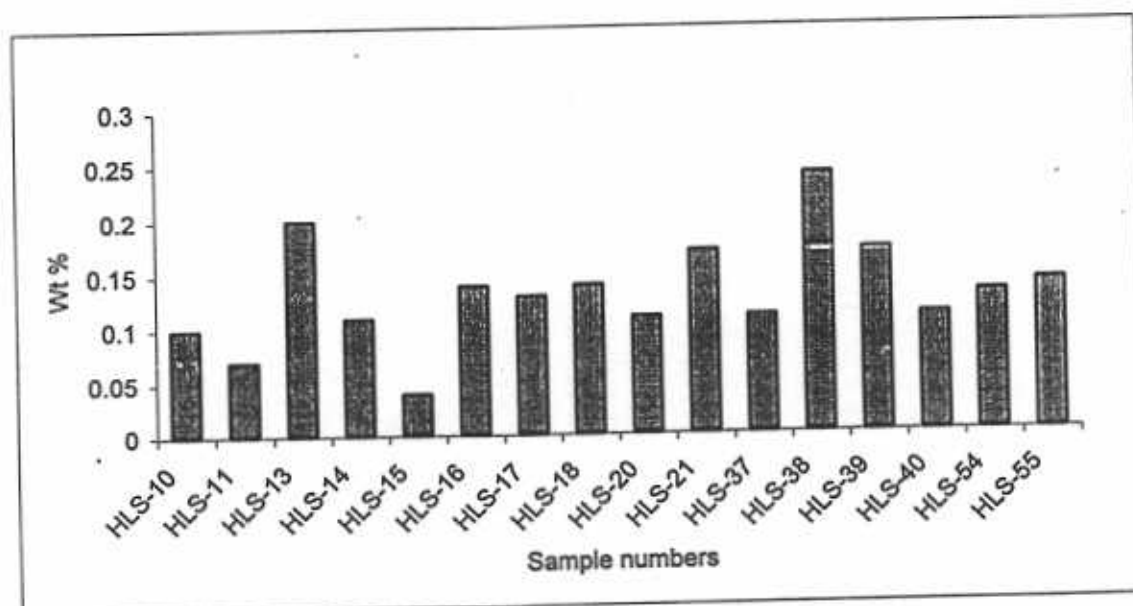


Figure 4.1 (f) Variation of sodium oxides (Na_2O) in the high-grade limestone samples.

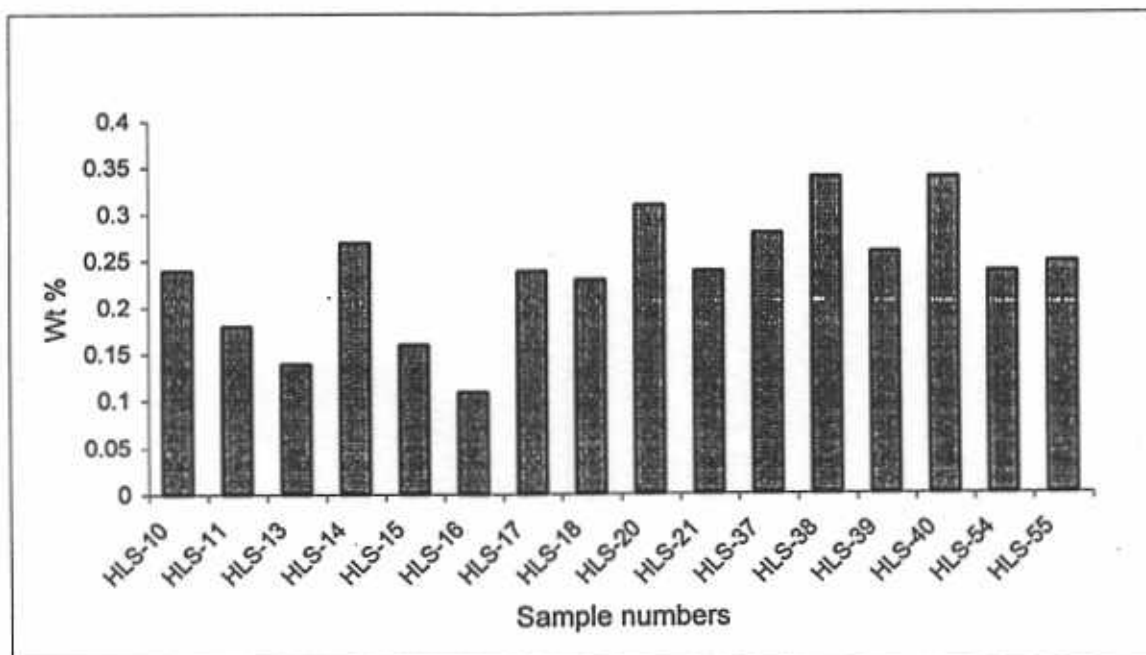


Figure 4.1 (g) Variation of potassium oxides (K_2O) in the high-grade limestone samples.

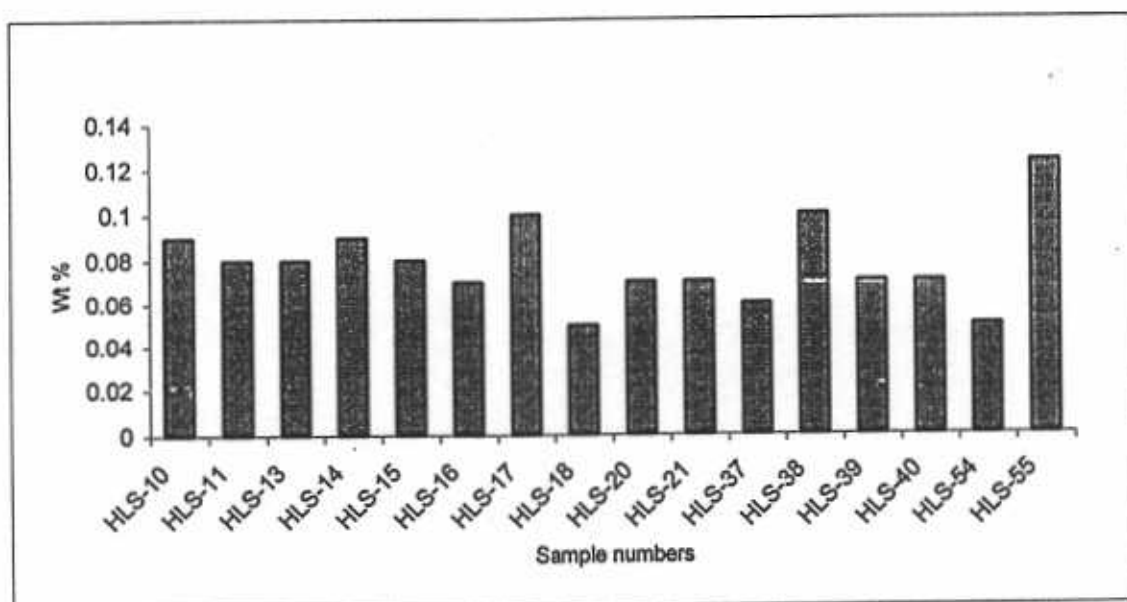


Figure 4.1 (h) Variation of sulphuric anhydride (SO_3) in the high-grade limestone samples.

4.1.2 Darukhula Limestone (DLS)

Darukhula limestone (DLS), mainly occurring in Darukhula area, is very hard and compact in texture. It is generally whitish in color. Table 4.2 and Figure 4.2 indicate that this limestone has variable chemical composition. SiO_2 varies from 1.17 to 7.66 wt%, Al_2O_3 from 0.11 to 1.84 wt %, Fe_2O_3 from 0.04 to 0.67 wt % CaO from 47.35 to 51.44 wt % MgO from 0.31 to 1.58 wt %, Na_2O from 0.04 to 0.35 wt %, K_2O from 0.18 to 0.27 wt % and SO_3 varies from 0.01 to 0.07 wt %.

The average wt% of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O and SO_3 of the studied limestone is 4.95 %, 1.32 %, 0.32%, 49.03 %, 0.83 %, 0.12 %, 0.22 % and 0.04 % respectively as indicated in Table 4.2. The alumina modulus (MA), silica modulus (MS) and lime saturation factor (LSF), calculated on bases of average composition of the studied limestone are 4.13, 3.02 and 3.14 respectively.

Table 4.2 Chemical Analysis of Darukhula Limestone Samples (DLS)

Analyte	Wt. %																Average
	DLS-22	DLS-23	DLS-24	DLS-25	DLS-26	DLS-27	DLS-28	DLS-29	DLS-30	DLS-31	DLS-32	DLS-33	DLS-34	DLS-35	DLS-36		
SiO ₂	2.05	6.74	1.17	4.68	3.55	5.43	4.25	5.84	6.77	3.67	5.78	6.68	7.66	5.18	4.83	4.95	
Al ₂ O ₃	0.66	1.84	0.87	0.11	1.94	0.83	1.77	0.91	0.37	1.47	1.62	0.76	0.39	4.52	1.68	1.32	
Fe ₂ O ₃	0.11	0.04	0.67	0.24	0.33	0.47	0.81	0.34	0.17	0.26	0.24	0.33	0.18	0.21	0.33	0.32	
CaO	50.40	48.70	51.40	49.50	50.10	47.40	48.30	49.20	47.40	50.40	48.50	47.40	48.70	48.60	49.50	49.03	
MgO	0.99	0.57	0.85	0.75	0.69	1.05	1.24	1.34	0.87	1.58	0.57	0.28	0.87	0.48	0.31	0.83	
Na ₂ O	0.04	0.14	0.35	0.08	0.15	0.07	0.16	0.05	0.11	0.06	0.14	0.07	0.09	0.10	0.14	0.12	
K ₂ O	0.22	0.21	0.18	0.22	0.18	0.23	0.18	0.24	0.27	0.16	0.24	0.27	0.24	0.22	0.27	0.22	
SO ₃	0.02	0.04	0.07	0.02	0.06	0.05	0.01	0.06	0.04	0.07	0.06	0.04	0.04	0.05	0.04	0.04	
LOI	40.40	38.90	41.20	39.40	40.00	40.00	38.80	39.70	38.70	40.80	38.60	38.90	39.10	40.20	39.50	39.61	
Total	95	97.2	96.8	95	97.1	95.4	95.5	97.7	94.6	98.5	95.8	94.7	97.2	99.6	96.6	96.44	

Calculated on average basis: MA = 2.87; MS = 0.69; LSF = 20

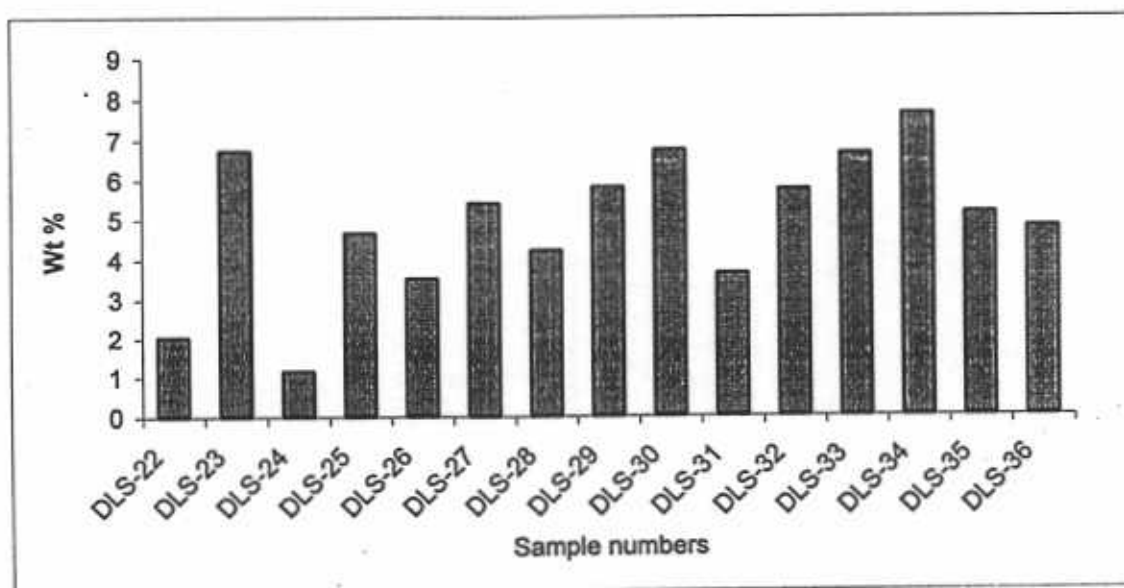


Figure 4.2 (a) Variation of silicon dioxide (SiO_2) in Darukhula limestone samples.

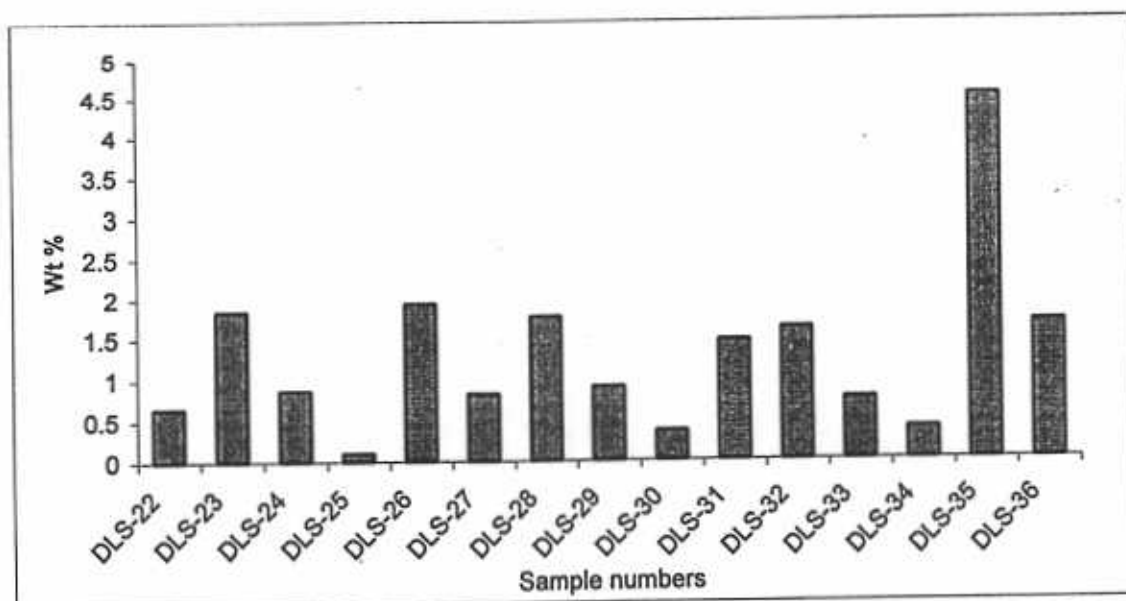


Figure 4.2 (b) Variation of aluminum oxide (Al_2O_3) in Darukhula limestone samples.

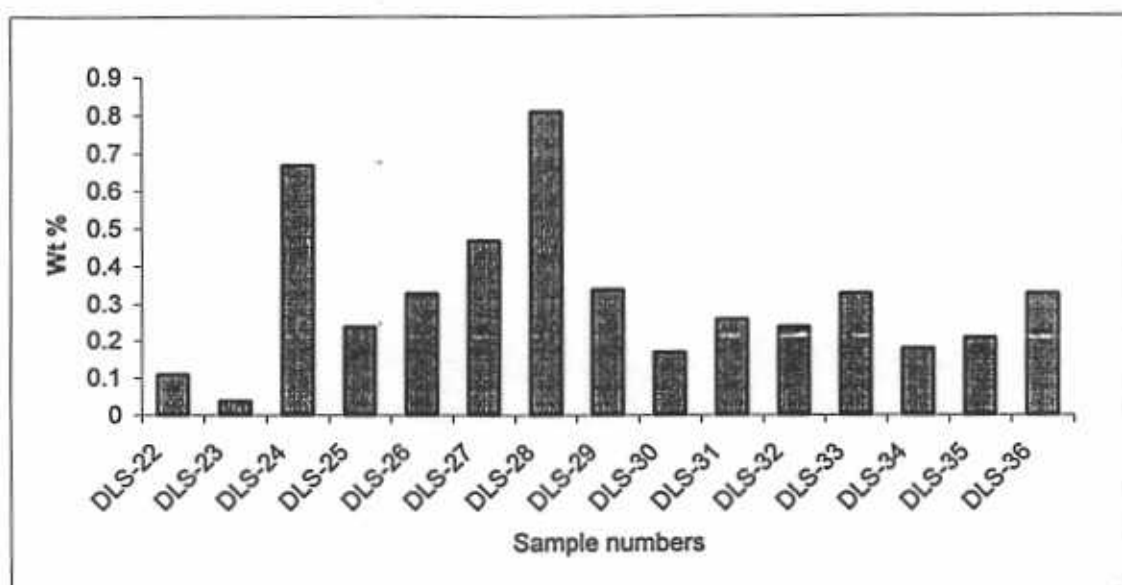


Figure 4.2 (c) Variation of iron oxide (Fe_2O_3) in Darukhula limestone samples.

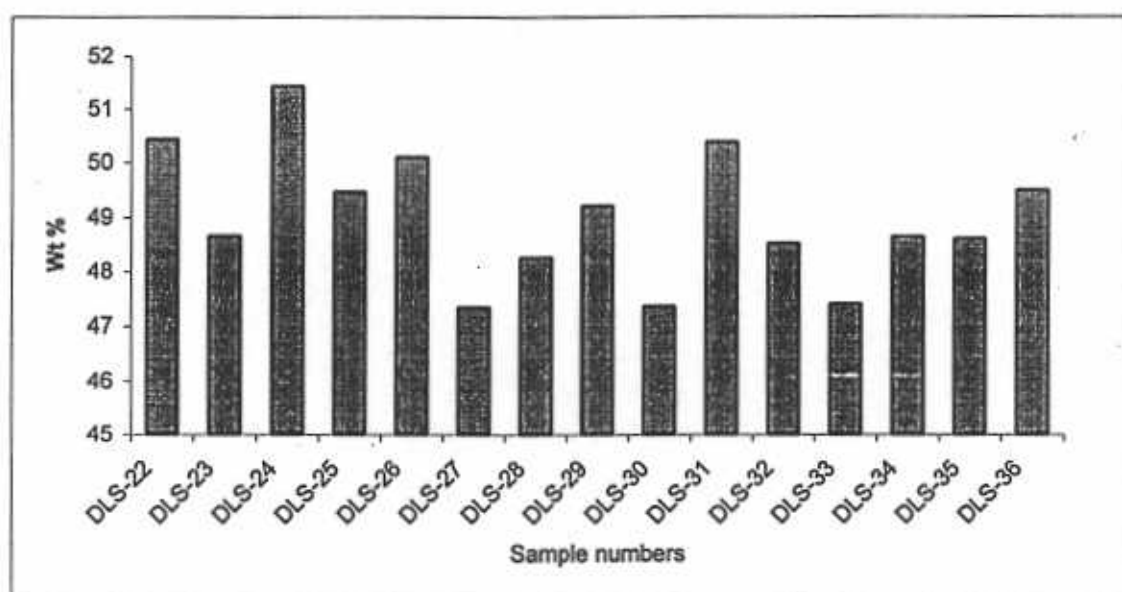


Figure 4.2 (d) Variation of calcium oxide (CaO) in Darukhula limestone samples.

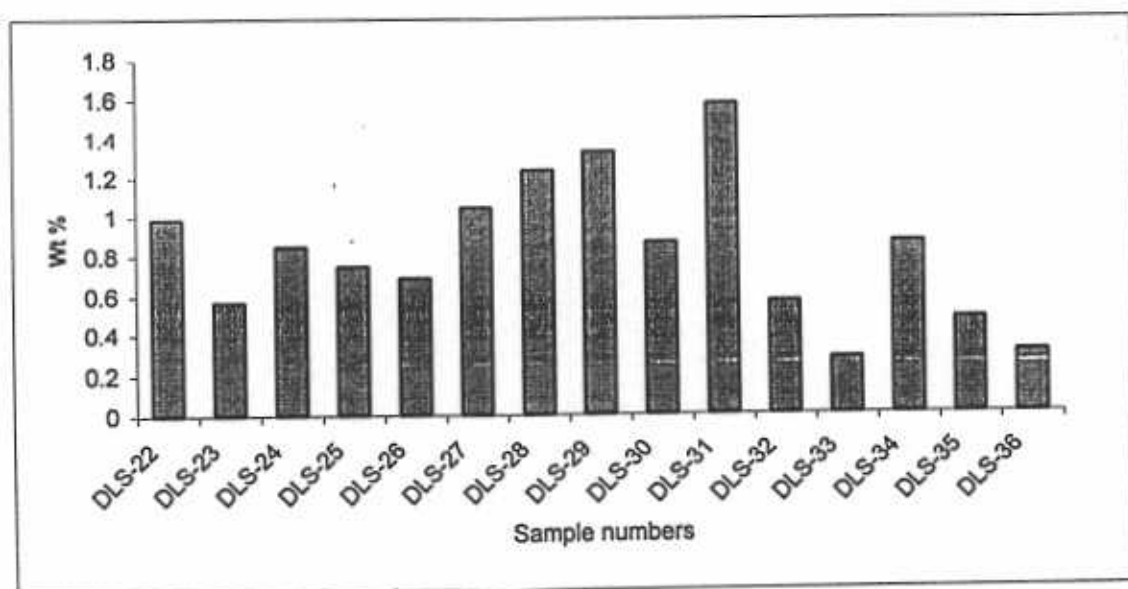


Figure 4.2 (e) Variation of Magnesium oxide (MgO) in Darukhula limestone samples.

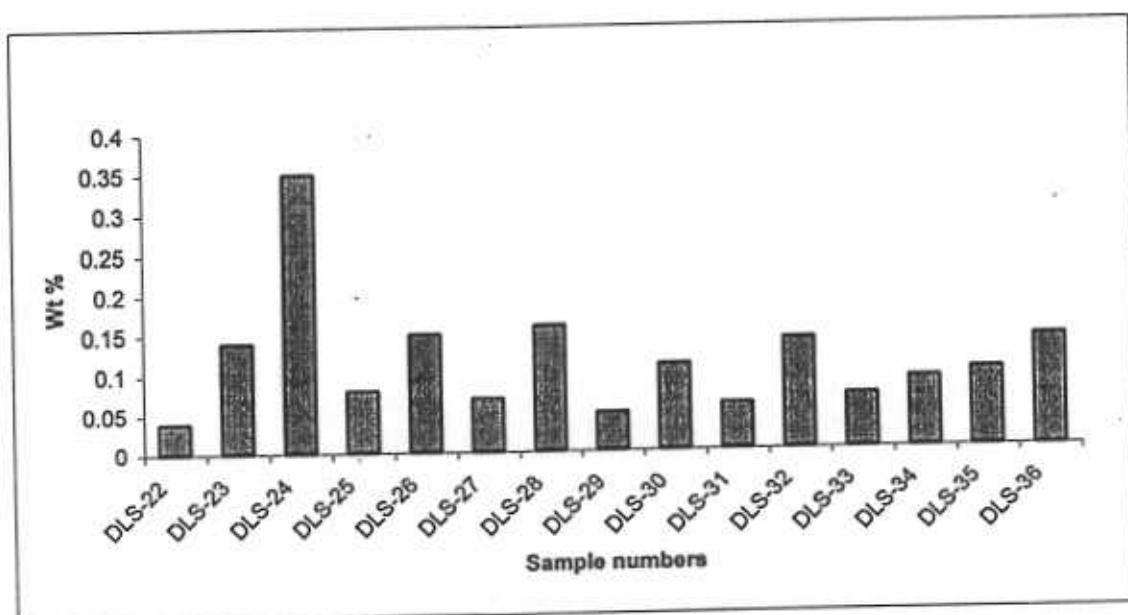


Figure 4.2 (f) Variation of sodium oxides (Na_2O) in Darukhula limestone samples.

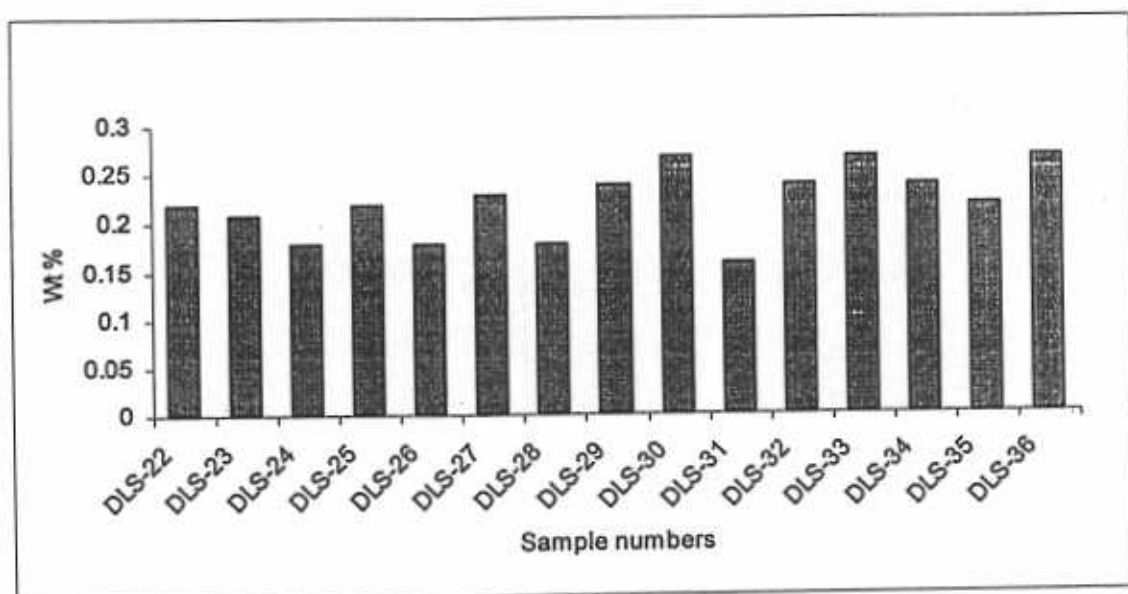


Figure 4.2 (g) Variation of potassium oxides (K_2O) in Darukhula limestone samples.

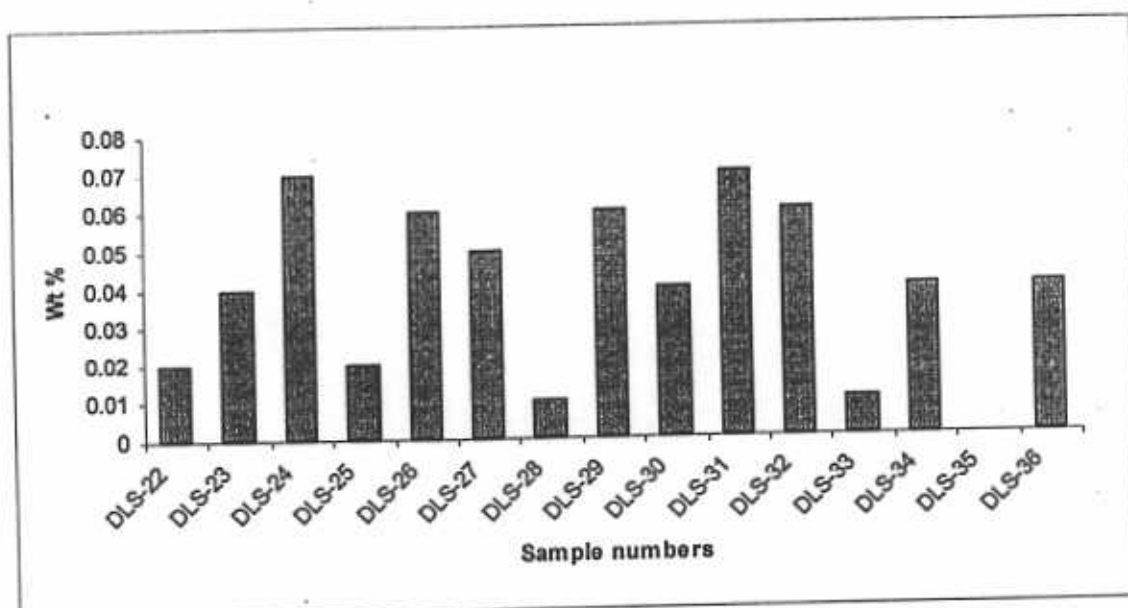


Figure 4.2 (h) Variation of sulphuric anhydride (SO_3) in Darukhula limestone samples.

4.1.3 Siliceous Limestone (SLS)

Siliceous limestone (SLS) is occurring as minor bodies within Darukhula and its surrounding areas. It is very hard and compact and whitish in colour on fresh surface. Chemically this limestone contain relatively high SiO_2 (8.72 to 15.69 wt %) and low CaO (42.67 to 46.73 wt %) and LOI (35.26 to 36.89 wt %), when compared with a foresaid limestone. The other oxides are also present in variable amounts such as Al_2O_3 (0.34 to 0.65 wt %), Fe_2O_3 (0.19 to 0.21wt %), MgO (0.71to 1.43 wt %), Na_2O (0.10 to 0.19 wt %), K_2O (0.33 to 0.71 wt %) and SO_3 (0.04 to 0.11 wt %) as indicated in Table 4.3 and Figure 4.3. The moduli i.e. MA, MS and LSF of siliceous limestone calculated on the basis of average composition are 2.19, 20.38 and 1.16 respectively.

Table 4.3 Chemical Analysis of Siliceous Limestone Samples (SLS)

Analyte	Wt. %					Average
	SLS-56	SLS-57	SLS-58	SLS-59	SLS-60	
SiO ₂	14.56	11.39	14.56	15.69	11.99	13.64
Al ₂ O ₃	0.41	0.44	0.46	0.34	0.65	0.46
Fe ₂ O ₃	0.19	0.19	0.21	0.21	0.25	0.21
CaO	44.80	46.73	45.01	42.67	46.73	45.19
MgO	0.71	0.98	0.71	1.28	1.43	1.02
Na ₂ O	0.16	0.11	0.15	0.19	0.10	0.14
K ₂ O	0.39	0.71	0.33	0.33	0.35	0.42
SO ₃	0.04	0.10	0.05	0.06	0.11	0.07
LOI	35.35	36.89	36.14	35.26	35.88	35.90
Total	96.61	97.54	97.62	96.03	97.49	97.06

Calculated on average basis: MA = 2.19; MS = 20.38; LSF = 1.16

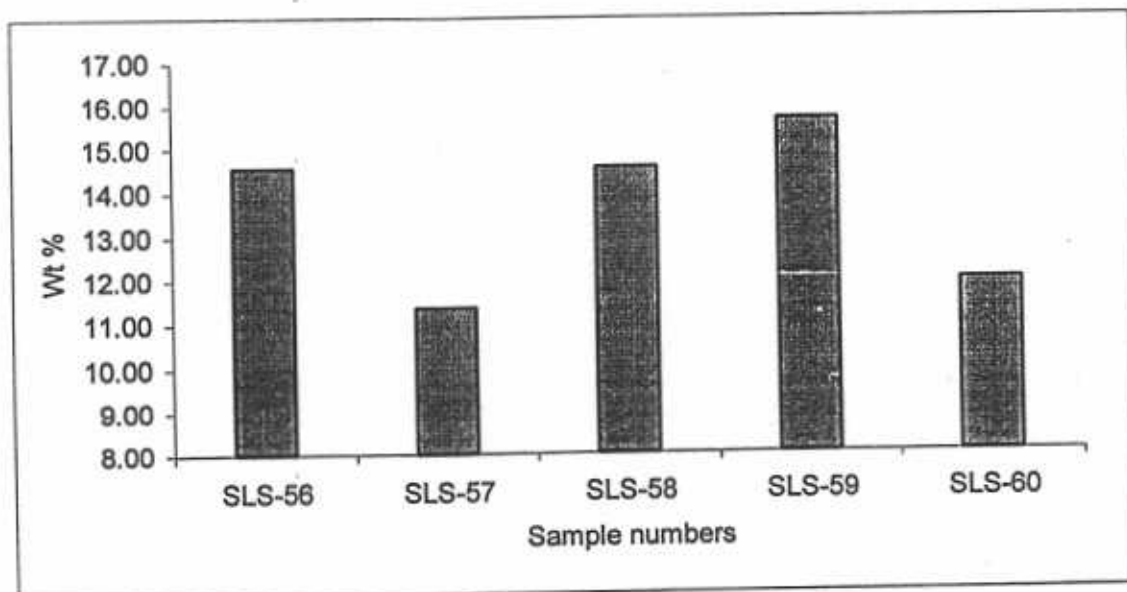


Figure 4.3 (a) Variation of silicon dioxide (SiO_2) in siliceous limestone samples.

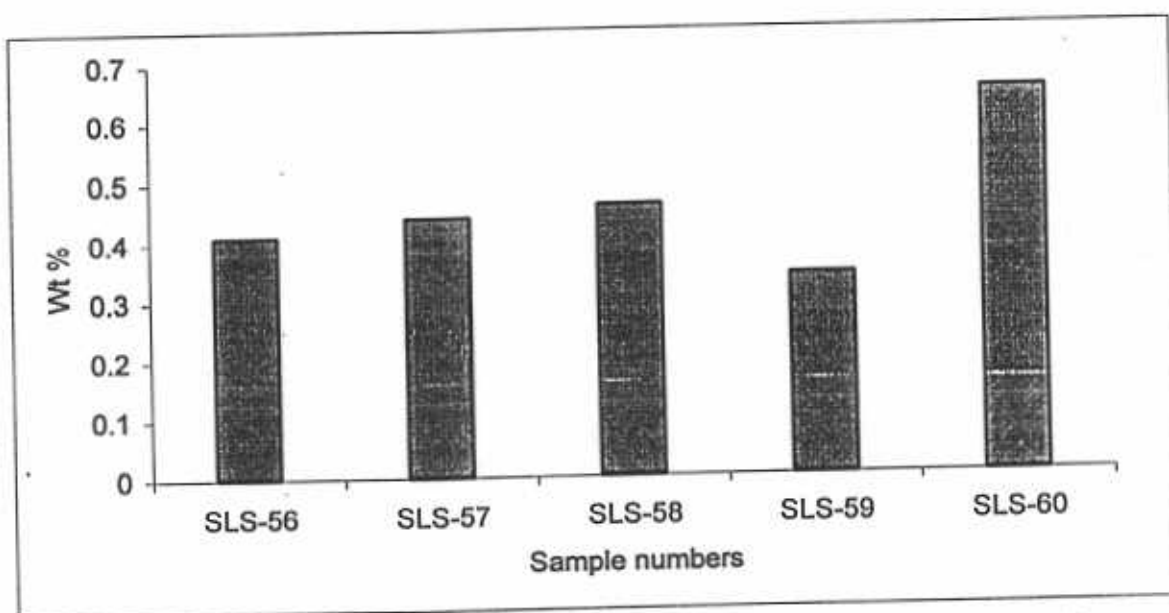


Figure 4.3 (b) Variation of aluminum oxide (Al_2O_3) in siliceous limestone samples.

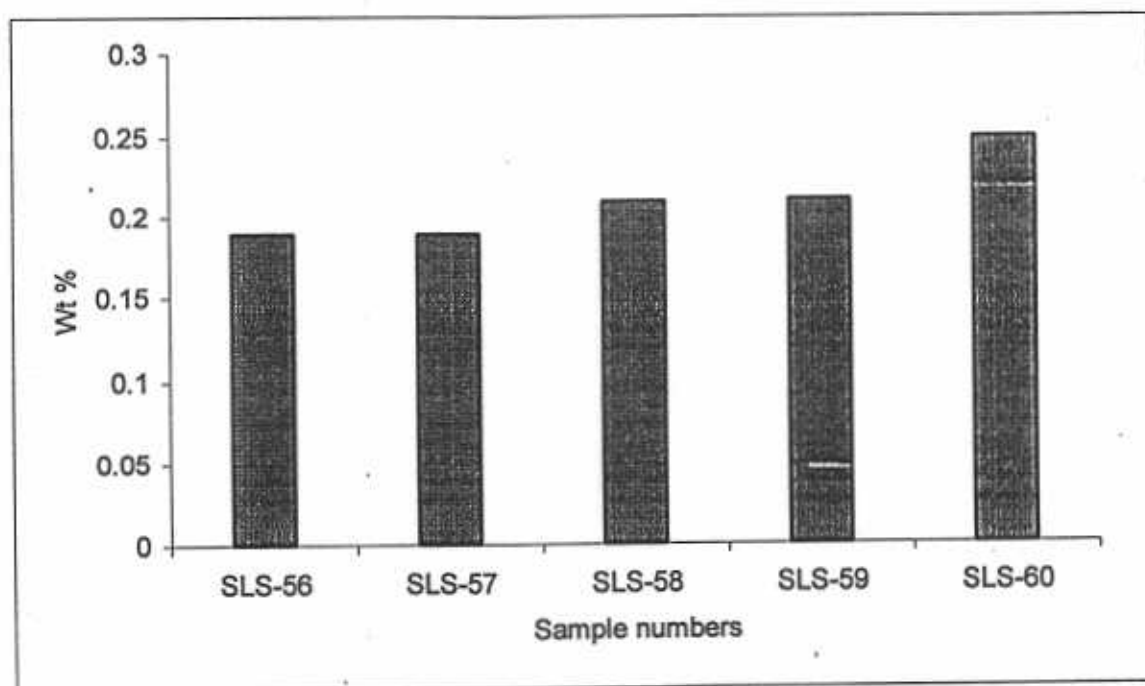


Figure 4.3 (c) Variation of iron oxide (Fe_2O_3) in siliceous limestone samples.

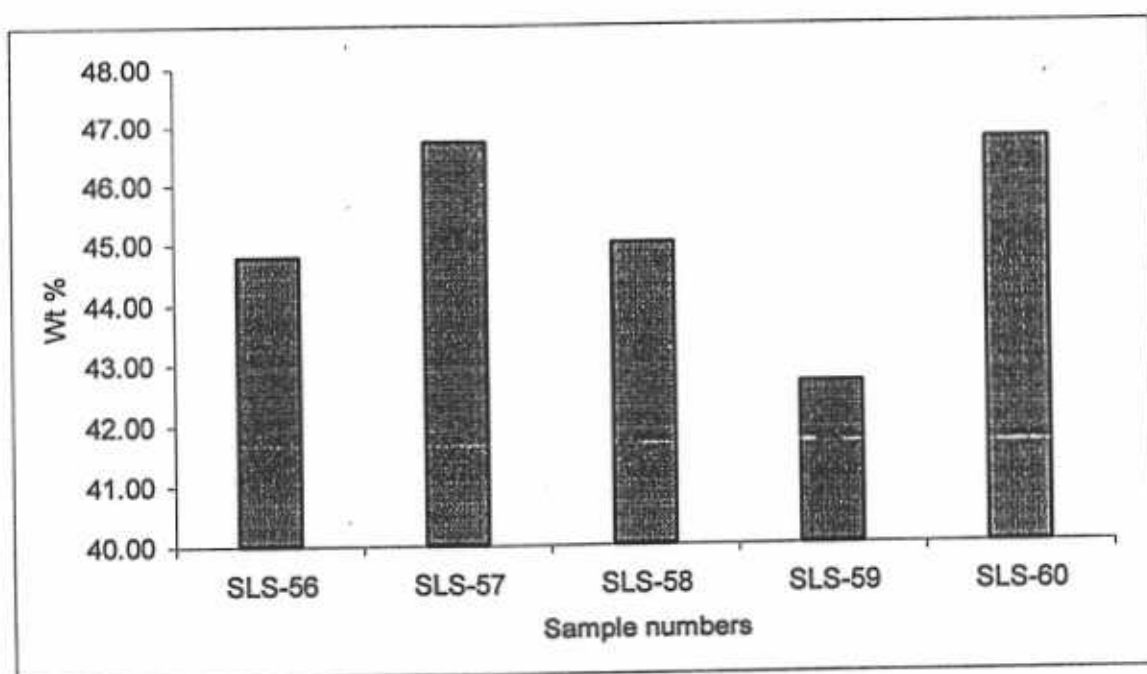


Figure 4.3 (d) Variation of calcium oxide (CaO) in siliceous limestone samples.

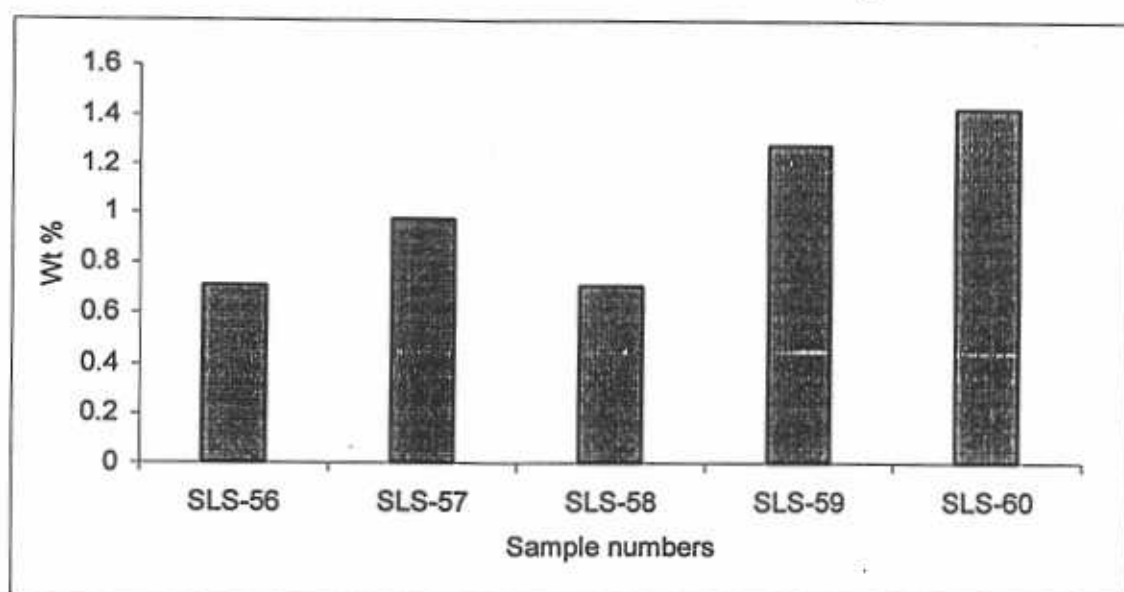


Figure 4.3 (e) Variation of magnesium oxide (MgO) in siliceous limestone samples.

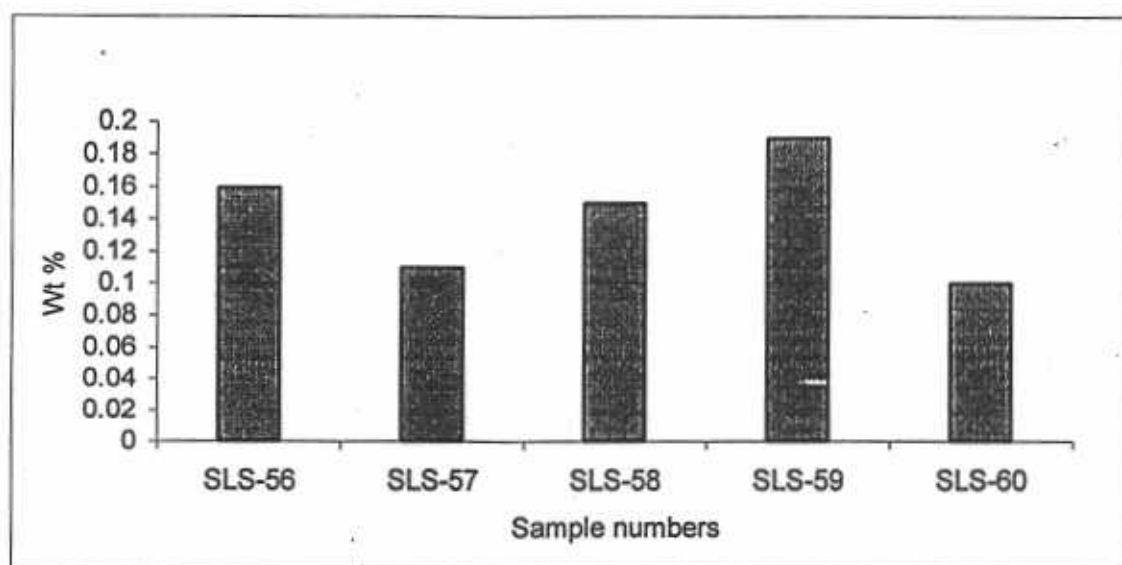


Figure 4.3 (f) Variation of sodium oxides (Na₂O) in siliceous limestone samples.

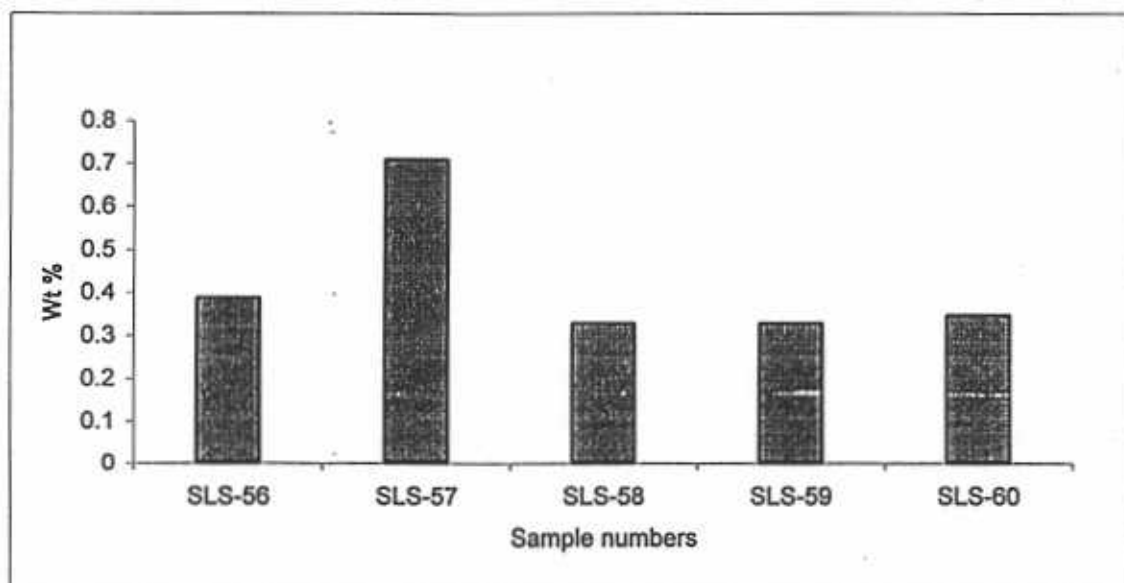


Figure 4.3 (g) Variation of potassium oxides (K_2O) in siliceous limestone samples.

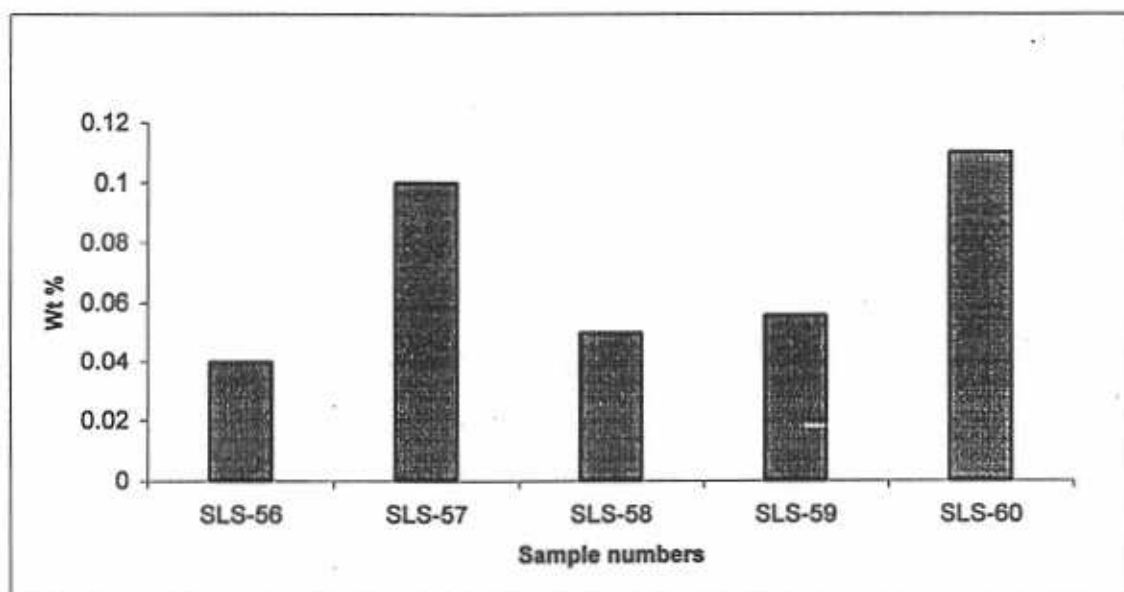


Figure 4.3 (h) Variation of sulphuric anhydride (SO_3) in siliceous limestone samples.

4.1.4 Maroon color clay

Maroon color clay is widely exposed in the study area. It is generally maroon in color and is soft in texture. The composition of these clay samples are given in Table 4.4 and the variation of various constituents are presented in Figure 4.4. It is clear from the Table and Figure that SiO_2 varies from 50.70 to 62.25 wt%, Al_2O_3 from 16.36 to 20.26 wt %, Fe_2O_3 from 5.69 to 9.24 wt % CaO from 5.25 to 11.35 wt % MgO from 2.55 to 5.10 wt %, Na_2O from 0.15 to 0.36 wt %, K_2O from 0.25 to 0.85 wt % and SO_3 varies from 0.05 to 0.26 wt %.

The average composition of the studied clay suggest that this clay on average contain $\text{SiO}_2 = 57.76$ wt%, $\text{Al}_2\text{O}_3 = 18.56$, $\text{Fe}_2\text{O}_3 = 7.59$ wt%, $\text{CaO} = 8.36$ wt%, $\text{MgO} = 3.87$ wt%, $\text{Na}_2\text{O} = 0.25$ %, $\text{K}_2\text{O} = 0.54$ % and $\text{SO}_3 = 0.16$ %. The alumina modulus (MA), silica modulus (MS) and lime saturation factor (LSF) of the studied limestone are 2.45, 2.21 and 0.04 respectively as shown in Table 4.4.

Table 4.4 Chemical Analysis of Maroon Color Clay Samples.

Analyte	Wt. %							Average
	MC-1	MC-2	MC-3	MC-4	MC-5	MC-8	MC-9	
SiO ₂	50.70	55.21	60.21	57.65	62.25	60.05	58.23	57.76
Al ₂ O ₃	19.85	19.21	18.30	17.32	18.65	20.26	16.36	18.56
Fe ₂ O ₃	7.54	7.69	7.25	9.24	5.69	6.98	8.74	7.59
CaO	11.35	9.67	5.25	9.82	7.25	7.20	7.98	8.36
MgO	3.82	4.62	5.10	2.55	3.45	3.3	4.25	3.87
Na ₂ O	0.36	0.21	0.25	0.15	0.24	0.25	0.29	0.25
K ₂ O	0.48	0.62	0.52	0.53	0.52	0.25	0.85	0.54
SO ₃	0.26	0.21	0.05	0.14	0.11	0.15	0.20	0.16
LOI	6.54	3.25	3.52	3.26	2.52	2.50	3.42	3.57
Total	100.90	100.70	100.50	100.70	100.70	100.90	100.30	100.67

Calculated on average basis: MA = 2.45; MS = 2.21; LSF = 0.04

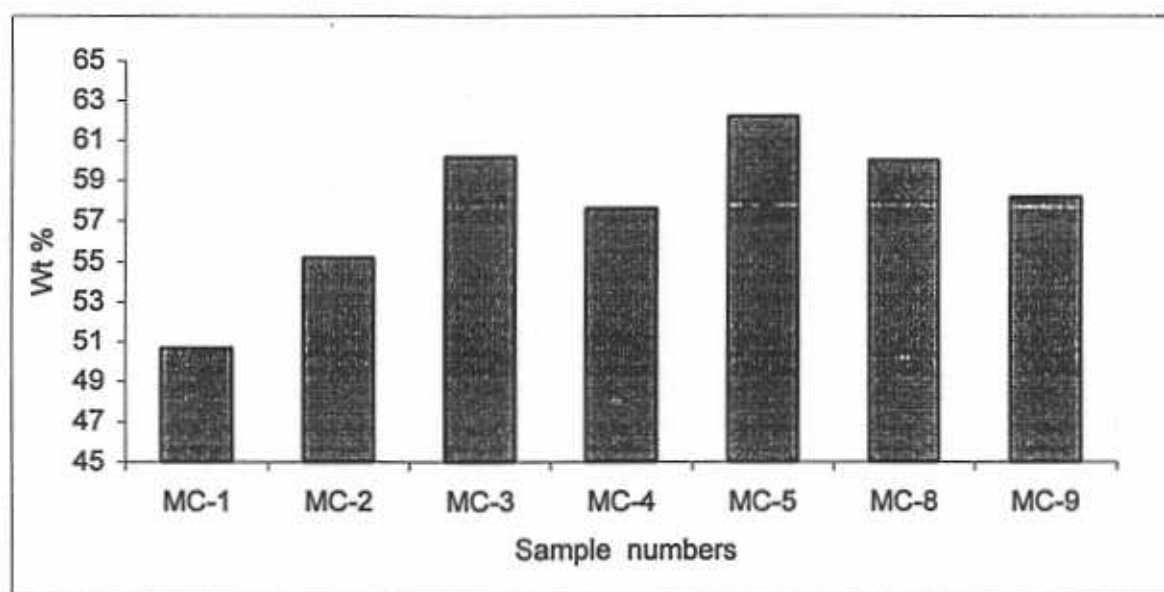


Figure 4.4 (a) Variation of silicon dioxide (SiO_2) in maroon color clay samples.

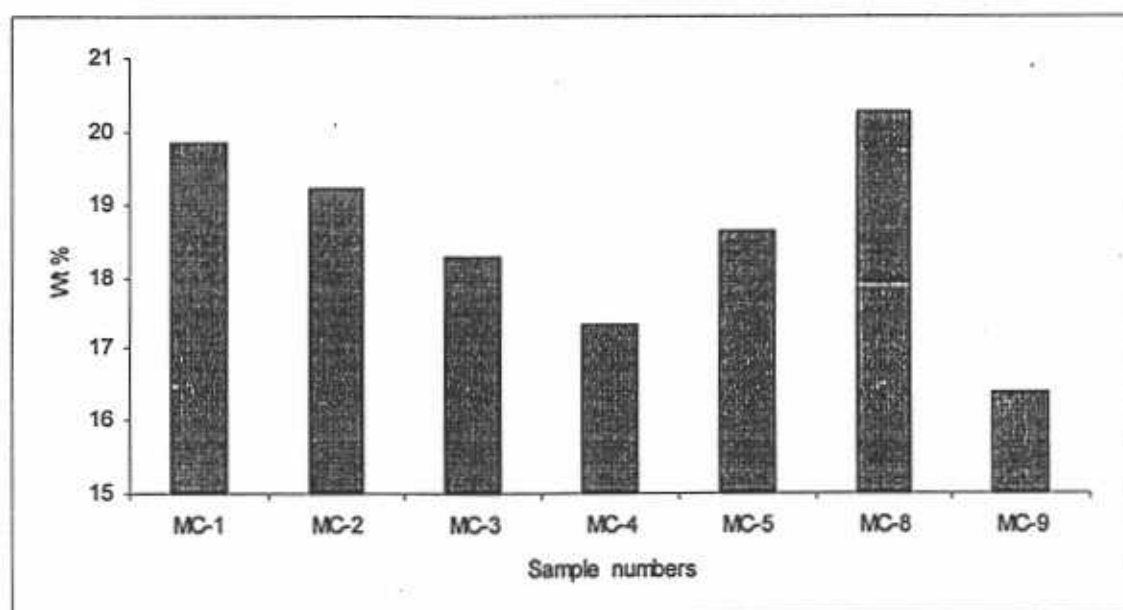


Figure 4.4 (b) Variation of aluminum oxide (Al_2O_3) in maroon color clay samples.

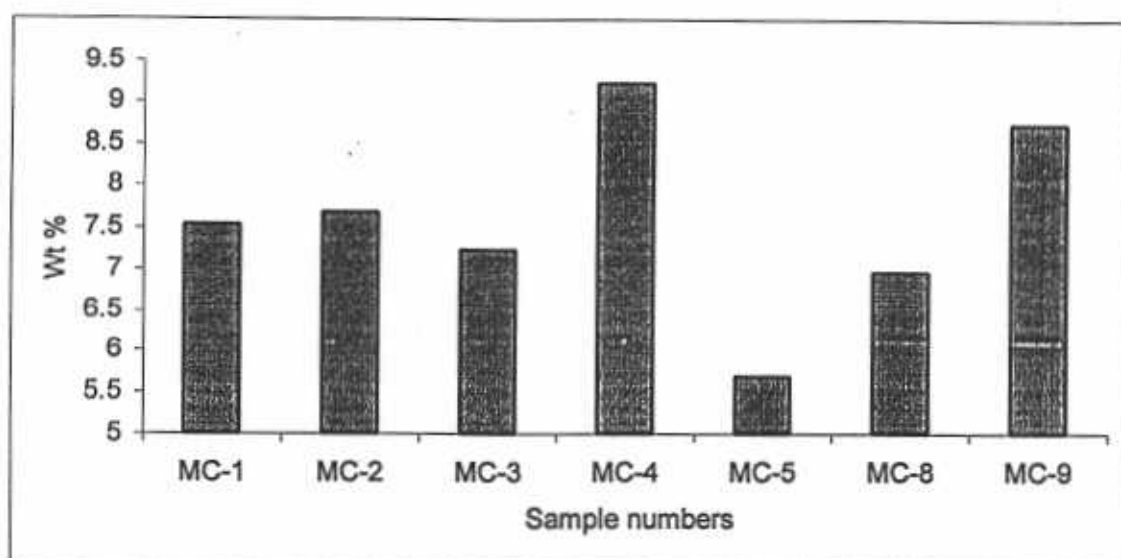


Figure 4.4 (c) Variation of iron oxide (Fe_2O_3) in maroon color clay samples.

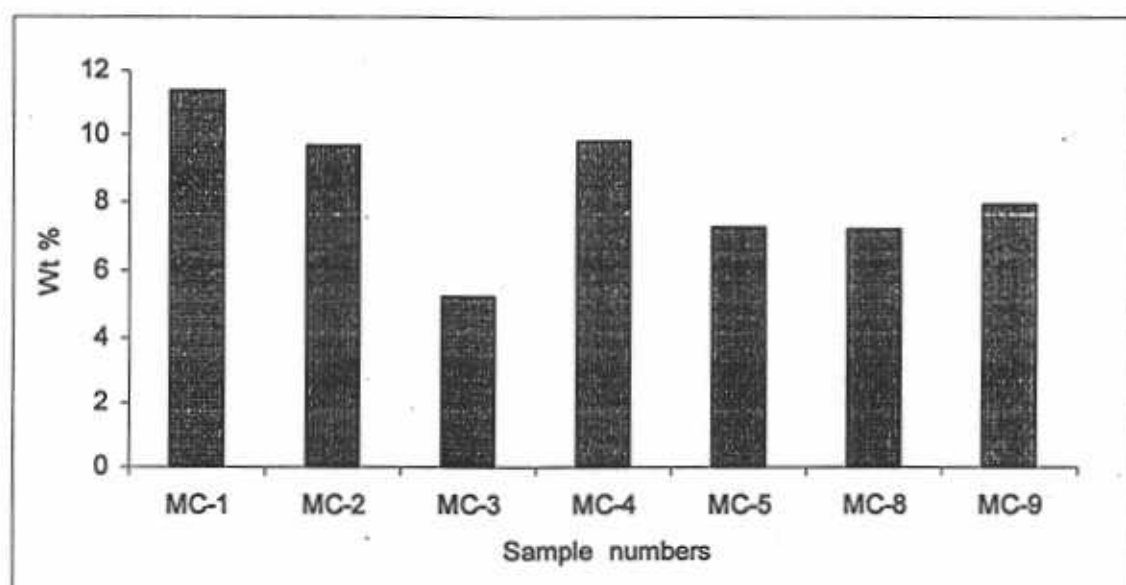


Figure 4.4 (d) Variation of calcium oxide (CaO) in maroon color clay samples.

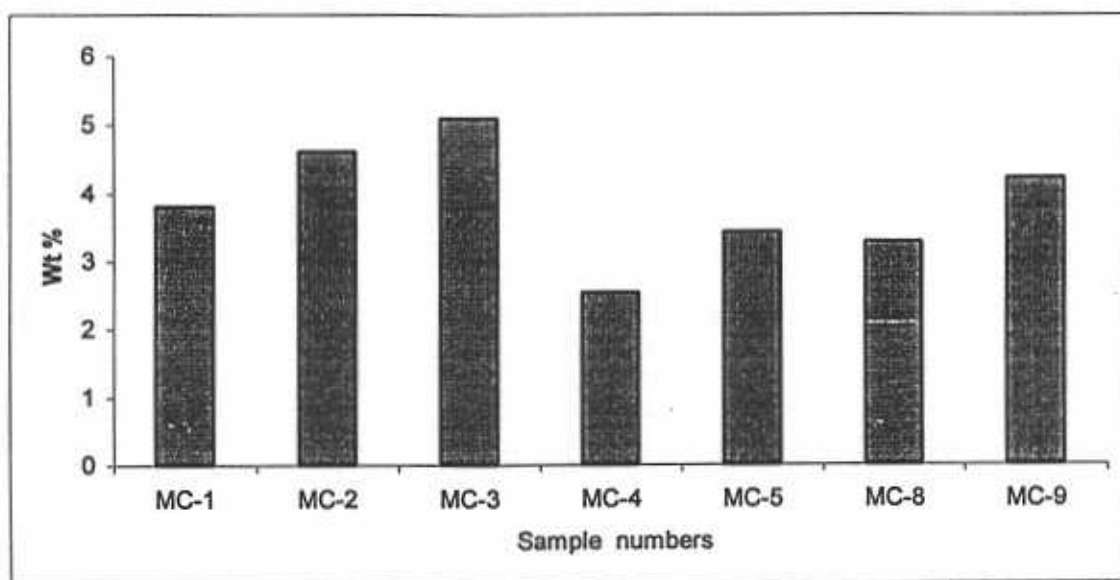


Figure 4.4 (e) Variation of magnesium oxide (MgO) in maroon color clay samples.

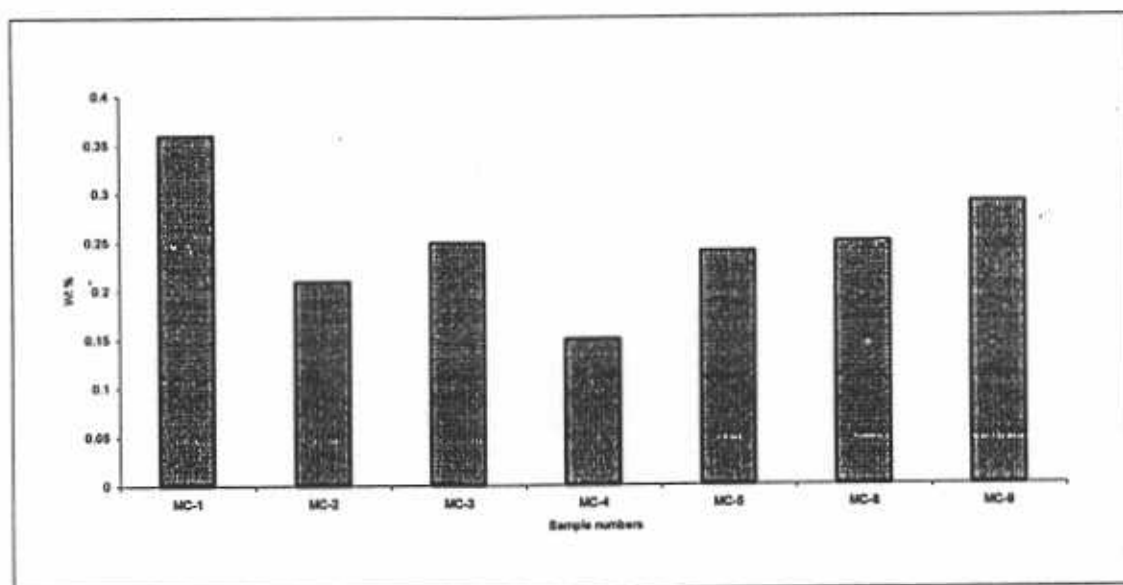


Figure 4.4 (f) Variation sodium oxides (Na_2O) in maroon color clay samples.

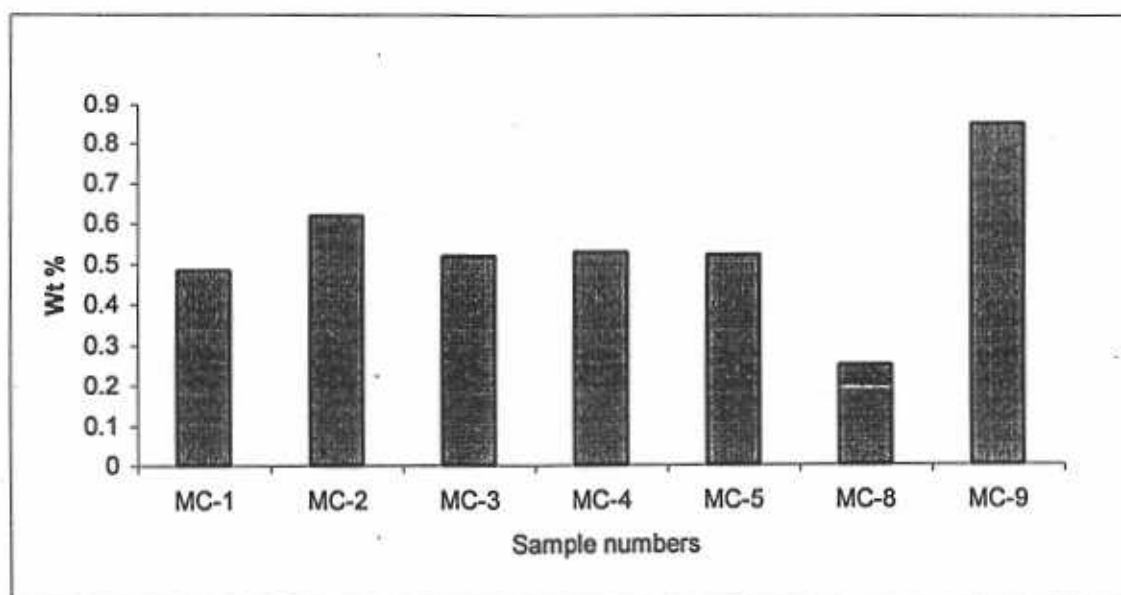


Figure 4.4 (g) Variation of potassium oxides (K_2O) in maroon color clay samples.

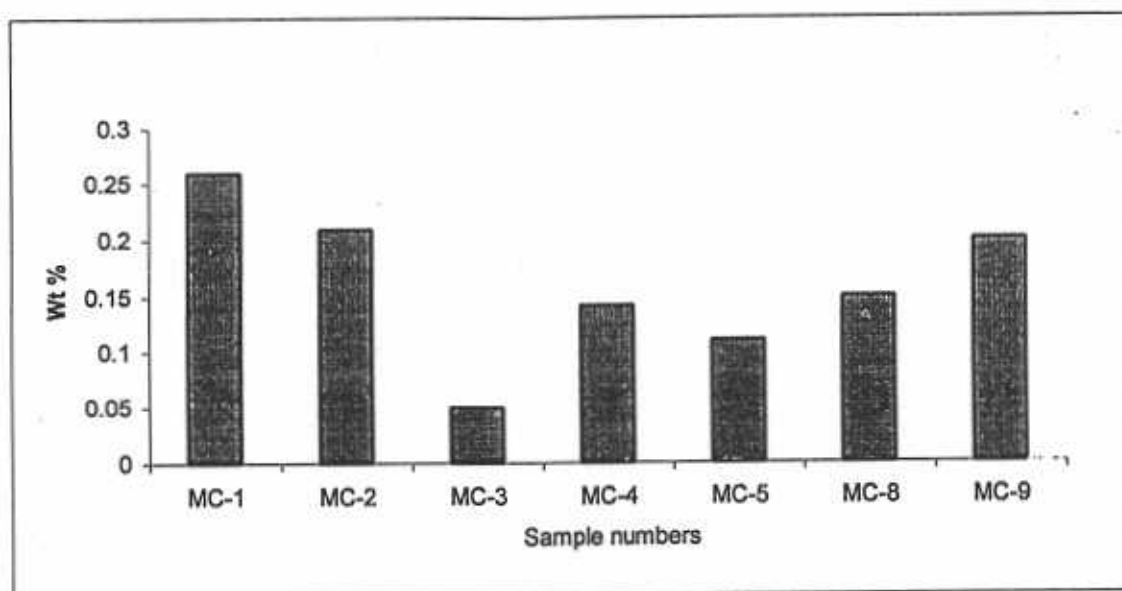


Figure 4.4 (h) Variation of sulphuric anhydride (SO_3) in maroon color clay samples.

4.1.5 Lacustrine Clay (LC)

Lacustrine clay (LC) is present in a vast area within Nizampur. It is various in colour from yellow to yellowish green. The composition of these clay samples are given in Table 4.5 and the variation of various constituents are presented in Figure 4.5. It is clear from the Table and Figure that SiO_2 varies from 57.57 (LC-49) to 66.85 wt% (LC-53), Al_2O_3 from 10.65 (LC-47) to 15.85 wt % (LC-19), Fe_2O_3 from 3.55 (LC-46) to 9.65 wt % (LC-47) CaO from 5.62 (LC-52) to 9.36 wt % (LC-49) MgO from 1.21 (LC-53) to 2.55 wt % (LC-49), Na_2O from 0.09 (LC-46) to 1.03 wt % (LC-47), K_2O from 1.26 (LC-19) to 1.97 wt % (LC-46) and SO_3 varies from 0.10 (LC-46) to 0.22 wt % (LC-47).

The average composition of the studied clay suggest that this clay on average contain $\text{SiO}_2 = 65.47$ wt%, $\text{Al}_2\text{O}_3 = 6.82$ wt%, $\text{Fe}_2\text{O}_3 = 6.82$ wt%, $\text{CaO} = 6.77$ wt%, $\text{MgO} = 1.79$ wt%, $\text{Na}_2\text{O} = 0.35$ %, $\text{K}_2\text{O} = 1.61$ % and $\text{SO}_3 = 0.18$ %. The alumina modulus (MA), silica modulus (MS) and lime saturation factor (LSF) of the studied limestone are 2.13, 3.06 and 0.03 respectively as shown in Table 4.5.

Table 4.5 Chemical Analysis of the Lacustrine Clay Samples.

Analyte	Wt. %									Average
	LC-19	LC-46	LC-47	LC-48	LC-49	LC-50	LC-51	LC-52	LC-53	
SiO ₂	64.23	69.5	66.35	65.90	57.57	66.65	66.85	65.35	66.85	65.47
Al ₂ O ₃	15.85	14.55	10.65	15.69	15.46	13.65	14.98	15.00	15.24	14.56
Fe ₂ O ₃	7.25	3.55	9.65	6.52	8.65	5.87	6.66	6.81	6.45	6.82
CaO	6.50	6.82	6.35	6.25	9.36	7.75	6.54	5.62	5.73	6.77
MgO	1.58	1.86	1.78	1.38	2.55	2.14	1.48	2.10	1.21	1.79
Na ₂ O	0.12	0.09	1.03	0.36	0.42	0.30	0.25	0.36	0.21	0.35
K ₂ O	1.26	1.97	1.67	1.66	1.66	1.68	1.52	1.56	1.54	1.61
SO ₃	0.10	0.10	0.22	0.18	0.21	0.21	0.21	0.21	0.21	0.18
LOI	3.25	2.31	2.55	2.05	4.25	2.54	2.15	3.21	2.65	2.77
Total	100.14	100.75	100.25	99.99	100.13	100.79	100.64	100.22	100.09	100.33

Calculated on average basis: MA = 2.13; MS = 3.06; LSF = 0.03

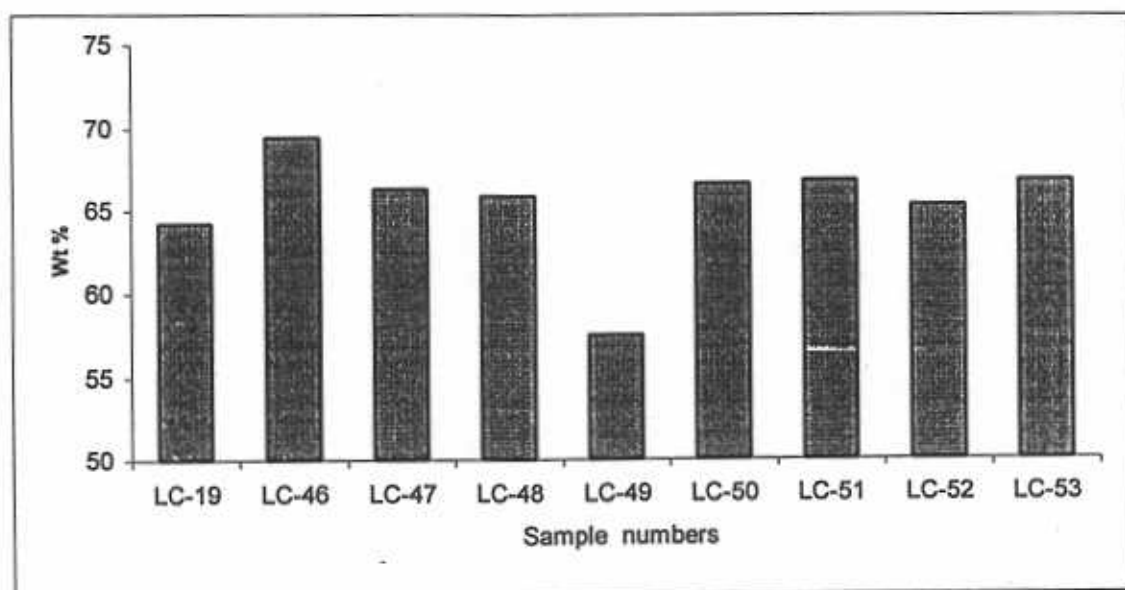


Figure 4.5 (a) Variation of silicon dioxide (SiO_2) in lacustrine clay samples.

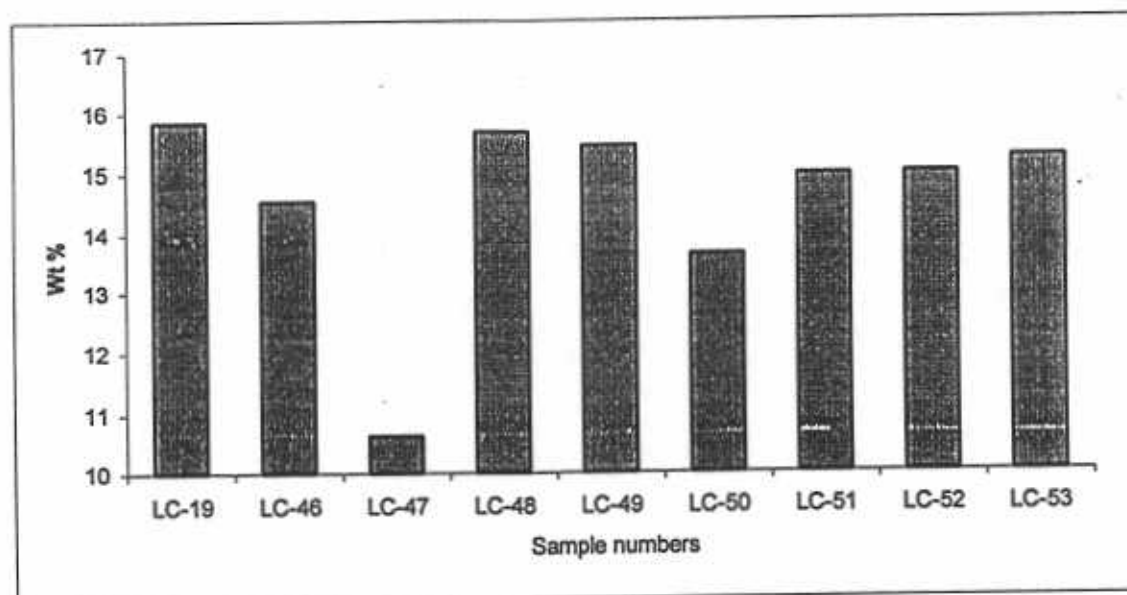


Figure 4.5 (b) Variation of aluminum oxide (Al_2O_3) in lacustrine clay samples.

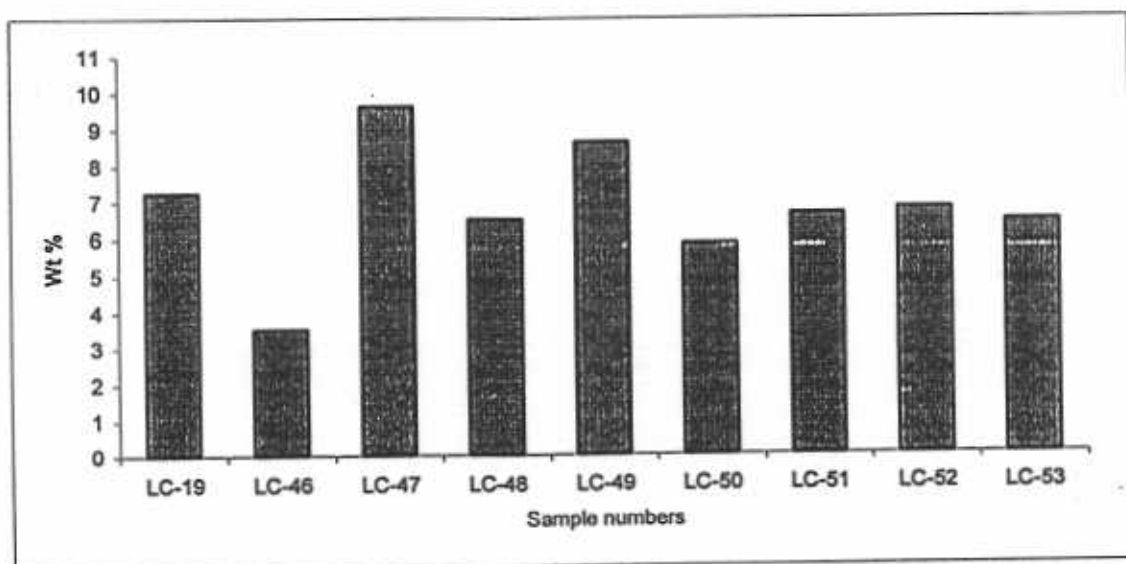


Figure 4.5 (c) Variation of iron oxide (Fe_2O_3) in lacustrine clay samples.

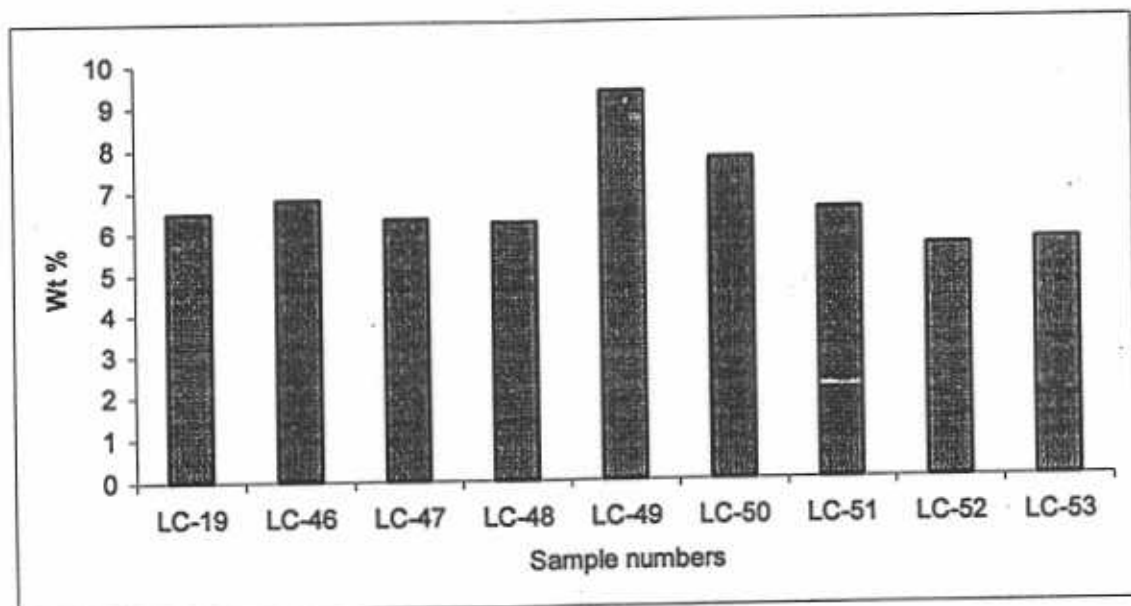


Figure 4.5 (d) Variation of calcium oxide (CaO) in lacustrine clay samples.

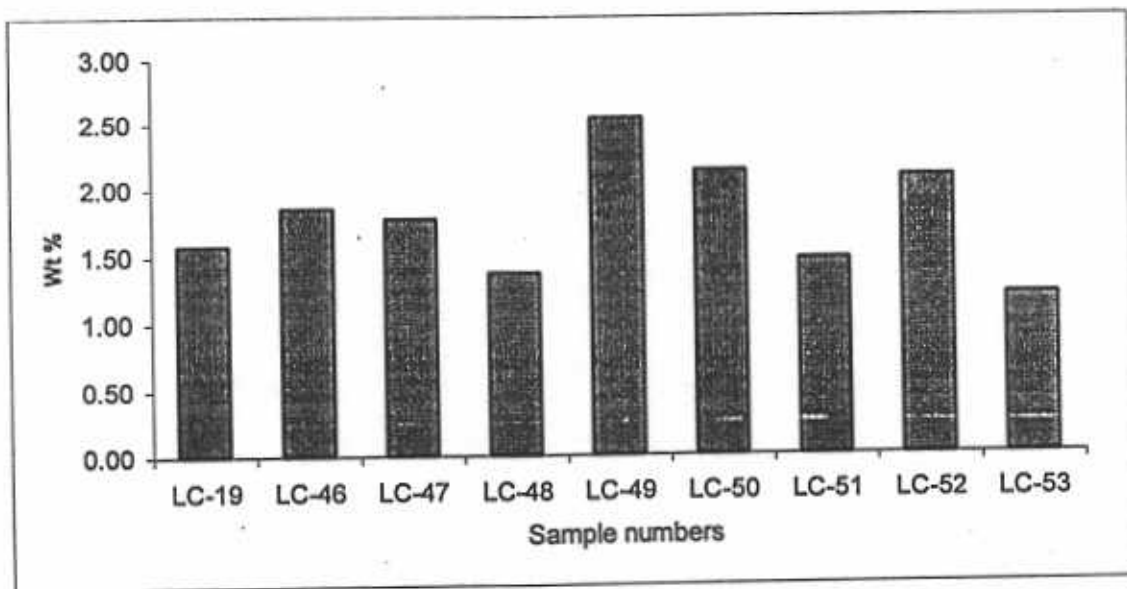


Figure 4.5 (e) Variation of magnesium oxide (MgO) in lacustrine clay samples.

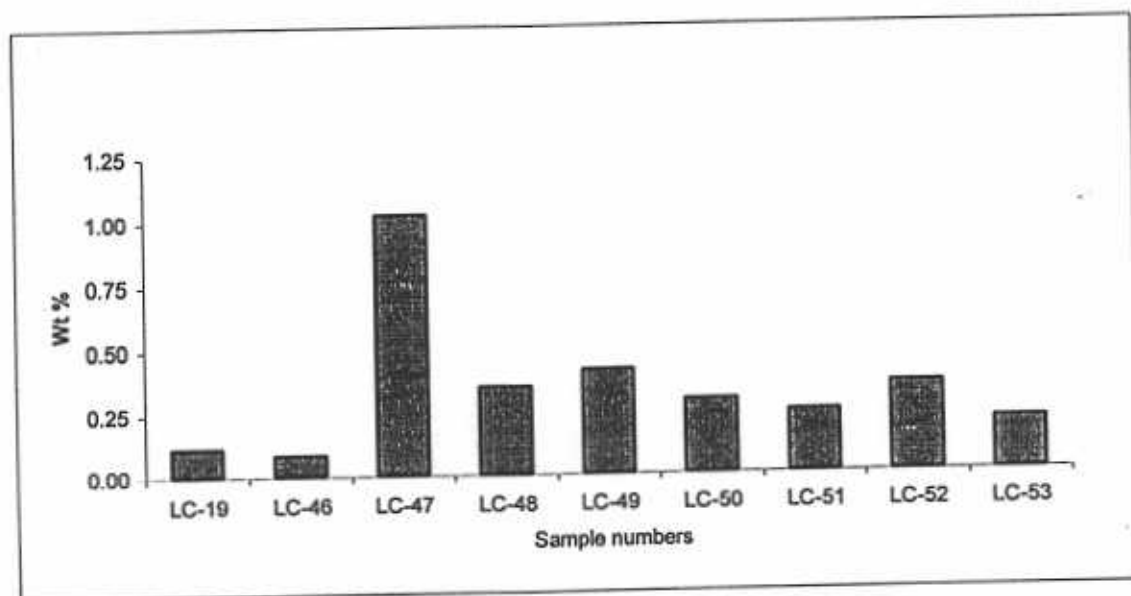


Figure 4.5 (f) Variation of sodium oxides (Na_2O) in lacustrine clay samples.

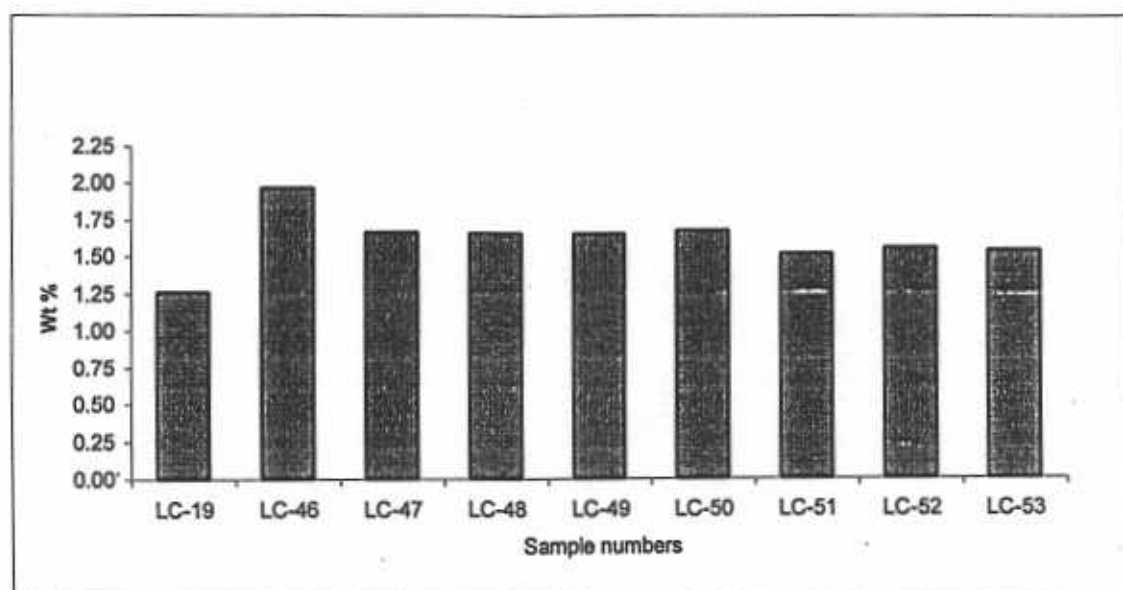


Figure 4.5 (g) Variation of potassium oxides (K_2O) in lacustrine clay samples.

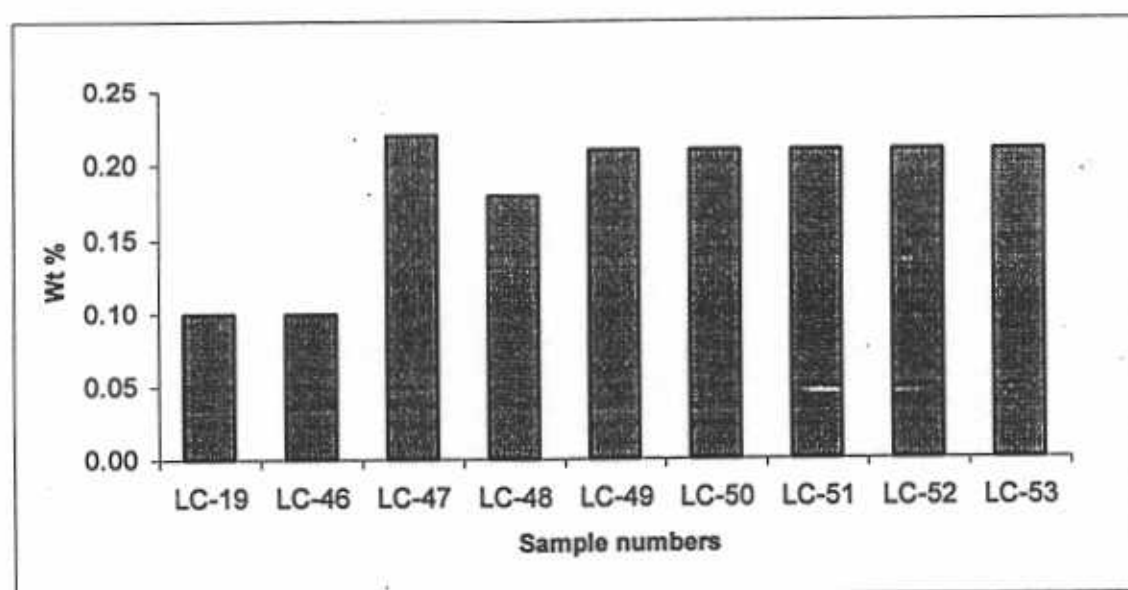


Figure 4.5 (h) Variation of sulphuric anhydride (SO_3) in lacustrine clay samples.

4.1.6 Green Colour Clay

Green colour clay is greenish in colour and is very hard. It is found in Darukhula and adjoining area of Nizampur. The chemical composition of green colour clay is indicated in Table 4.6 and Figure 4.6. From the Figure it is clear that this clay has variable composition. SiO_2 is ranging from 55.56 to 65.32 wt%, Al_2O_3 from 12.25 to 16.35 wt %, Fe_2O_3 from 6.31 to 8.35 wt %, CaO from 4.52 to 8.49 wt %, MgO from 1.27 to 2.55 wt %, Na_2O from 0.11 to 0.21 wt %, K_2O from 0.98 to 2.01 wt % and SO_3 is ranging from 0.09 to 0.18 wt %.

The average composition of the studied clay suggest that this clay on average contain SiO_2 , Al_2O_3 , Fe_2O_3 , CaO, MgO, Na_2O , K_2O and SO_3 , as 61.24 %, 14.38 %, 6.81 %, 7.49 %, 1.63 %, 0.17 %, 1.35 % and 0.15 % respectively as indicated in Table 4.6 The alumina modulus (MA) of the studies clay, calculated on average bases is 2.11, silica modulus (MS) is 2.89 and lime saturation factor (LSF) is 0.04.

Table 4.6 Chemical Analysis of the Green Colour Clay Samples.

Analyte	Wt. %					Average
	GC-12	GC-41	GC-42	GC-43	GC-44	
SiO ₂	65.32	63.65	62.35	59.32	55.56	61.24
Al ₂ O ₃	15.85	16.35	14.21	13.24	12.25	14.38
Fe ₂ O ₃	8.35	7.02	6.31	4.85	7.52	6.81
CaO	4.52	5.65	7.52	8.49	11.26	7.49
MgO	2.55	1.59	1.27	1.77	0.99	1.63
Na ₂ O	0.11	0.15	0.21	0.18	0.21	0.17
K ₂ O	0.98	1.26	1.45	2.01	1.05	1.35
SO ₃	0.18	0.18	0.16	0.16	0.09	0.15
LOI	3.69	5.00	7.25	10.31	11.41	7.53
Total	101.55	100.85	100.74	100.33	100.34	100.76

Calculated on average basis: MA = 2.11; MS = 2.89; LSF = 0.04

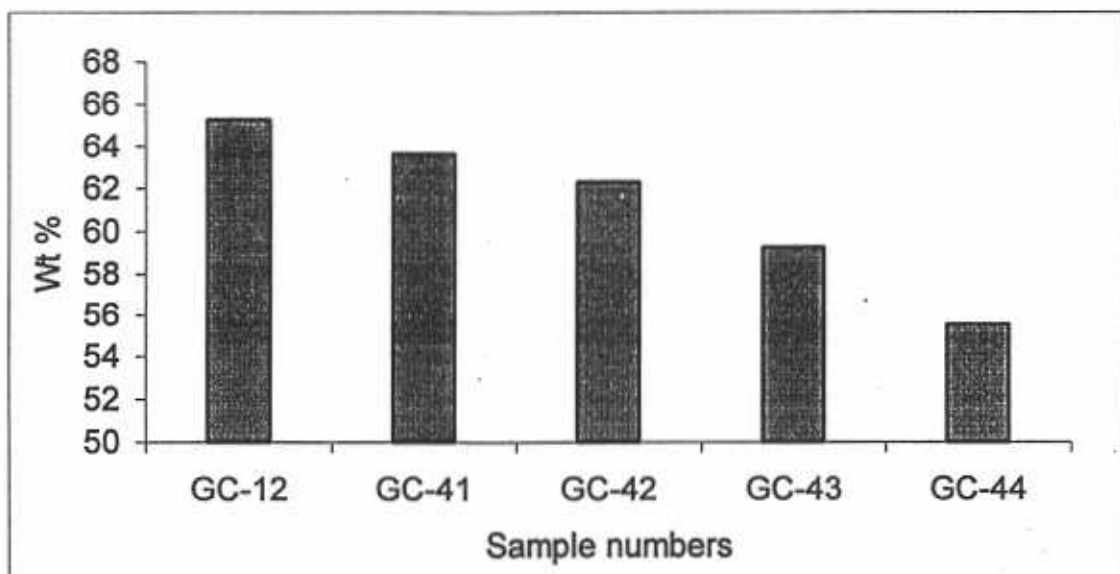


Figure 4.6 (a) Variation of silicon dioxide (SiO₂) in green colour clay samples.

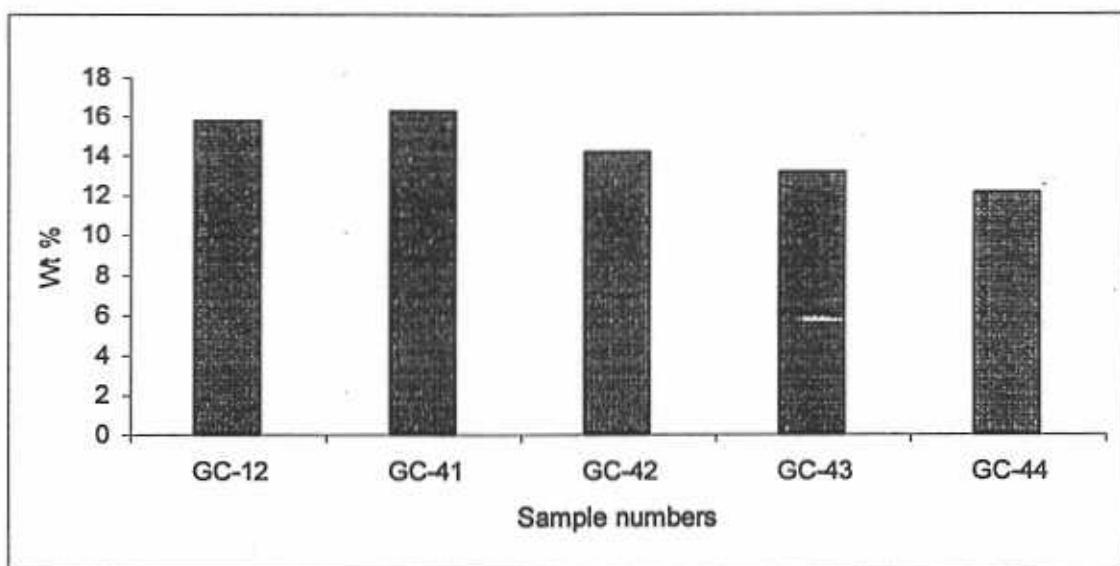


Figure 4.6 (b) Variation of aluminum oxide (Al₂O₃) in green colour clay samples.

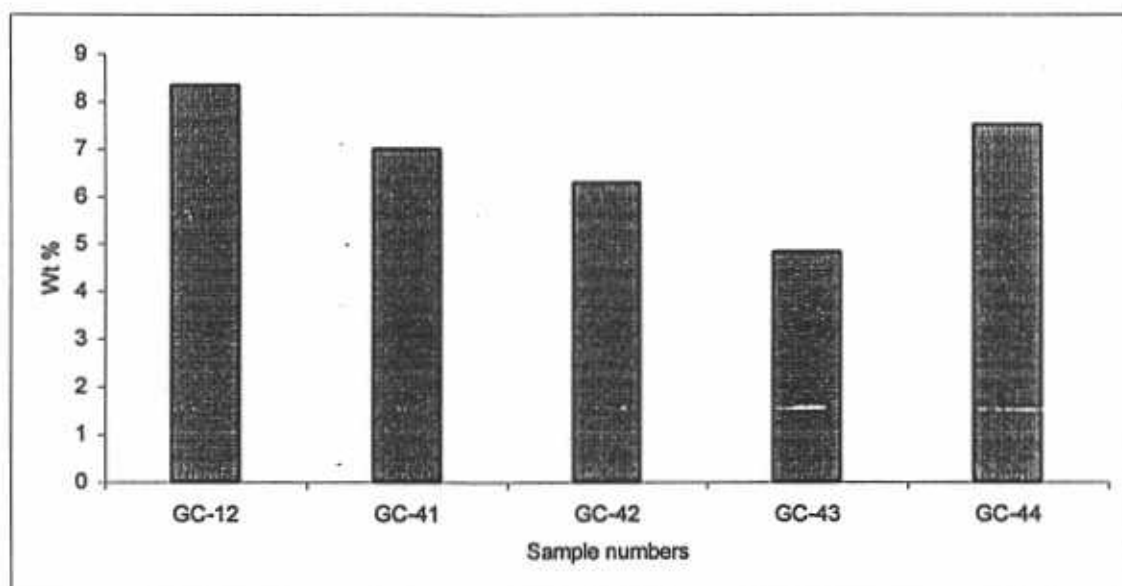


Figure 4.6 (c) Variation of iron oxide (Fe_2O_3) in green colour clay samples.

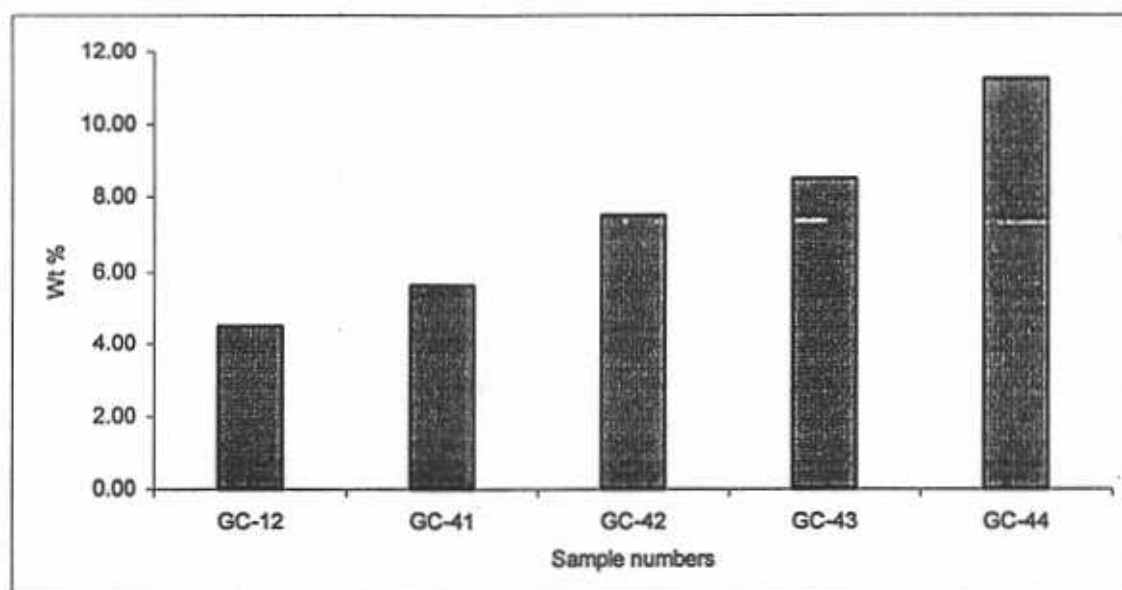


Figure 4.6 (d) Variation of calcium oxide (CaO) in green colour clay samples.

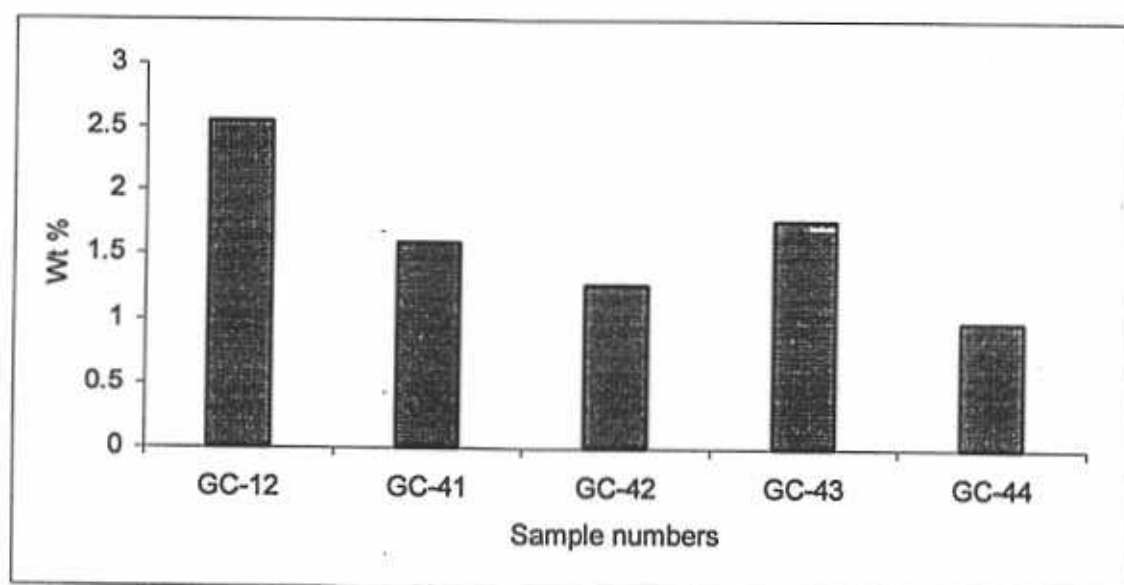


Figure 4.6 (e) Variation of magnesium oxide (MgO) in green colour clay samples.

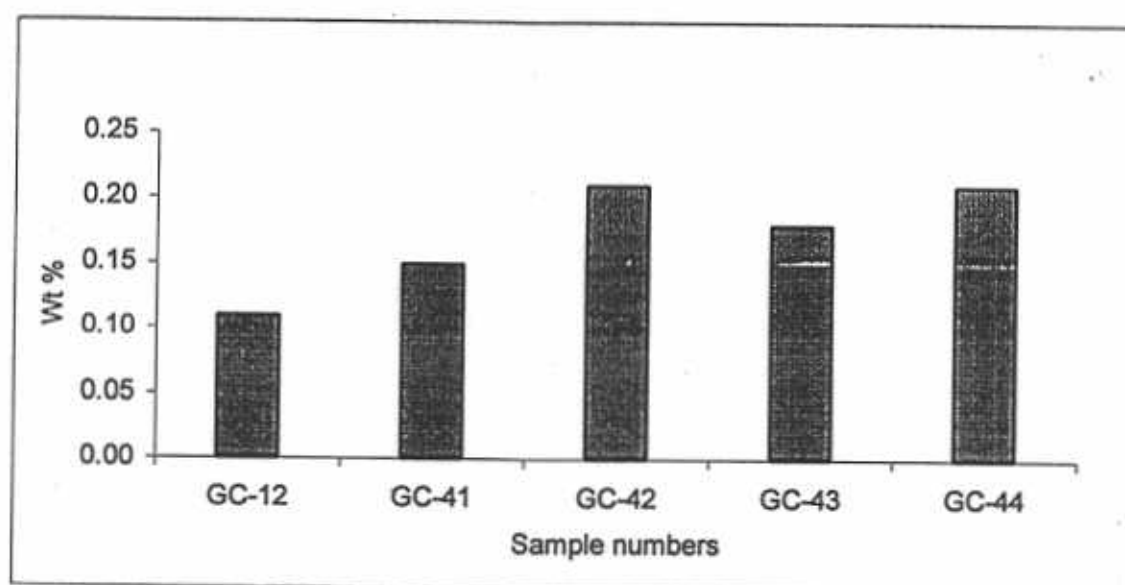


Figure 4.6 (f) Variations of sodium oxides (Na_2O) in green colour clay samples.

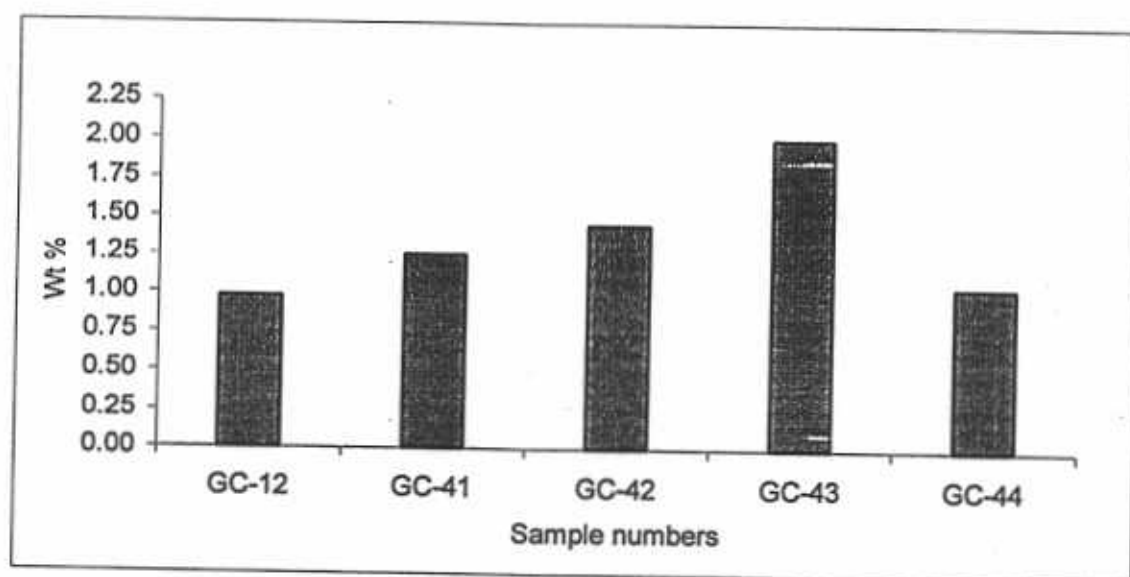


Figure 4.6 (g) Variations of potassium oxides (K_2O) in green colour clay samples.

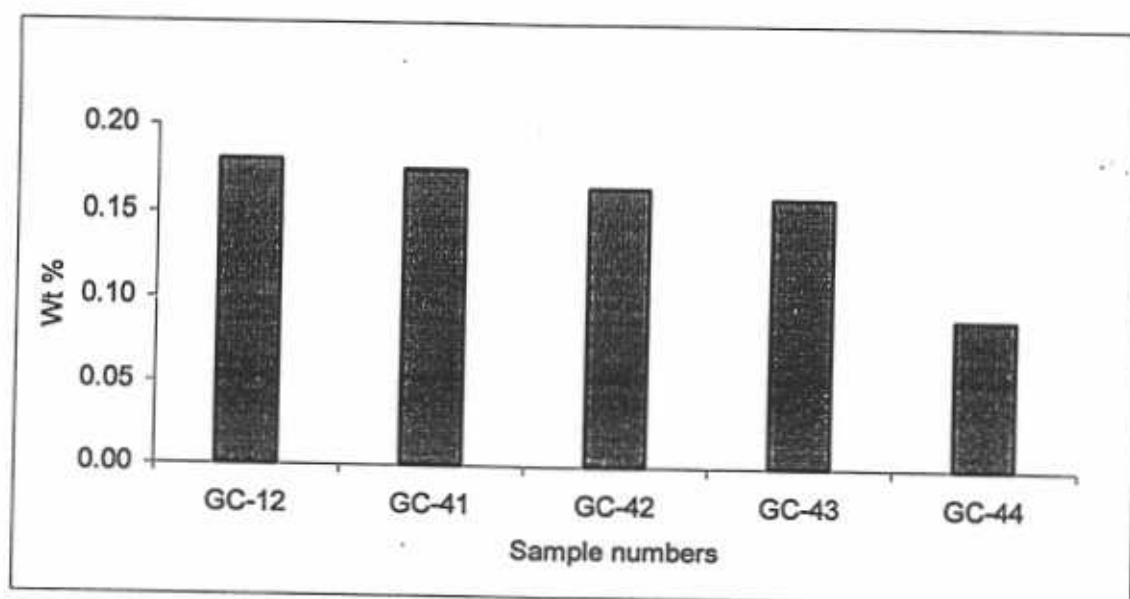


Figure 4.6 (h) Variations of sulphuric anhydride (SO_3) in green colour clay samples.

4.2 SUITABILITY OF LIMESTONE AND CLAY OF THE STUDY AREA FOR CEMENT MANUFACTURING

4.2.1 Lime Stone

It is clear from the chemical data of various types of limestone of the study area that high grade limestone (Table 4.1) has a very high lime content and low silica, iron, and alumina which, resulted in a very high lime saturation factor (LSF) and low silica modulus (MS). It is very suitable for cement manufacturing, but the requirement of iron in preparing high strength Portland cement and sulfate resisting cement from this limestone can not be fulfilled by adding only clay with it. The only solution to this problem is that some amount of iron rich material like laterite should be used with this limestone. The low alkalis (Na_2O and K_2O) in the high grade limestone is good for cement manufacturing.

Since in the manufacturing of white cement, negligible amount of iron is preferred, therefore, this limestone can be used for the manufacturing of such cement. The white cement requires higher amount of alumina in order to have high alumina modulus. For this purpose small amount of high alumina clay may be used in the manufacturing of white cement.

Darukhula limestone (Table 4.2) contains comparatively greater amount of silica and alumina and smaller amount of calcium which make it more important for high strength Portland cement. The silica and alumina contents of Darukhula limestone can be compensated by clay but the iron content can not be fulfilled by clay. The alkalis in this limestone are in smaller quantities which make it suitable for all types of cements. For the manufacturing of high strength Portland cement and sulfate resisting cement some laterite may be used to compensate for the percentage of iron. This lime stone is not appropriate to be used alone in the manufacture of white cement due to its comparatively low calcium and high silica.

Siliceous limestone (Table 4.3), on the other hand, is different from both high grade limestone and Darukhula limestone due to a greater percentage of silica. This lime stone can be very easily used in cement manufacturing due to its high silica contents. As the alumina and iron in this limestone are low, this makes it comparatively more suitable for manufacturing sulfate resisting cement. Because of

the high silica contents of siliceous limestone, its use in cement manufacturing is not possible, except by mixing with the high grade lime of the study area.

4.2.2 Clay

Maroon color clay of (Table 4.4) has 58 % silica which makes it suitable for the manufacturing of all types of high strength Portland and sulfate resisting cements. The silica content of this clay is smaller while the alumina content is greater than other types of clays found in the study area. Alkalies are in permissible a range which makes it more suitable for high strength and sulphate resisting cements. Thus this clay can be used with all types of limestones and can also be mixed with other types of clays.

Lauustrine clay (Table 4.5) is the richest clay in silica which can be used in very small quantity in cement manufacturing. Its high alkalies contents make it less important. However, it can be easily used with high grade lime stone or in combination with other clays for the manufacturing of high strength Portland and sulphate resisting cement.

Green colour clay (Table 4.6) is somewhat similar to that of laustrine clay with a very little variation in chemical composition. It has calcium oxide in comparatively greater quantity. This clay can be used in combination of all types of the clay of the study area for the manufacture of cement.

RESULTS AND DISCUSSIONS

Part – 2

4.3 RAW MIX DESIGNING AND CLINKERIZATION

In the first part of this research work, the raw material was analyzed. In this part different raw mixes were designed and subjected to clinkerization. The clinkers thus formed were analyzed and compared with the Standard Specifications. Only those raw mixes have been reported which meet the Standard Specification. It should be noted that the designing of raw mixes were made on prediction bases, such that the prospective clinker would contain constituents meeting the standard specification. However, some of the raw mixes did not meet the specifications and not included in this report.

4.3.1 Raw mix Designing for High Strength Portland Cement (HSPC)

Raw material such as limestone and clay of the studied area were mixed in different proportions and various types of raw mix were prepared for further processing for the preparation of cement. Four types of raw mix are given in Table 4.7. It is clear from the Table that all the three types of limestone and clay are used in raw mix designing for high strength Portland cement. In the first blend high grade limestone was mixed with lacustrine clay. In the second blend, Darukhula limestone was mixed with green colour clay. In the third blend, Darukhula limestone and lacustrine clay were mixed, while in the fourth blend two types of limestones i.e. siliceous and high grade limestone were mixed with maroon colour clay.

In order to bring the iron concentration as per with the standard specification of cement, laterite (iron rich clay) of chemical composition, given in Table 4.8, were also mixed in different proportions in these raw mix. The chemical compositions of these raw mixes are presented in Table 4.9. The Table shows that the Raw mix-1 has 14.60% SiO_2 , 3.38% Al_2O_3 , 2.28% Fe_2O_3 , 42.55% CaO , 0.98% MgO , 0.18% Na_2O , 0.46% K_2O , 0.10% SO_3 ; Raw mix-2 has 14.46% SiO_2 , 3.65% Al_2O_3 , 2.11% Fe_2O_3 , 42.29% CaO , 0.97% MgO , 0.23% Na_2O , 0.42% K_2O , 0.07% SO_3 ; Raw mix-3 has 14.53% SiO_2 , 3.38% Al_2O_3 , 2.28% Fe_2O_3 , 42.55% CaO , 0.98% MgO , 0.18% Na_2O ,

0.46% K_2O , 0.10% SO_3 ; and raw mix-4 has 14.17% SiO_2 , 4.29% Al_2O_3 , 2.37% Fe_2O_3 , 42.18% CaO , 1.31% MgO , 0.16% Na_2O , 0.34% K_2O , 0.10% SO_3 (Table 4.9)

MA, MS and LSF in raw mix -1 are 1.68, 2.39, 0.91, in raw mix -2 are 1.74, 2.50 and 0.92, in raw mix-3 are 1.74, 2.60 and 0.91 and in raw mix-4 are 1.81, 2.13 and 0.91 respectively. The normal range of MA is 1.3 - 2.5. If it goes above 2.5, viscous slag and high early strength occur and if it goes below 1.3, then fluid slag, low early strength and low heat of hydration occur. The usual range of MS is 2 - 3. For MS less than 2, burning become very easy but excessive liquid phase and low strength cement is obtained. On the other hand if the MS reaches up to 3, then the high strength cement is obtained, however the burning become very difficult. For MS more than 3, no clinkerization takes place at all. The normal range of LSF is 0.90 - 0.98 but if it is 0.8, it does not create any problem in cement manufacturing process and cement strength, however it should not go below 0.80. From the Table 4.9 it is clear that MA, MS and LSF of all the four raw mixes for high strength Portland cements are within the range.

The raw mixes of different composition were subjected to clinkerization. The clinker thus formed were named as clinker-1, clinker-2, clinker-3 and clinker-4, and analyzed according to British and Pakistan Standard Specifications (BS and PS). The chemical composition along with the moduli and clinker potential are presented in Table 4.10, and are graphically compared in Figure 4.7 - 4.10. Figure 4.7 and 4.8 shows the comparison of major and minor element oxides in clinker for high strength Portland cements. The percentages of major and minor element oxides of all the four clinkers are almost the same which shows that all types of limestone and clay of the study area are suitable for cement manufacturing, when used in different proportion. MA of the resulting clinkers ranges from 1.67 to 1.74, MS from 2.37 to 2.55 and LSF from 0.91 to 0.92 (Figure 4.9). The comparison of clinker potential of the four clinkers for high strength Portland cement is shown in Figure 4.10 which shows that C_3S varies from 50.89 to 53.54, C_2S 23.74 to 26.42, C_3A 8.97 to 9.82 and C_4AF from 9.94 to 10.84.

The clinkers were converted into cement, which were named as HSPC-1, HSPC-2, HSPC-3, and HSPC-4. The cements were tested for all possible physical parameters as per requirement of British and Pakistan Standard Specifications (BS

and PS) like blaine, compressive strength, setting time, consistency, and expansion and chemical parameters like insoluble residue, loss on ignition, and percent composition etc represented in Table 4.12. Table 4.12 also shows the British and Pakistan Standard Specifications. The minimum limit of compressive strength for three, seven, and twenty eight days is 3336, 4690, 5960 PSI respectively according to British and Pakistan Standard Specifications. Similarly the minimum initial setting time for high strength Portland cement is 45 minutes and the maximum final setting time is 10 hours, while the minimum range of consistency is 27 %. The upper limit of Lechatlier expansion of high strength Portland cement is 10 mm while the minimum limit of blaine is 2250 Sq. cm / gram according to British and Pakistan Standard Specifications. The upper limit of loss on ignition and insoluble residue are 3.0 % and 1.5 % respectively. Figure 4.11 to 4.16 show the comparison of compressive strength, blaine, setting time, Lechatlier expansion, loss on ignition, and insoluble residue of high strength Portland cements obtained from the raw material of the study area with the Standard. As clear from the Figures, all the mentioned physical and chemical parameters meet the British and Pakistan Standard Specifications.

Table 4.7 Blending ratio of Raw Mix for High Strength Portland Cement

Raw Mix Title	Material taken	Percentage
Raw mix -1	High grade lime stone	78
	Lacustrine clay	20
	Laterite	2
	Total	100
Raw mix -2	Darukhula Lime stone	82
	Green colour clay	16
	Laterite	2
	Total	100
Raw mix -3	Darukhula Limestone	83
	Lacustrine clay	15
	Laterite	2
	Total	100
Raw mix -4	High grade lime stone	63
	Siliceous Limestone	16
	Maroon Color Clay	19
	Laterite	2
	Total	100

Table 4.8 Chemical Composition of Laterite

Analyte	Wt. %
SiO ₂	43.53
Al ₂ O ₃	13.54
Fe ₂ O ₃	37.66
CaO	0.88
MgO	1.55
Na ₂ O	0.45
K ₂ O	0.88
SO ₃	0.85

Table 4.9 Chemical Analysis of Raw Mixes for High Strength Portland Cement

Analyte	Wt. %			
	Raw Mix-1	Raw Mix-2	Raw Mix-3	Raw Mix-4
SiO ₂	14.60	14.46	14.53	14.17
Al ₂ O ₃	3.83	3.65	3.55	4.29
Fe ₂ O ₃	2.28	2.11	2.04	2.37
CaO	42.55	42.29	42.09	42.18
MgO	0.98	0.97	0.99	1.31
Na ₂ O	0.18	0.23	0.25	0.16
K ₂ O	0.46	0.42	0.44	0.34
SO ₃	0.10	0.07	0.08	0.10
LOI	34.00	33.85	34.12	34.22
Total	98.98	98.05	98.09	99.14
Moduli				
MA	1.68	1.74	1.74	1.81
MS	2.39	2.50	2.60	2.13
LSF	0.91	0.92	0.91	0.91

Table 4.10 Chemical Analysis of Clinker for High Strength Portland Cement

Analyte	wt. %			
	Clinker-1	Clinker-2	Clinker-3	Clinker-4
SiO ₂	22.60	22.4	22.50	22.36
Al ₂ O ₃	5.98	5.68	5.58	5.48
Fe ₂ O ₃	3.56	3.27	3.28	3.28
CaO	65.95	65.59	65.24	65.18
MgO	0.88	0.55	0.88	0.75
Na ₂ O	0.34	0.20	0.18	0.12
K ₂ O	0.61	0.68	0.64	0.73
SO ₃	0.20	0.11	0.14	0.13
LOI	1.10	0.98	0.99	1.08
Free lime (CaO _{free})	1.26	1.26	1.26	1.22
Liquid Phase	27.98	25.94	25.96	25.55
Moduli				
MA	1.68	1.74	1.70	1.67
MS	2.37	2.5	2.54	2.55
LSF	0.91	0.92	0.91	0.92
Clinker Potential				
C ₃ S	50.89	53.63	52.02	53.54
C ₂ S	26.42	23.78	25.29	23.74
C ₃ A	9.82	9.52	9.237	8.97
C ₄ AF	10.82	9.94	9.97	9.97
Burnability Factor (BF)	20.11	21.63	21.21	21.62

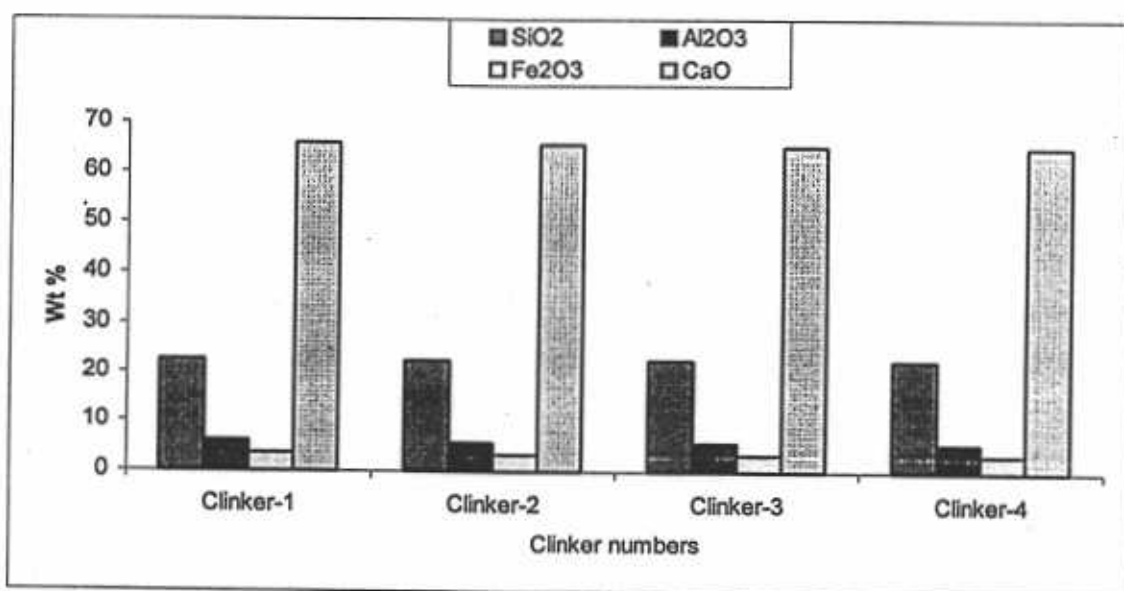


Figure 4.7 Comparison of major element oxides in clinker for high strength portland cement.

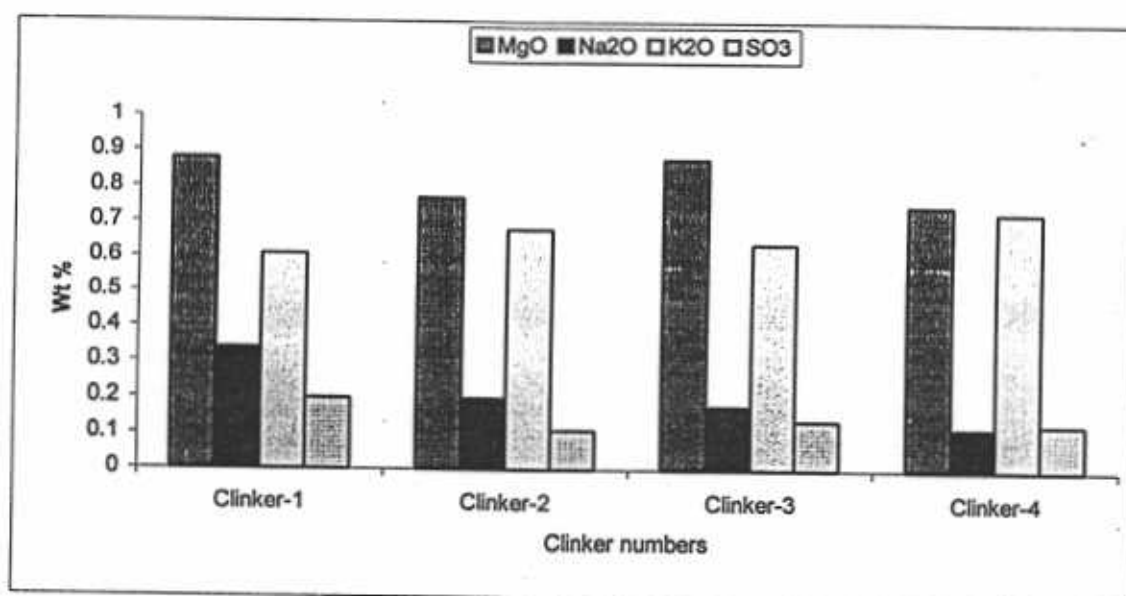


Figure 4.8 Comparison of minor element oxides in clinker for high strength portland cement.

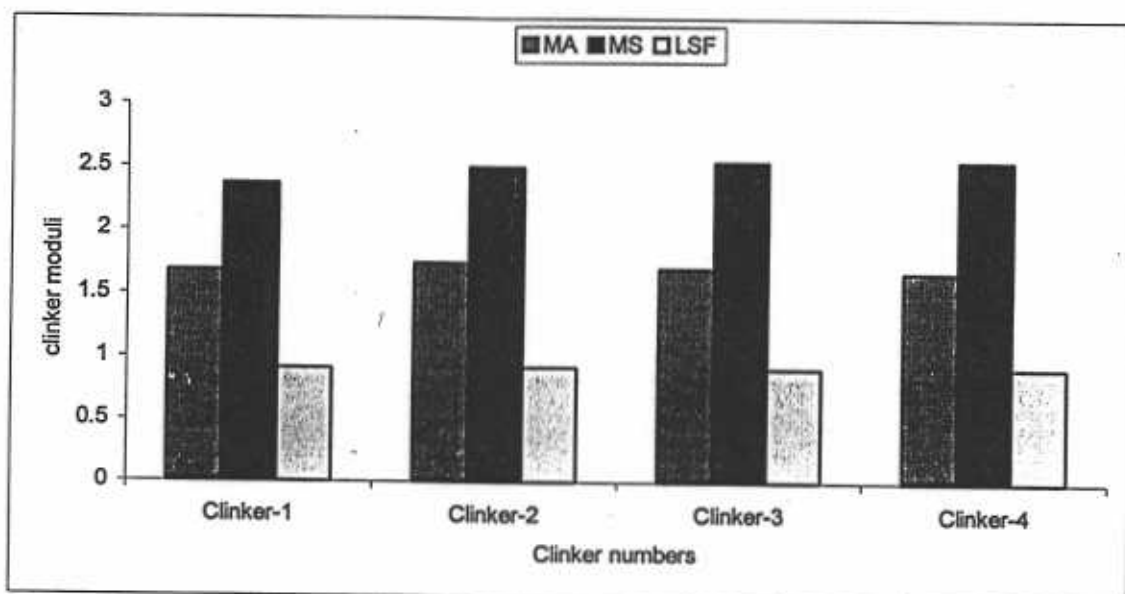


Figure 4.9 Comparison of the moduli in the clinker for high strength portland cement.

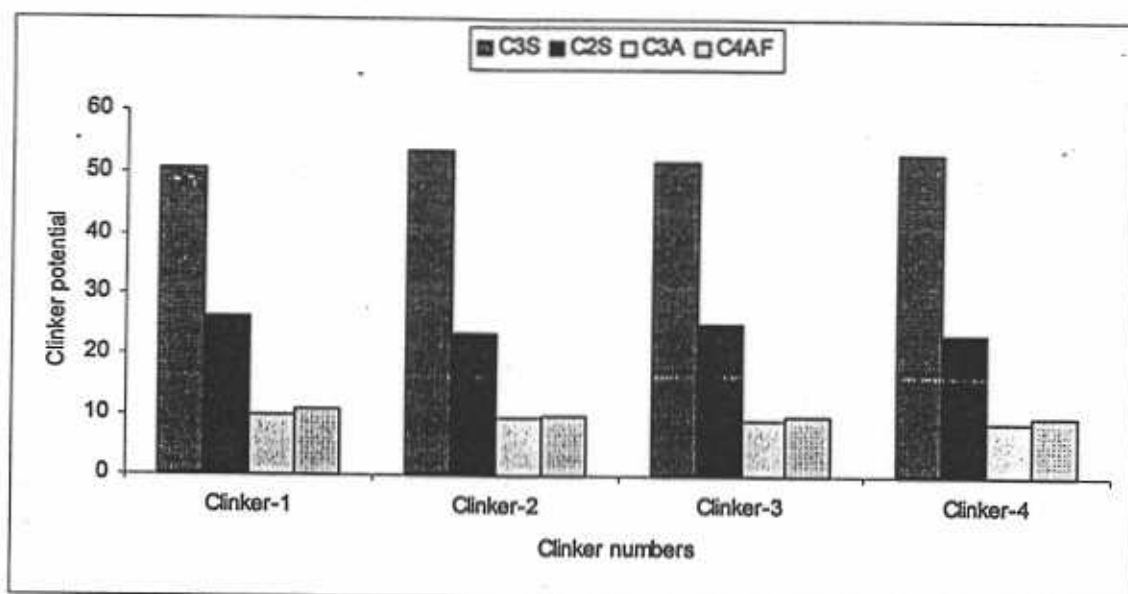


Figure 4.10 Comparison of clinker potential in the clinker for high strength portland cement.

Table 4.11 Chemical Composition of High Strength Portland Cement

Analyte	Wt. %			
	HSPC-1	HSPC-2	HSPC-3	HSPC-4
SiO ₂	21.55	21.36	21.46	21.32
Al ₂ O ₃	5.69	5.41	5.31	5.22
Fe ₂ O ₃	3.39	3.11	3.12	3.12
CaO	64.25	63.9	63.57	63.51
MgO	0.85	0.53	0.85	0.72
Na ₂ O	0.33	0.2	0.18	0.12
K ₂ O	0.59	0.65	0.62	0.70
SO ₃	2.47	2.38	2.41	2.40
Moduli				
MA	1.68	1.74	1.7	1.67
MS	2.37	2.51	2.54	2.56
LSF	0.93	0.94	0.93	0.94
Cement Potential				
C ₃ S	47.61	50.21	48.68	50.12
C ₂ S	25.90	23.39	24.81	23.34
C ₃ A	9.35	9.07	8.80	8.55
C ₄ AF	10.30	9.46	9.49	9.49

Table 4.12 Physical and Chemical Parameters of High Strength Portland Cement

Parameter	Results					
	HSPC-1	HSPC-2	HSPC-3	HSPC-4	Standard (BS &PS)	
Physical Testing						
Compressive Strength (PSI)	3 Days	3980	4580	4150	4110	3336 PSI (Min)
	7 Days	5430	5860	5460	5390	4690 PSI (Min)
	28 Days	6988	7140	6850	6520	5960 PSI (Min)
Setting Time (minute)	Initial	120	145	145	165	45 Minutes (Min)
	Final	210	290	260	270	10 Hours (Max)
Consistency (%)		30	29	29	29	27% minimum
Expansion (Lechatlier) mm		0.75	0.88	0.75	0.24	10mm (Max)
Blaine (sq cm/gram)		2900	3000	2950	2910	2250 Sq cm/g (Min)
Chemical Testing						
Loss on Ignition (%)		1.11	0.85	0.92	0.74	3.0 (Max)
Insoluble Residue (%)		0.18	0.31	0.33	0.44	1.5 (Max)

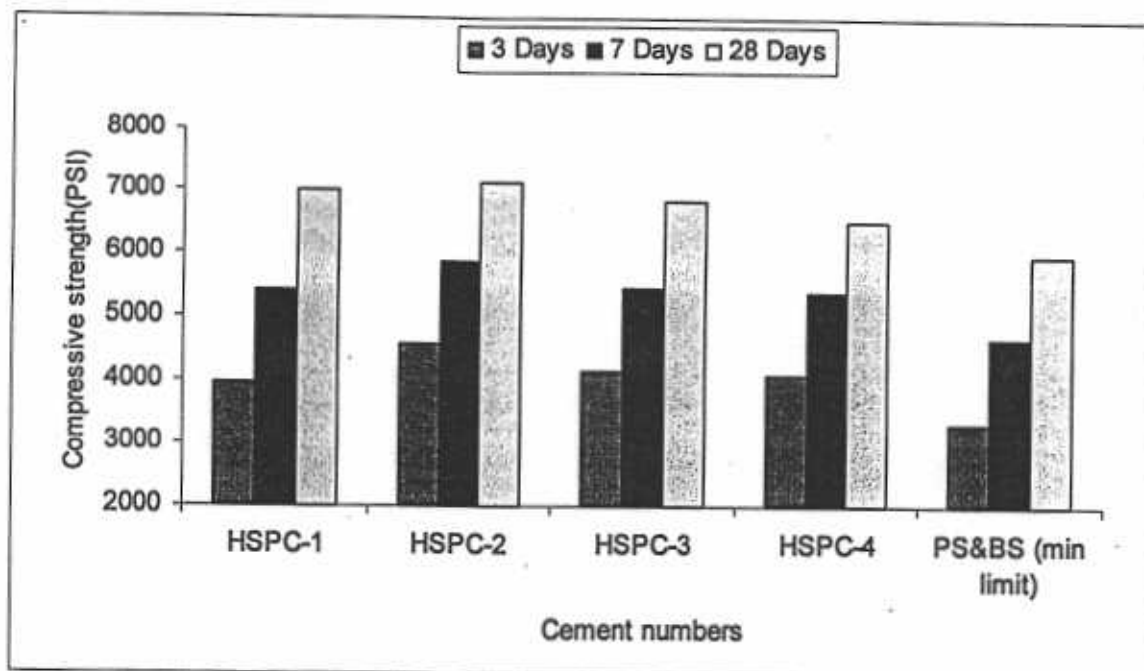


Figure 4.11 Comparison of compressive strength of the high strength portland cement.

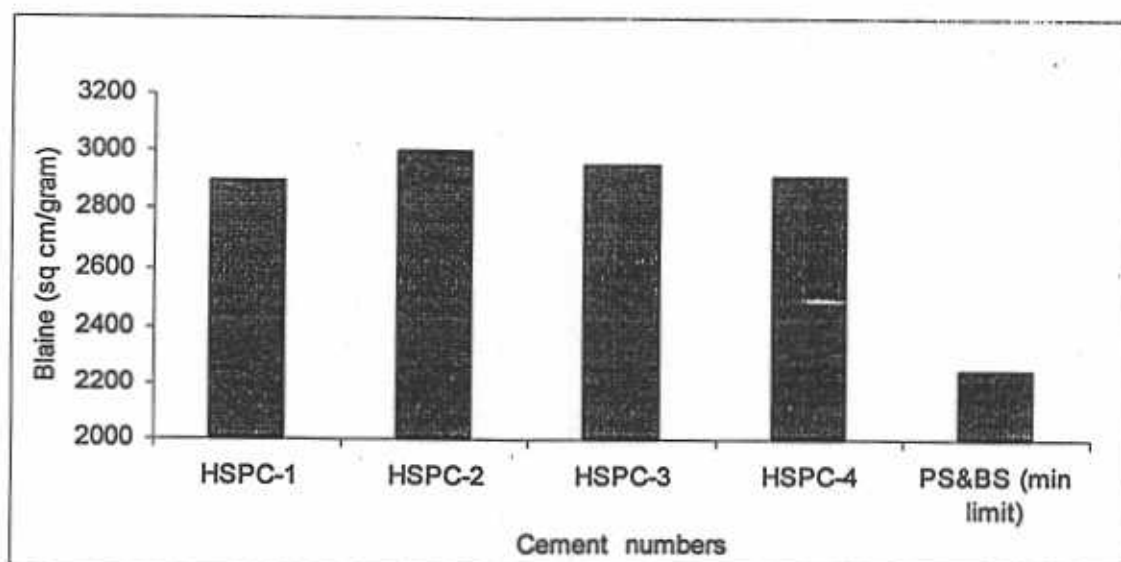


Figure 4.12 Comparison of blaine of the high strength portland cement.

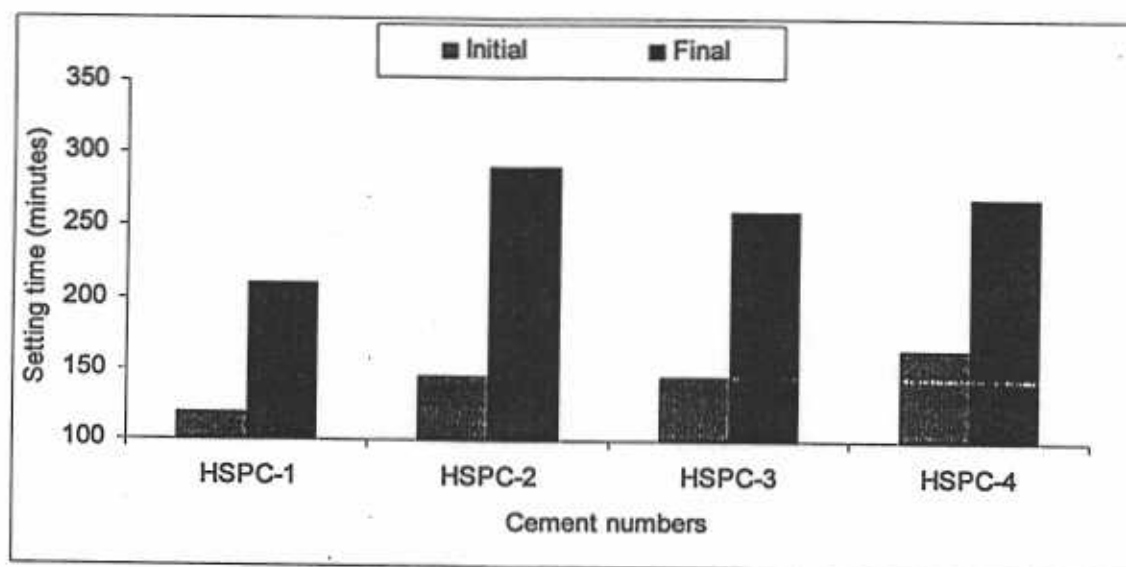


Figure 4.13 Comparison of setting time and consistency of the high strength portland cement.

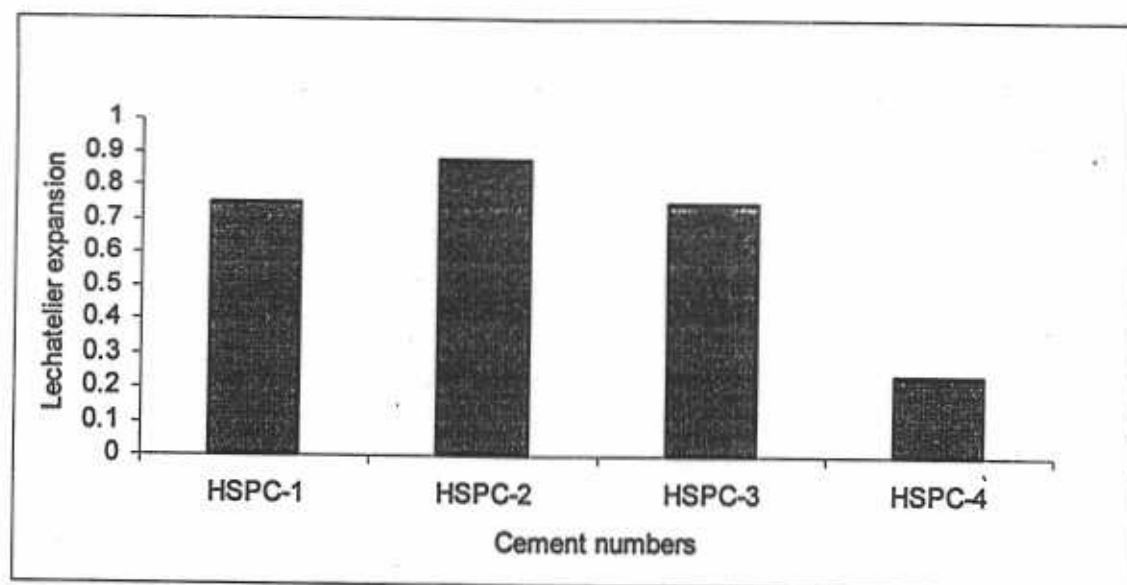


Figure 4.14 Comparison of Le chatelier expansion of the high strength portland cement.

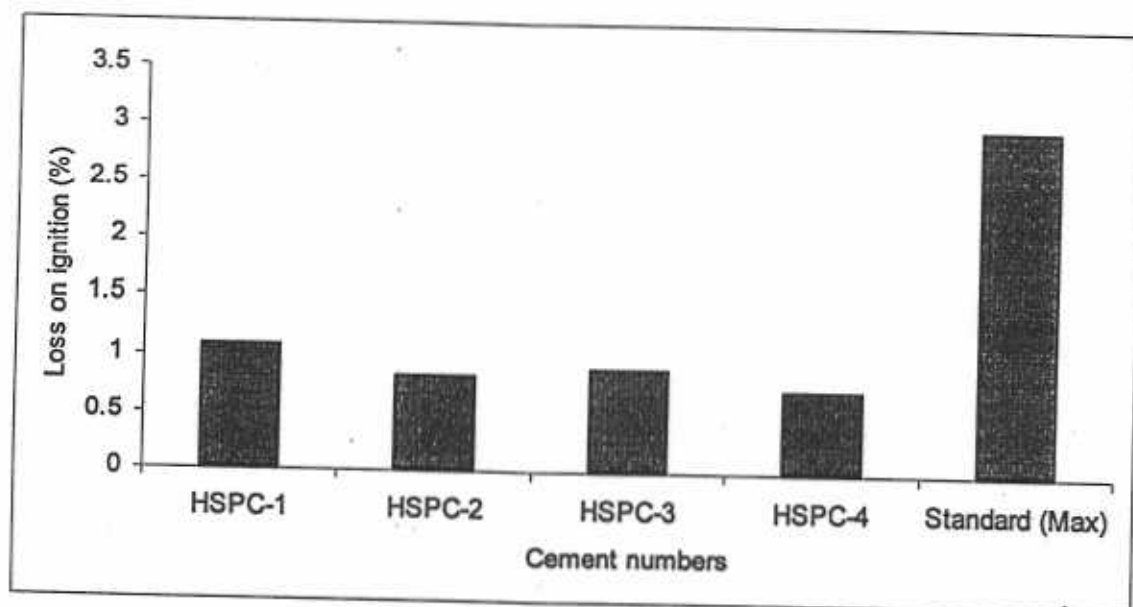


Figure 4.15 Comparison of loss on ignition of high strength portland cement

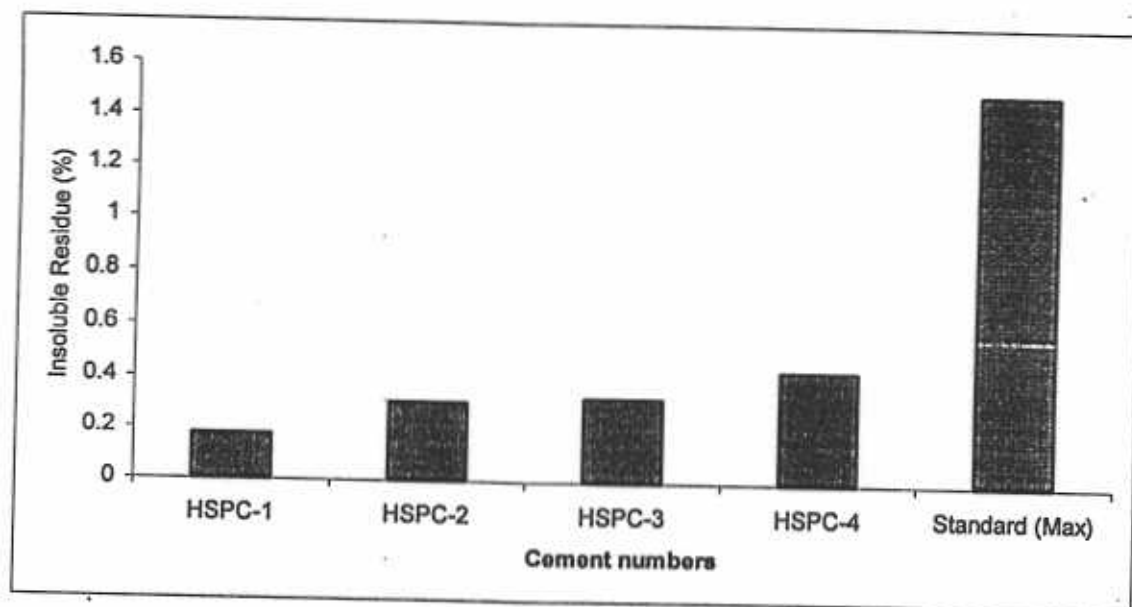


Figure 4.16 Comparison of insoluble residue of high strength Portland cement.

4.3.2 Raw Mix Designing for Sulfate Resisting Cement (SRC)

Different raw mixes for sulfate resisting cement were designed by combining different types of material in different percentages from different locations of the study area. Three types of raw mixes were used for further processing and are reported in Table 4.13, which shows that in the raw mix designing of sulphate resisting cements all the three types of limestone and only two types of clay are used. In the first blend high grade limestone was mixed with maroon colour clay. In the second blend two types of limestones i.e. Darukhula and siliceous limestone were mixed with maroon colour clay while in the third blend for sulphate resisting cement, high grade limestone and green colour clay were mixed.

In order to bring the iron concentration as per with the standard specification of sulphate resisting cement, laterite (iron rich clay) of chemical composition, given in Table 4.8, and that of silica modulus (MS) silica sand of chemical composition given in Table 4.14 were also mixed in different proportions in these raw mixes.

The chemical composition of these raw mixes is presented in Table 4.15. This Table shows that the Raw mix-1 has 14.69% SiO_2 , 2.85% Al_2O_3 , 3.69% Fe_2O_3 , 41.67% CaO , 0.74% MgO , 0.27% Na_2O , 0.56% K_2O , 0.17% SO_3 ; Raw mix-2 has 14.02% SiO_2 , 3.08% Al_2O_3 , 3.71% Fe_2O_3 , 41.08% CaO , 1.15% MgO , 0.58% Na_2O , 0.72% K_2O , 0.12% SO_3 and Raw mix-3 has 15.03% SiO_2 , 2.85% Al_2O_3 , 3.16% Fe_2O_3 , 42.63% CaO , 0.40% MgO , 0.15% Na_2O , 0.48% K_2O , 0.18% SO_3 . MA, MS and LSF of raw mix -1 are 0.77, 2.25, 0.89; raw mix -2 are 0.83, 2.07, 0.91 and that of raw mix-3 are 0.90, 2.50 and 0.90 respectively.

The raw mixes of different composition were subjected to clinkerization. The clinkers thus formed were named as clinker-1, clinker-2 and clinker-3, and analyzed according to British and Pakistan Standard Specifications (BS and PS). The chemical composition along with the moduli and clinker potential are presented in Table 4.16 and are graphically compared in Figure 4.17 - 4.20. The comparison of major and minor elements oxide in clinker for sulphate resisting cement are shown in Figure. 4.17 and 4.18. MA of the resulting clinkers ranges from 0.77 to 0.89, MS from 2.25 to 2.47 and LSF from 0.89 to 0.91 as shown in Figure 4.19. The clinker potential of the three clinker for sulphate resisting cement is shown in Figure 4.20. It is clear from

the Figure that C_3S varies from 51.71 to 55.16, C_2S 22.50 to 26.29, C_3A 2.03 to 2.95 and C_4AF from 15.14 to 17.51.

The clinkers were converted into cement, which were named as SRC-1, SRC-2, and SRC-3. The cements are tested for all possible physical parameters as per requirement of British and Pakistan Standard Specifications (BS and PS) similar to high strength Portland cement, and the results are presented in Table 4.18. Table 4.18 also shows the British and Pakistan Standard Specifications for sulphate resisting cement. According to British and Pakistan Standard Specifications, the minimum limit of compressive strength for three, seven, and twenty eight days is 2176, 3409 and 4932 PSI respectively. The minimum initial setting time for sulphate resisting cement is 165 minutes and the maximum final setting time is 10 hours, while the minimum consistency is 27.25 %. The upper limit of lechatlier expansion of sulphate resisting cement is 10 mm while the minimum limit of blaine is 2500 Sq. cm / gram according to British and Pakistan Standard Specifications. The upper limit of loss on ignition and insoluble residue is 3.00 % and 2.00 % respectively.

Figure 4.21 to 4.26 show the comparison of compressive strength, blaine, setting time, Lechatlier expansion, loss on ignition, and insoluble residue of sulfate resisting cements obtained from the raw material of the study area with the Standard. As clear from the Figures, all the mentioned physical and chemical parameters meet the British and Pakistan Standard Specifications.

Table 4.13 Blending Ratio of Raw Mix for Sulphate Resisting Cement

Raw Mix Title	Material Taken	Percentage
Raw mix -1	High grade lime stone	80
	Maroon color clay	5
	Silica Sand	8
	Laterite	7
	Total	100
Raw mix -2	Darukhula Limestone	55
	Siliceous Limestone	30
	Maroon Color clay	6
	Silica Sand	1
	Laterite	8
	Total	100
Raw mix -3	High grade lime stone	78
	Green colour clay	10
	Silica sand	6
	Laterite	6
	Total	100

Table 4.14 Chemical Composition of Silica Sand

Analyte	Percent Composition
SiO ₂	97.00
Al ₂ O ₃	1.36
Fe ₂ O ₃	0.66
CaO	0.10
MgO	0.14
Na ₂ O	0.18
K ₂ O	0.20
SO ₃	0.11

Table 4.15 Chemical Composition of Raw Mixes for Sulfate Resisting Cement

Analyte	Percent Composition		
	Mix-1	Mix-2	Mix-3
SiO ₂	14.69	14.02	15.03
Al ₂ O ₃	2.85	3.08	2.85
Fe ₂ O ₃	3.69	3.71	3.16
CaO	41.67	41.08	42.63
MgO	0.74	1.15	0.40
Na ₂ O	0.27	0.58	0.15
K ₂ O	0.56	0.72	0.48
SO ₃	0.17	0.12	0.18
LOI	33.00	32.87	34.00
Total	97.64	97.33	98.88
Moduli			
MA	0.77	0.83	0.90
MS	2.25	2.07	2.50
LSF	0.89	0.91	0.90

Table 4.16 Chemical Composition of Clinkers for Sulfate Resisting Cement

Analyte	Percent Composition		
	Clinker-1	Clinker-2	Clinker-3
SiO ₂	22.77	21.77	23.2
Al ₂ O ₃	4.42	4.79	4.42
Fe ₂ O ₃	5.72	5.76	4.98
CaO	64.59	63.67	65.98
MgO	0.59	0.99	0.96
Na ₂ O	0.26	0.26	0.21
K ₂ O	0.42	0.58	0.58
SO ₃	0.11	0.14	0.11
LOI	1.50	1.05	0.99
Free lime (CaO _{free})	0.85	1.26	1.26
Liquid Phase	27.49	29.30	26.33
Moduli			
MA	0.77	0.83	0.89
MS	2.25	2.01	2.47
LSF	0.89	0.91	0.90
Clinker Potential			
C ₃ S	51.71	52.93	55.16
C ₂ S	26.29	22.5	24.93
C ₃ A	2.03	2.95	3.29
C ₄ AF	17.39	17.51	15.14
Burnability Factor (BF)	19.64	16.02	20.35

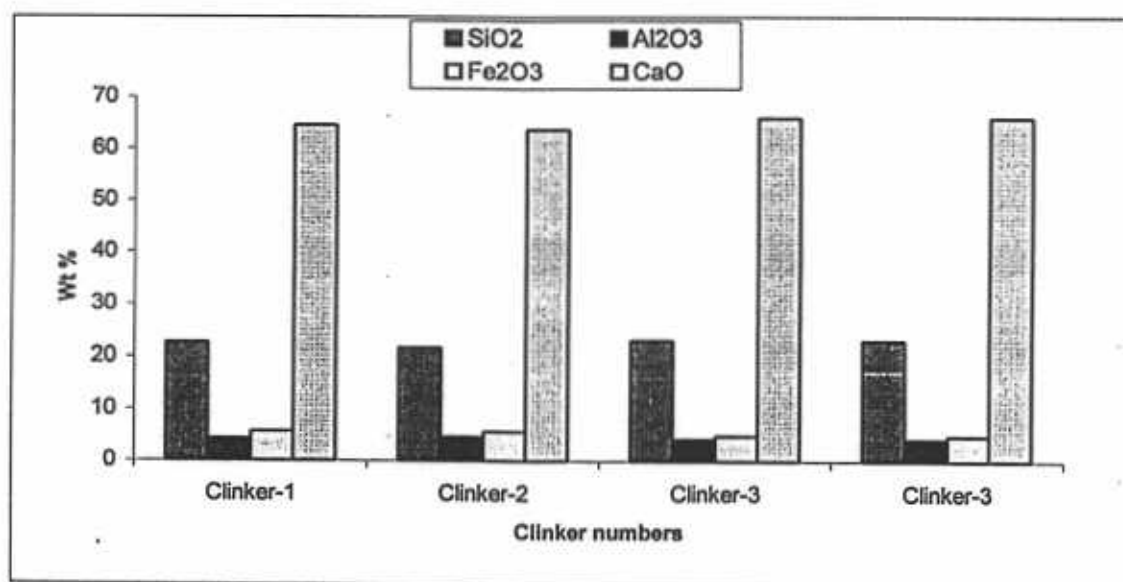


Figure 4.17 Comparison of major element oxides in the clinker for sulfate resisting cement.

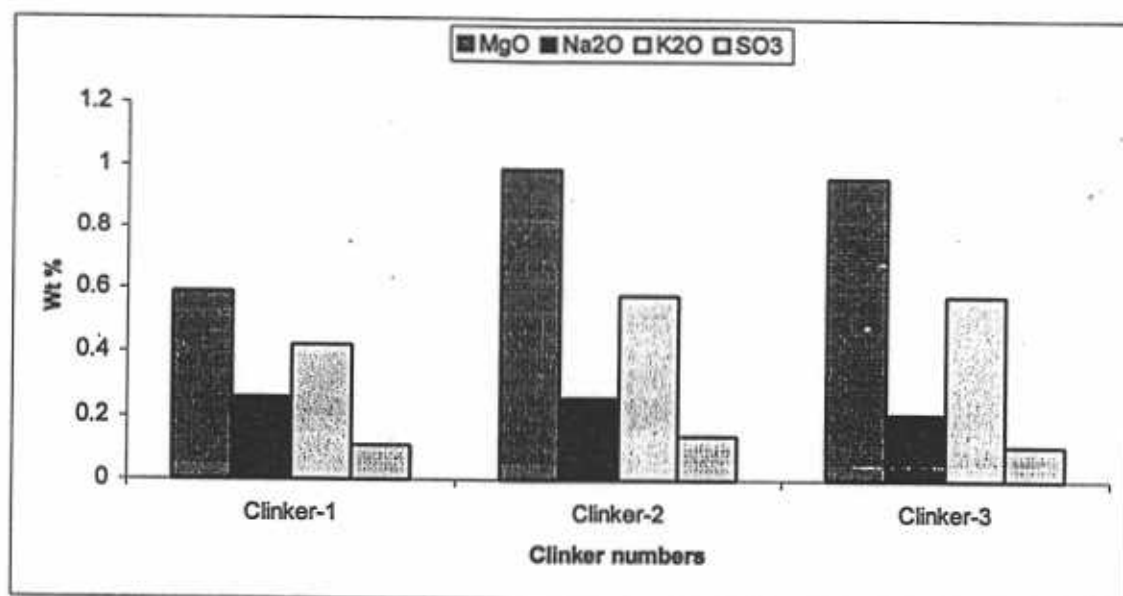


Figure 4.18 Comparison of minor element oxides in clinker for sulfate resisting cement.

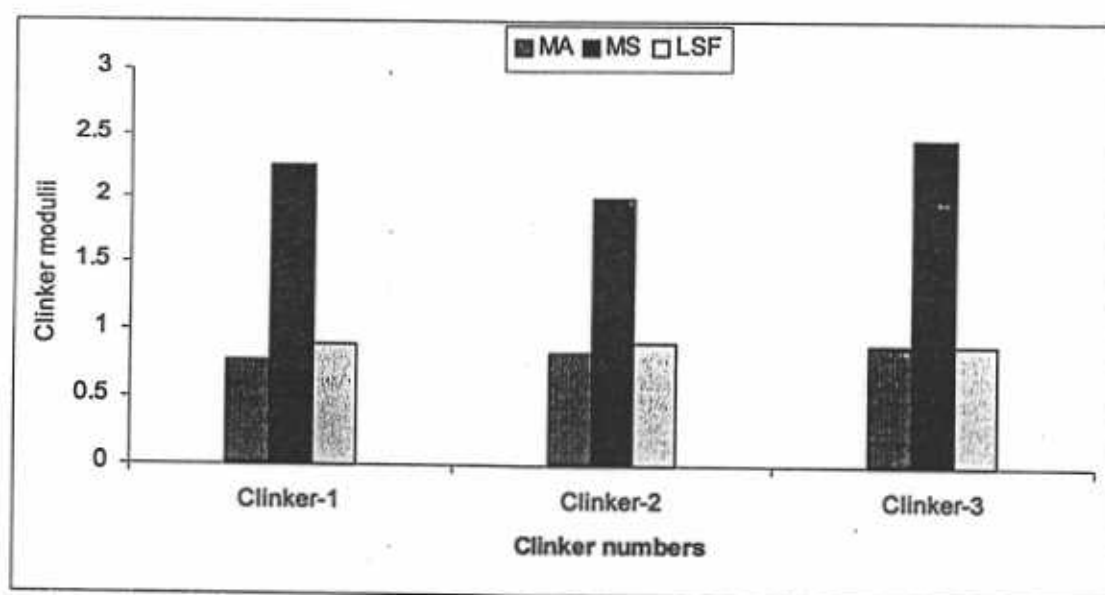


Figure 4.19 Comparison of moduli of clinker for sulfate resisting cement.

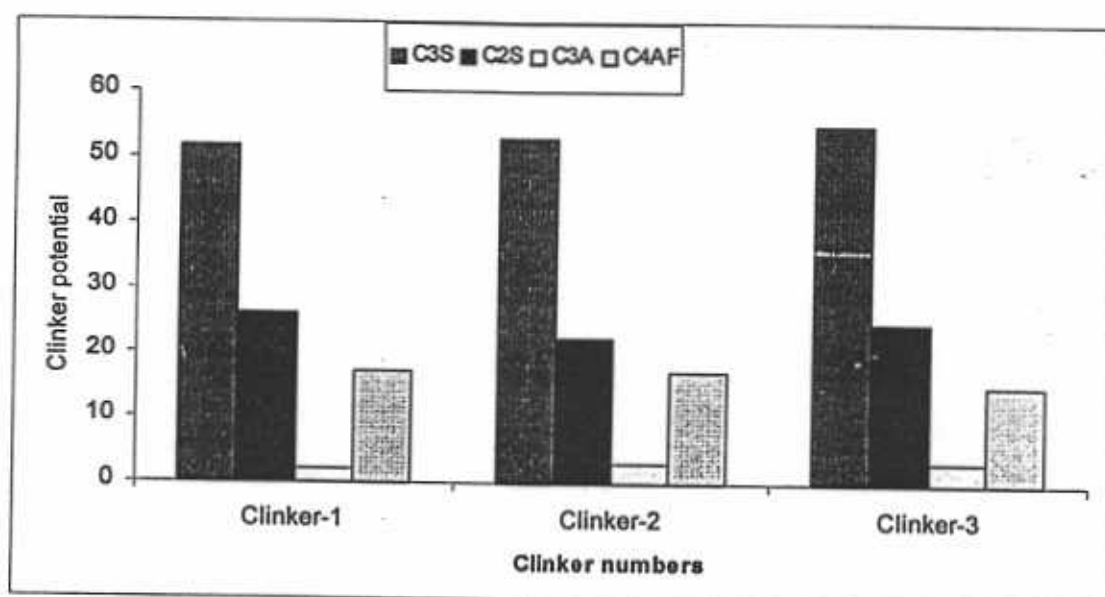


Figure 4.20 Comparison of the clinker potential for sulfate resisting cement

Table 4.17 Chemical Composition of Sulfate Resisting Cement

Analyte	Percent Composition		
	SRC-1	SRC-2	SRC-3
SiO ₂	21.71	20.76	22.12
Al ₂ O ₃	4.21	4.56	4.21
Fe ₂ O ₃	5.44	5.48	4.74
CaO	62.95	62.08	64.27
MgO	0.55	0.95	0.92
Na ₂ O	0.25	0.25	0.21
K ₂ O	0.41	0.56	0.56
SO ₃	2.38	2.41	2.38
Moduli			
MA	0.77	0.83	0.89
MS	2.25	2.07	2.47
LSF	0.91	0.93	0.92
Cement Potential			
C ₃ S	48.39	49.55	51.66
C ₂ S	25.77	22.17	24.47
C ₃ A	1.956	2.823	3.145
C ₄ AF	16.54	16.65	14.4

Table 4.18 Physical and Chemical Parameters of Sulfate Resisting Cement

Parameter		Results			
		SRC-1	SRC-2	SRC-3	Standard (BS & PS)
Physical Testing					
Compressive Strength (PSI)	3 Days	3945	3885	4575	2176 PSI (Min)
	7 Days	4869	5970	5980	3409 PSI (Min)
	28 Days	6870	6982	7860	4932 PSI (Min)
Setting Time (minute)	Initial	142	145	165	165 Minutes(Min)
	Final	210	225	270	10 Hours (Max)
Consistency (%)		28	30	29	27.25
Expansion (Lechatlier) mm		0.36	0.68	0.69	10mm(Max)
Blaine (sq cm/gram)		2944	3045	3150	2500 Sq cm/g (Min)
Chemical Testing					
Loss on Ignition (%)		0.75	0.99	0.78	3.0 (Max)
Insoluble Residue (%)		0.68	0.39	0.25	2.00 (Max)

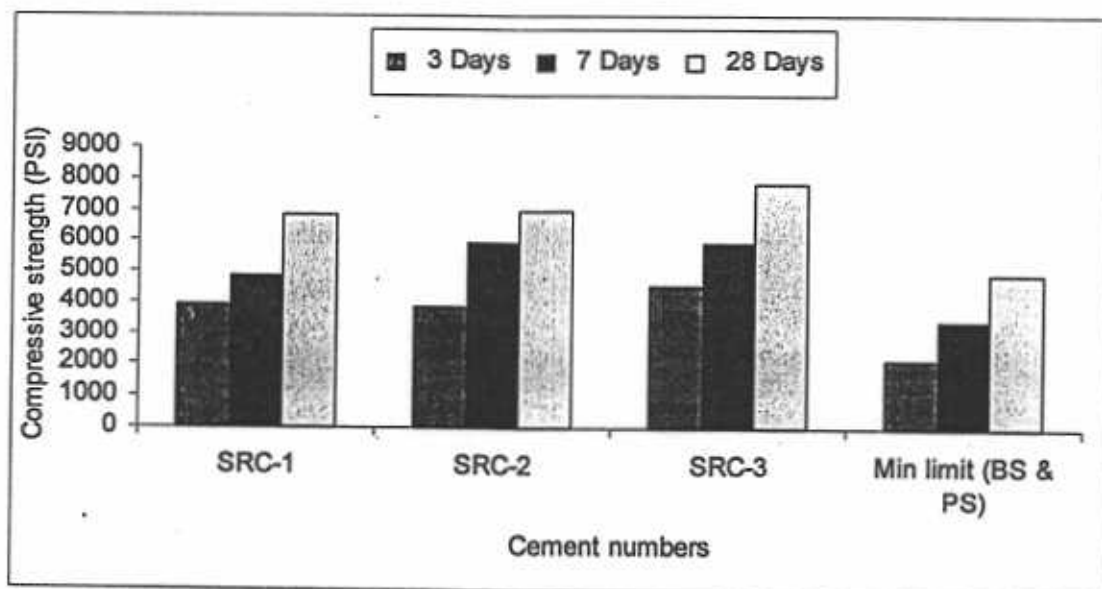


Figure 4.21 Comparison of compressive strength of the sulfate resisting cement.

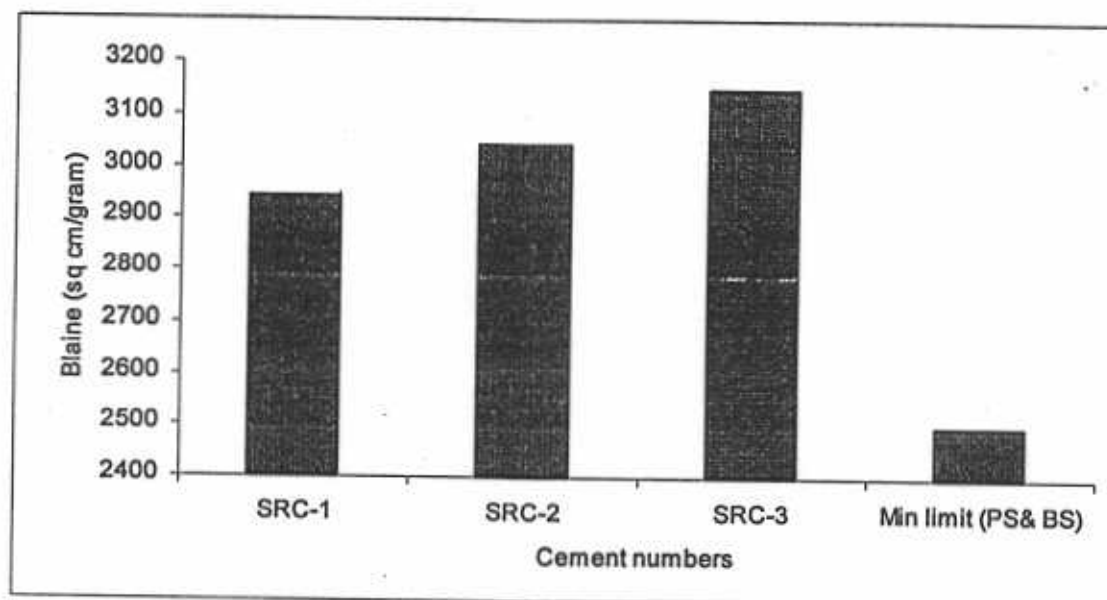


Figure 4.22 Comparison of blaine of the sulfate resisting cement.

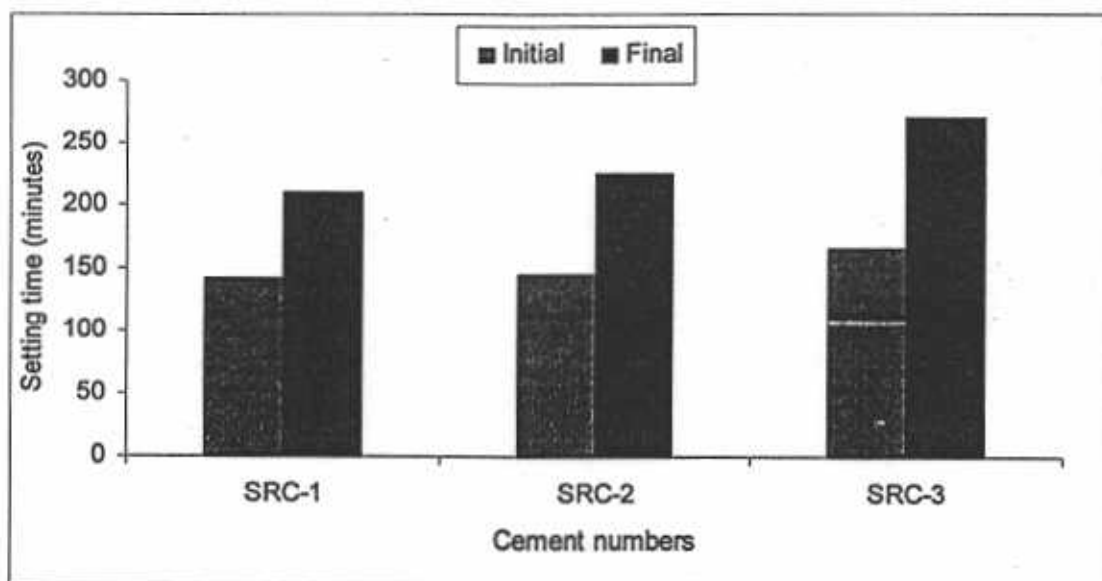


Figure 4.23 Comparison of setting time of sulfate resisting cement.

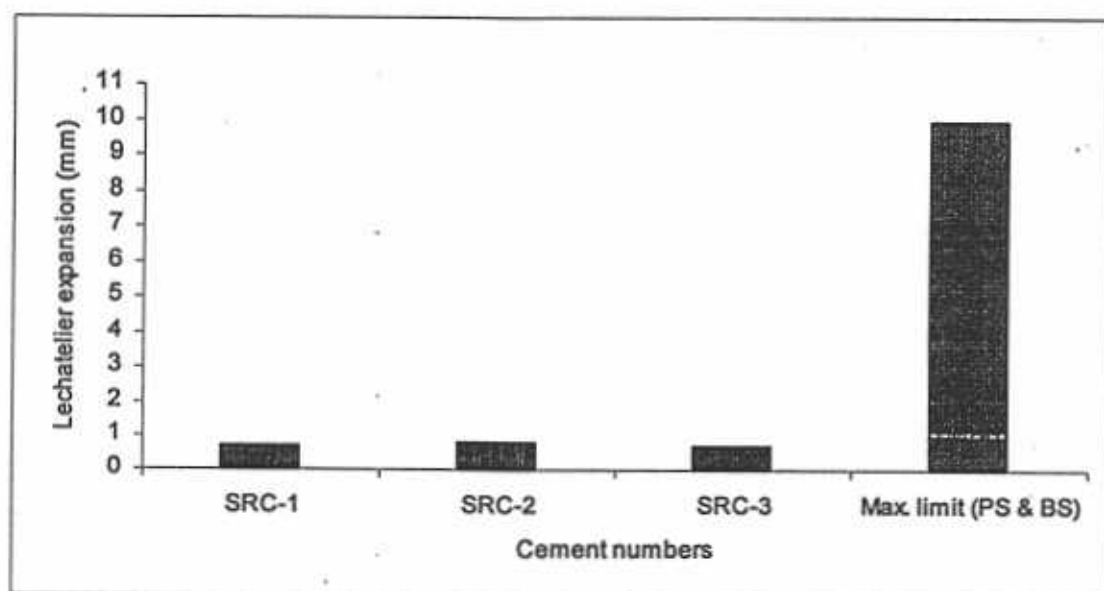


Figure 4.24 Comparison of Lechatelier expansion of sulfate resisting cement.

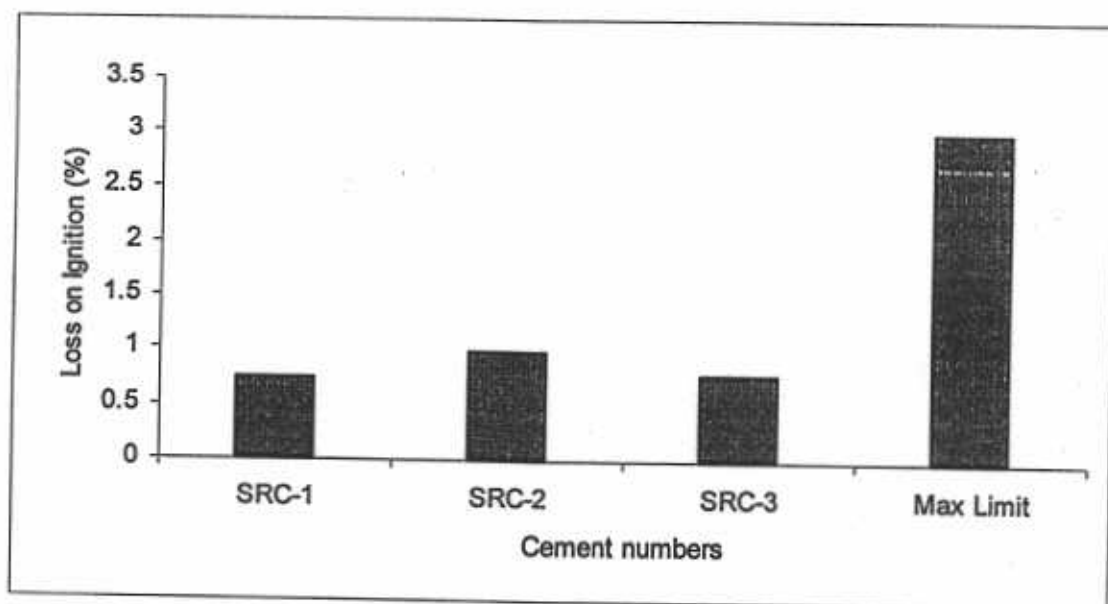


Figure 4.25 Comparison of loss on ignition of sulfate resisting cement.

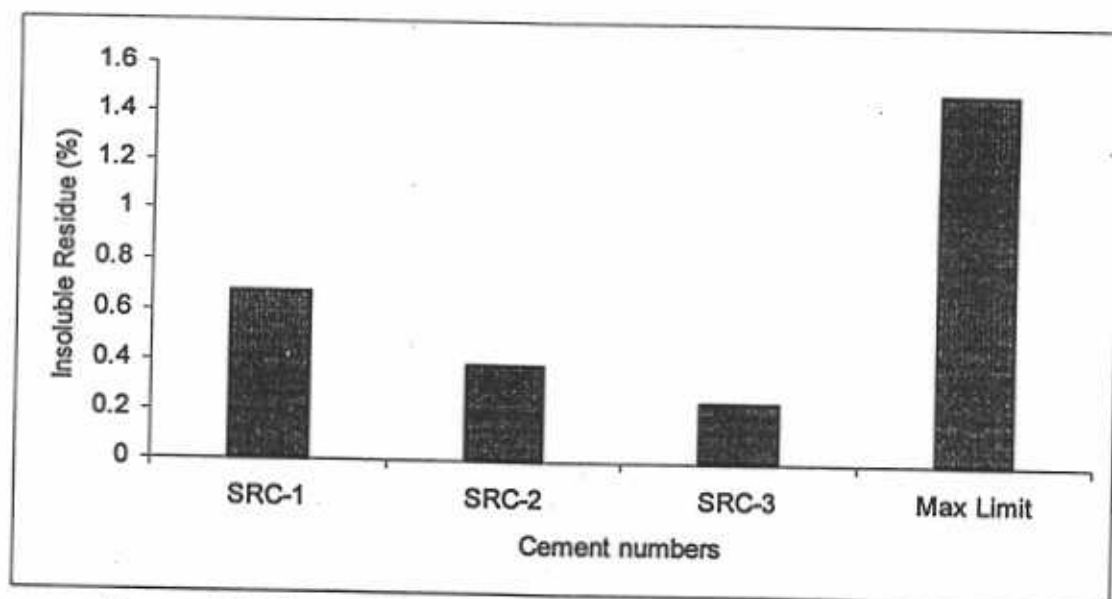


Figure 4.26 Comparison of insoluble residue of sulfate resisting cement.

4.3.3 Raw mix Designing for White Cement.

Raw material from the study area was used for the raw mix designing of white cement. Different raw mixes were prepared in different proportion, three of which were used for further processing and are given in Table 4.19. It is clear from the table that in the raw mix designing of white cement, all the three types of limestone i.e. high grade limestone, siliceous limestone and Darukhula limestone and only one type of clay i.e. green colour clay sampled from the study area were used. In the first blend high grade limestone and siliceous limestone were mixed with high alumina clay. In the second blend only Darukhula limestone was mixed with high alumina clay and silica sand. In this blend no clay of the study area was used. In the third blend for white cement, high grade limestone and green colour clay were mixed. In order to bring the MA as per with the standard specification of cement, high alumina clay of chemical composition, given in Table 4.20, were also mixed in different proportions in these raw mix. The percent composition of the resulting three raw mixes for white cements is shown in Table 4.21.

It is clear from the Table that the raw mix-1 has 14.85% SiO_2 , 4.85% Al_2O_3 , 0.38% Fe_2O_3 , 42.65% CaO , 0.34% MgO , 0.11% Na_2O , 0.42% K_2O , 0.13% SO_3 ; raw mix-2 has 13.84% SiO_2 , 5.89% Al_2O_3 , 0.46% Fe_2O_3 , 41.91% CaO , 0.72% MgO , 0.71% Na_2O , 0.20% K_2O , 0.05% SO_3 ; and raw mix-3 has 14.57% SiO_2 , 5.55% Al_2O_3 , 0.43% Fe_2O_3 , 42.40% CaO , 0.58% MgO , 0.14% Na_2O , 0.21% K_2O , 0.07% SO_3 . (Table 4.21) MA, MS and LSF in raw mix -1 are 12.76, 2.84, 0.90, in raw mix -2 are 12.78, 2.18 and 0.91 and in raw mix-3 are 13.06, 2.44 and 0.89 respectively.

The raw mix of different composition were subjected to clinkerization. The clinker thus obtained are named as clinker-1, clinker-2 and clinker-3 and analyzed according to British and Pakistan Standard Specifications (BS and PS). The chemical composition along with the moduli and clinker potential are presented in Table 3.22 and are graphically compared in Figure 4.27 - 3.30. Figure. 4.27 and 4.28 shows the comparison of major and minor element oxides in clinker for white cements. The percentages of major and minor element oxides of all the four cements are almost the same which shows that all types of limestone and clay of the study area are suitable for manufacturing of white cement, when used in different proportion. MA, MS and

LSF of the resulting clinker-1 are 13.83, 2.51 and 0.90; clinker-2 are 13.05, 2.54 and 0.90 and that of clinker-3 are 18.39, 2.88 and 0.90 respectively (Figure 4.29).

The comparison of the clinker potential of the three clinkers for white cements is reported in Figure 4.30. It is clear from the figure that C_3S varies from 39.47 to 44.23, C_2S , 30.58 to 33.75, C_3A 19.29 to 20.98. and C_4AF form 1.25 to 1.88

The clinkers were converted into cement, which named as WC-1, WC-2, and WC-3. The cements are tested for all possible physical parameters as per requirement of British and Pakistan Standard Specifications (BS and PS) like blaine, compressive strength, setting time, consistency, and expansion and chemical parameters like insoluble residue, loss on ignition, and percent composition etc and presented in Table 4.23. The Table 4.23 also shows the British and Pakistan Standard Specifications for white cement. The minimum limit of compressive strength for three and seven days is 1740 and 2755 respectively, while the compressive strength of twenty eight days has no standard according to British and Pakistan Standard Specifications. Similarly the minimum initial setting time for White cement is 45 minutes and the maximum final setting time is 10 hours, while the minimum range of consistency is 28 %. The upper limit of lechatlier expansion of high strength Portland cement is 10 mm while the minimum limit of blaine is 2250 Sq. cm/gram according to British and Pakistan Standard Specifications. The upper limit of loss on ignition and insoluble residue is 4.7 % and 1.5 % respectively

Figure 4.31 to 4.36 shows the comparison of compressive strength, blaine, setting time, lechatlier expansion, loss on ignition, and insoluble residue of white Portland cements obtained from the raw material of the study area with the Standard. As clear from the Figures, all the mentioned physical and chemical parameters meet the British and Pakistan Standard Specifications.

Table 4.19 Blending ratio of Raw Mix for white Cement

Raw Mix Title	Material Taken	Percentage
Raw mix -1	High grade lime stone	65
	Siliceous Lime stone	18
	High Alumina Clay	9
	Silica Sand	8
	Total	100
Raw mix -2	Darukhula Limestone	85
	High Alumina Clay	10
	Silica Sand	5
	Total	100
Raw mix -3	High grade lime stone	51
	Green colour clay	31
	High Alumina Clay	10
	Silica sand	8
	Total	100

Table 4.20 Chemical Composition of High Alumina Clay

Analyte	Percent Composition
SiO ₂	50.66
Al ₂ O ₃	47.00
Fe ₂ O ₃	1.56
CaO	1.24
MgO	0.11
Na ₂ O	0.03
K ₂ O	0.15
SO ₃	0.20

Table 4.21 Chemical Composition of Raw Mix for White Cement

Analyte	Percent composition		
	Mix-1	Mix-2	Mix-3
SiO ₂	14.85	13.84	14.57
Al ₂ O ₃	4.85	5.89	5.55
Fe ₂ O ₃	0.38	0.46	0.43
CaO	42.65	41.91	42.40
MgO	0.34	0.72	0.58
Na ₂ O	0.11	0.71	0.14
K ₂ O	0.42	0.20	0.21
SO ₃	0.13	0.05	0.07
LOI	33.00	33.35	33.85
Total	97.98	97.63	97.6
Moduli			
MA	12.76	12.78	13.06
MS	2.84	2.18	2.44
LSF	0.90	0.91	0.89

Table 4.22 Chemical Composition of Clinker for White Cement

Analyte	Percent composition		
	Clinker-1	Clinker-2	Clinker-3
SiO ₂	22.30	22.15	22.89
Al ₂ O ₃	8.30	8.09	7.54
Fe ₂ O ₃	0.60	0.62	0.41
CaO	66.60	64.81	65.78
MgO	0.66	0.96	0.56
Na ₂ O	0.34	0.34	0.18
K ₂ O	0.60	0.61	0.24
SO ₃	0.28	0.28	0.11
LOI	1.50	0.98	0.96
Free lime (CaO _{free})	5.23	4.11	3.65
Liquid Phase	28.14	27.86	24.63
MODULI			
MA	13.83	13.05	18.39
MS	2.51	2.54	2.88
LSF	0.90	0.90	0.90
Clinker Potential			
C ₃ S	44.23	39.47	42.27
C ₂ S	30.58	33.75	33.75
C ₃ A	20.98	20.39	19.29
C ₄ AF	1.82	1.88	1.25
Burnability Factor (BF)	21.19	20.57	26.76

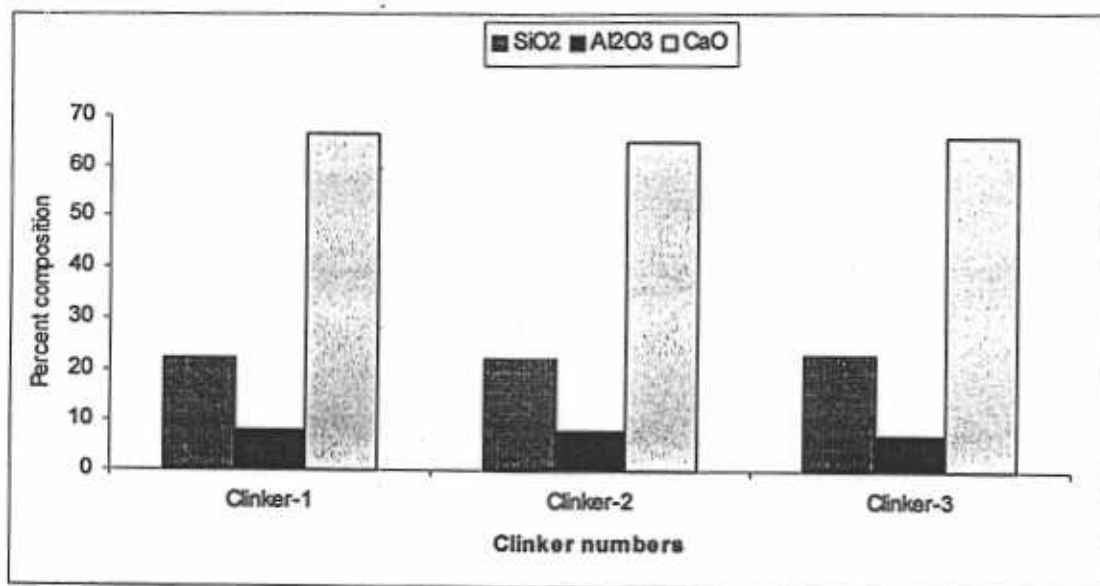


Figure 4.27 Comparison of major element oxides in clinker of white cement.

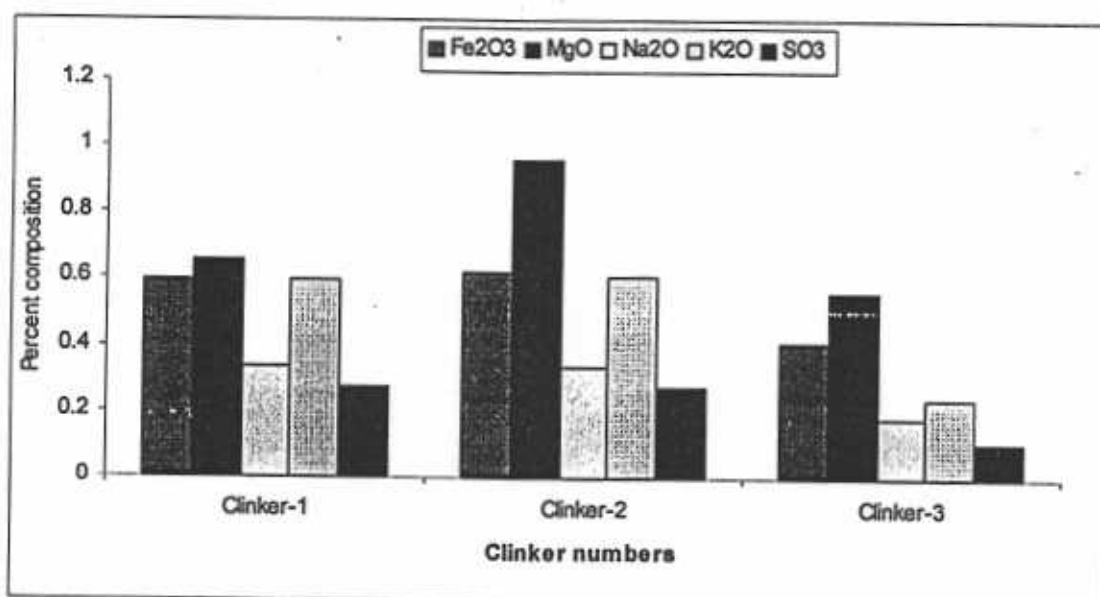


Figure 4.28 Comparisons of minor element oxides in the clinker of white cement.

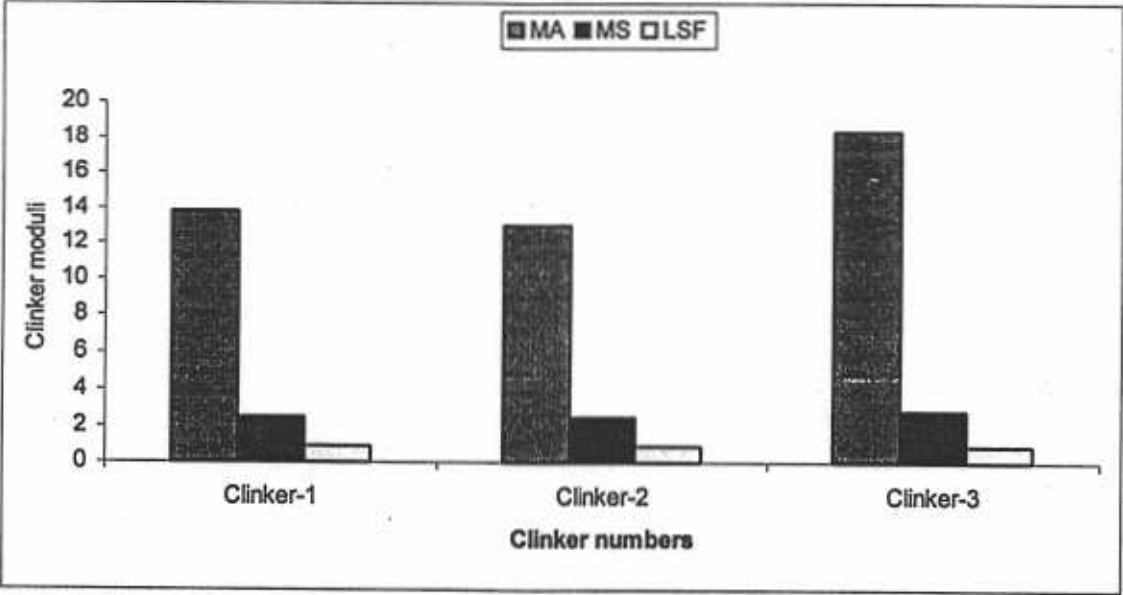


Figure 4.29 Comparison of moduli of clinker of white cement.

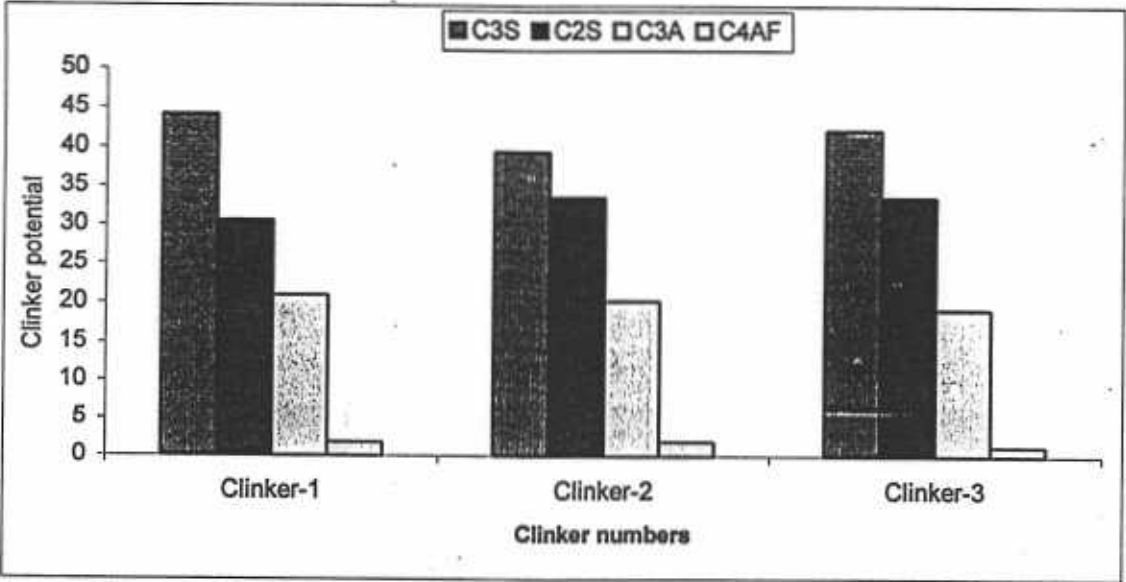


Figure 4.30 Comparison of clinker potential of clinker of white cement.

Table 4.23 Chemical Composition of White Cement

Analyte	Percent composition		
	WC-1	WC-2	WC-3
SiO ₂	21.27	21.13	21.83
Al ₂ O ₃	7.90	7.70	7.18
Fe ₂ O ₃	0.58	0.60	0.40
CaO	64.86	63.16	64.08
MgO	0.64	0.92	0.54
Na ₂ O	0.33	0.33	0.18
K ₂ O	0.59	0.59	0.24
SO ₃	2.55	2.55	2.38
Moduli			
MA	13.71	12.94	18.14
MS	2.51	2.55	2.88
LSF	0.94	0.92	0.92
Cement Potential			
C ₃ S	41.28	36.76	39.42
C ₂ S	29.85	32.82	32.86
C ₃ A	19.95	19.39	18.35
C ₄ AF	1.75	1.81	1.20

Table 4.24 Physical and Chemical Properties of White Cement

Parameters		Results			
		WC-1	WC-2	WC-3	Standard (BS % PS)
Physical Testing					
Compressive Strength (PSI)	3 Days	4150	3945	4100	1740 PSI (Min)
	7 Days	4825	4580	4850	2755 PSI (Min)
	28 Days	5640	5860	5890	No standard
Setting Time (minute)	Initial	150	124	145	45 min (Min)
	Final	240	280	265	10 Hours (Max)
Consistency (%)		28	29	28	28% (Min)
Expansion (Lechatlier) mm		1.69	1.92	1.68	10mm (Max)
Blaine (sq cm/gram)		4350	4200	4500	2250 Sq cm/g (Min)
Chemical Testing					
Loss on Ignition (%)		0.77	0.78	0.88	4.7 (Max)
Insoluble Residue (%)		0.9	0.27	0.47	1.59 (Max)

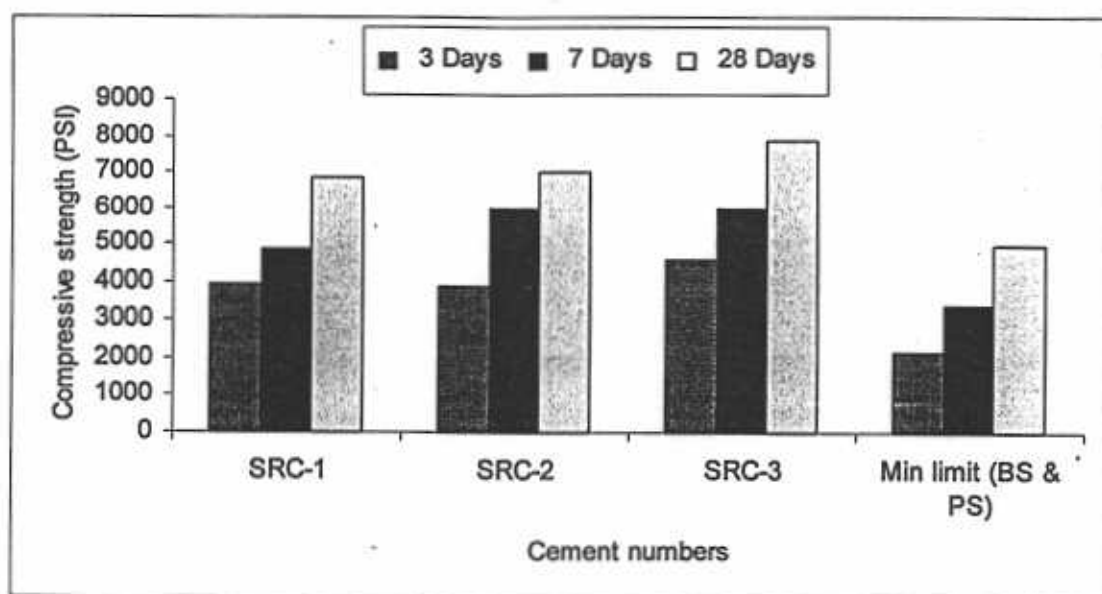


Figure 4.31 Comparison of the compressive strength of white cement.

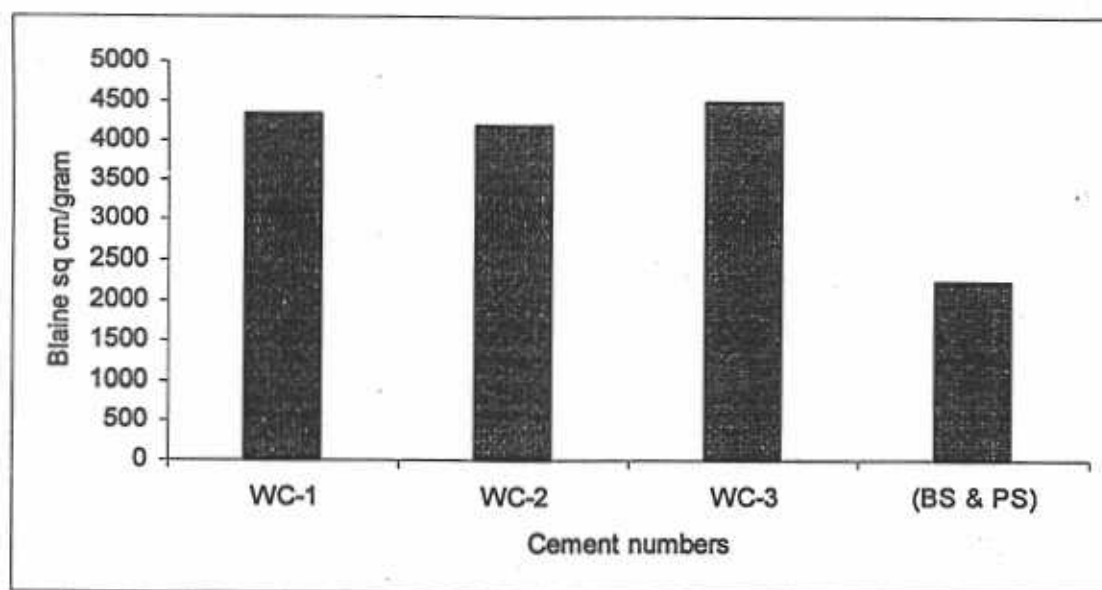


Figure 4.32 Comparison of the blaine of white cement.

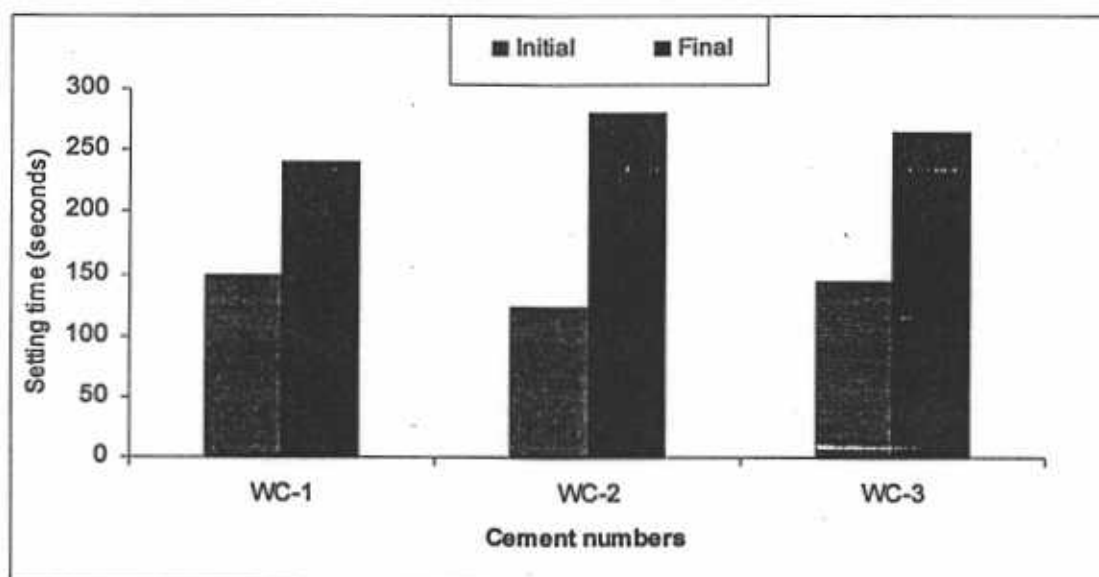


Figure 4.33 Comparison of setting time of white cement.

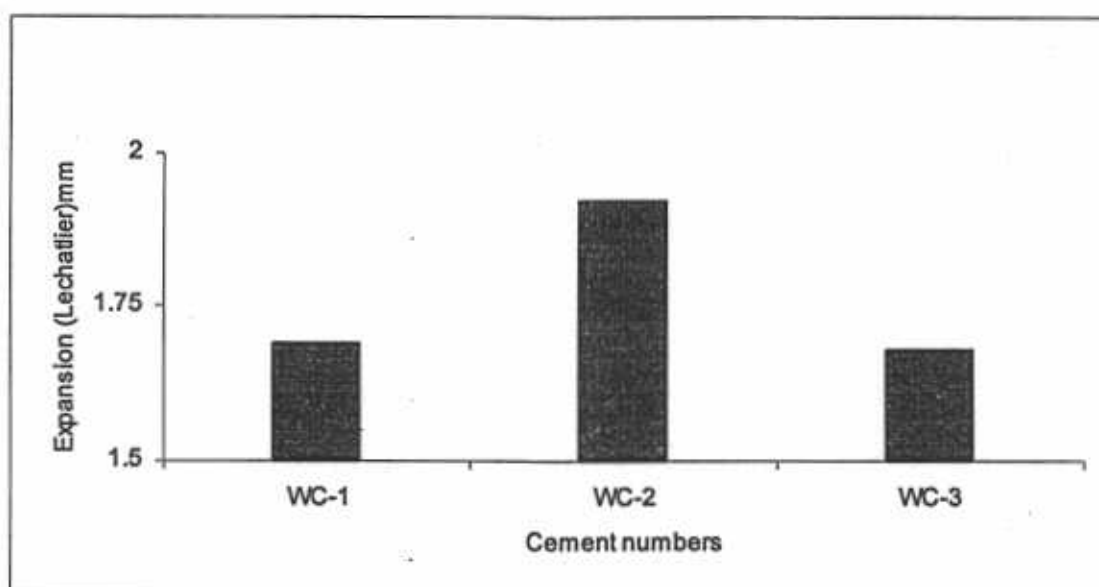


Figure 4.34 Comparison of Lechatlier expansion of the white cement

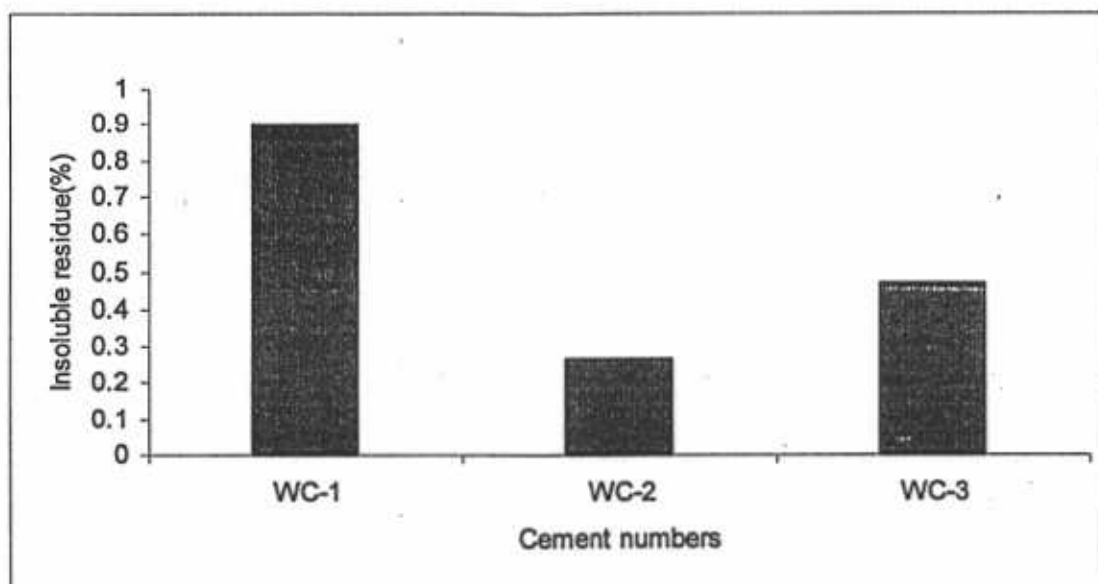


Figure 4.35 Comparison of insoluble residue of the white cement.

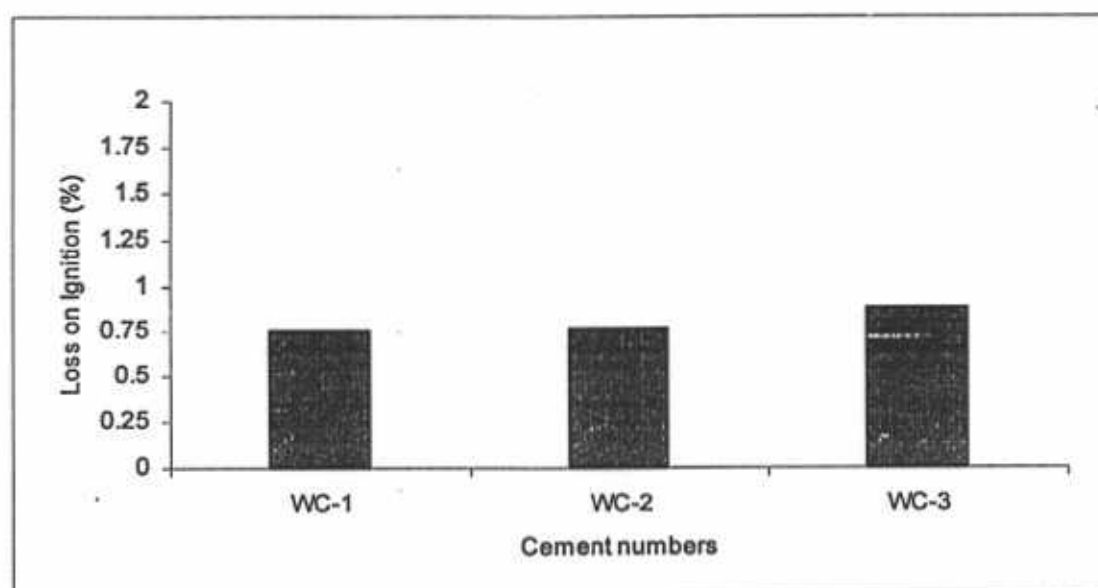


Figure 4.36 Comparison of loss on ignition of the white cement.

4.4 DISCUSSION AND CONCLUSION

The raw material collected from the study area was used for the manufacture of high strength Portland cement, sulphate resisting cement and white cement. The best limestone for cement should have high CaO. From the results it is clear that High grade limestone has the highest CaO (53.00%), which make it suitable for all types of cements. For white cement, less iron content is preferred, therefore high grade limestone due its low iron content, is more suitable. High grade limestone can be used alone, as well as in combination with other limestones for cement manufacturing. Moreover this limestone is soft in texture as compared with the Darukhula limestone which makes it more suitable for cement manufacturing.

Darukhula limestone differ from the high limestone only in CaO (49.15%) and SiO₂ (4.62%) content. Darukhula limestone require less amount of clay as compared to high grade lime stone which makes it good for high strength Portland cement and sulphate resisting cement. This limestone is hard in texture so its use in cement manufacturing on large scale will be more difficult as compared to the high grade limestone.

Siliceous limestone contain more SiO₂ (11.83%) and low CaO (44.91%) as compared to Darukhula limestone which needs less silica content but only clay can not bring MA and MS within range. If laterite is also used with clay, then LSF will go below the permissible range.

As laterite also contain 43.53% SiO₂ due which MS will go very high and LSF very low. In order to overcome this problem, some high grade or Darukhula limestone should be used in combination with siliceous limestone. So siliceous limestone can not be used alone in cement manufacturing of any type.

Maroon colour clay is the most suitable clay for cement manufacturing in the study area. It can be used both in high strength Portland and sulphate resisting cements. The only superiority of this clay over the other found in the study area is that, it contains low alkalies (Na₂O and K₂O) due to which it is more suitable for cement manufacturing. Other clay like lacustrine and green colour clay can also be used in the manufacturing of high strength Portland and sulphate resisting cements.

RESULTS AND DISCUSSIONS

Part – 3

4.5 DESIGNING OF RAW MIX WITH BAGGASE ASH AND ITS CLINKERIZATION

In the first part of this research work, the raw material collected from the study area was analyzed. In the second part different raw mixes were designed and subjected to clinkerization. The clinkers thus formed were analyzed and compared with the British and Pakistan Standard Specifications. In this part of the research work baggase and baggase ash samples were collected from the sugar industries of N.W.F.P, and analyzed for different physical and chemical parameters using different analytical techniques. Baggase ash was used for cement preparation along with other raw material like limestone and clay etc. The raw mixes thus formed were subjected to clinkerization. The clinker thus formed was analyzed, and compared with British and Pakistan Standard Specifications. Only those raw mixes have been reported in this section which meets the standard specification. It should be noted that some of the raw mixes did not meet the specifications and are not included in this report.

4.6 SAMPLING OF BAGGASE AND BAGGASE ASH

Samples of baggase and baggase ash were collected from different sugar industries of N.W.F.P and carried to the laboratory for analysis and further process. All the samples were properly numbered at the sampling points. Samples were collected from the following sugar industries.

1. Premier Sugar Mill Mardan (PSM)
2. Khazana Sugar Mill Peshawar (KSM)
3. Frontier Sugar Mill Thakt-Bhai (Mardan) (FSM)

4.7 ANALYSIS OF BAGGASE AND BAGGASE ASH

4.7.1 Analysis of Baggase

Baggase samples from the sugar mills of NWFP were collected and analyzed for moisture and ash. The analysis was performed through thermogravimetric analyzer (TGA). The results are reported in Table 4.25 and graphically presented in Figure 4.37(a) and (b)

The moisture in baggase varies from 8.78% to 9.55% (Figure 4.37 a) while Ash content of the baggase varies from 3.03% to 3.81%(4.37b)

Table 4.25 Physical Analysis of Baggase collected from Sugar Mills

Sampling Station	Sample numbers	Moisture (%)	Ash (%)
Premier Sugar Mill Mardan (PSM)	S ₁	9.21	3.23
	S ₂	9.26	3.01
	S ₃	9.07	4.05
Khazana Sugar Mill Peshawar(KSM)	S ₄	8.88	3.03
	S ₅	8.97	3.64
	S ₆	8.78	3.27
Frontier Sugar Mill Thakt-Bhai (Mardan) (FSM)	S ₇	9.52	3.51
	S ₈	9.55	3.81
	S ₉	9.34	3.62
Average		9.18	3.46

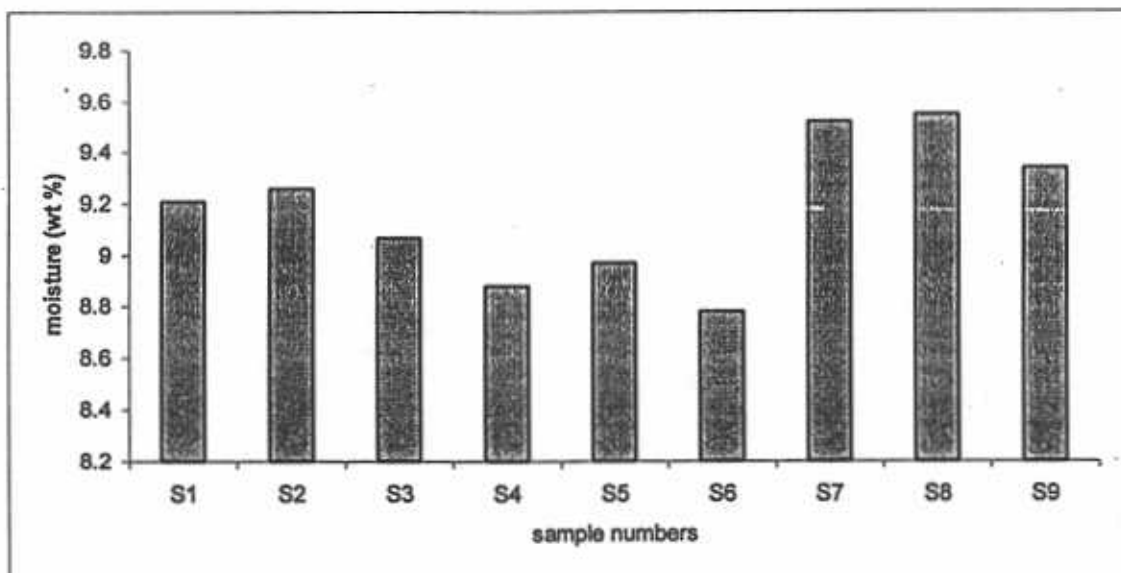


Figure 4.37 Moisture content in baggase (sugarcane).

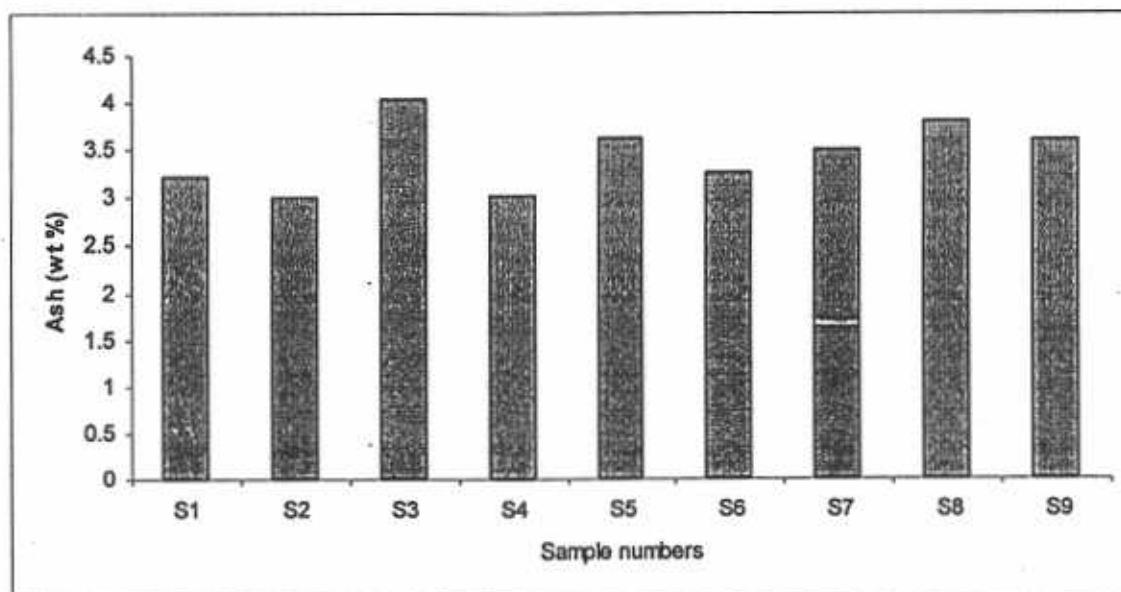


Figure 4.37 (b) Ash content in baggase (sugarcane).

4.7.2 Analysis of Baggage Ash (sugarcane)

Baggage ash is obtained from the burning of baggage in sugar mills. The ash was collected from the sugar mills of N.W.F.P. and studied for different physical and chemical parameters using different analytical techniques. The results are reported in Table 4.26 to 4.28.

Moisture, loss on ignition and ash was determined using thermogravimetric analyzer. Smaller variations in these parameters have been noticed. The results are presented in Table 4.26 and graphically shown in Figure 4.38. It is clear from the figure that moisture is ranging from 2.25 wt% to 3.68 wt%, Ash content from 85.21 wt% to 88.75 wt% and loss on ignition varies from 11.40 wt% to 14.80 wt%. The average composition of the studied baggage ash suggest that this ash on average contain moisture = 2.93 wt%, ash = 86.69 wt% and loss on ignition = 13.45 wt% (Table 4.26). The high loss on ignition is due to unburnt carbon, which on ignition changes in to carbon dioxide.

As discussed before that baggage on average contain 3.46% ash (Table 4.25), the remaining is almost carbon containing compounds. When baggage is burnt in the sugar mill, most of the carbon is converted into carbon dioxide and ash; still some of the carbon in baggage remains unburned, due to the incomplete burning in the sugar mills, which is good source of energy. The unburned carbon in the studied ash is shown in Table 4.27 and graphically presented in Figure 4.40 (a). The Table shows that carbon content varies from 15 to 24% and the average is 18.67%. The sulphur content of the studied baggage ash varies from 0.17 to 0.24% and the average is 0.21 wt% (Table 4.27)

The calorific value of the ash was studied using bomb calorimeter and the results are given in Table 4.28 and graphically shown in Figure 4.39. The figure shows that very small variations in calorific value have been noticed, which varies from 48 kcal/kg to 50 kcal/kg. The calorific value of baggage ash is 49.5 kcal/kg.

The ash of baggage obtained from sugar mills, contains almost all the constituents present in cement, due to which it has pozzolonic properties. The chemical composition of the ash after complete ignition in TGA was studied through

XRF for elements and the results obtained are presented in Table 4.29 and graphically shown in Figure 4.41.

Chemically variation in all the oxides has been noticed in the ash after ignition (Table 4.29 and Figure 4.41). SiO_2 is ranging from 85.65 to 90.09 wt%, Al_2O_3 from 1.72 to 3.65 wt %, Fe_2O_3 from 2.65 to 4.90 wt %, CaO from 2.49 to 3.39 wt %, MgO from 0.62 to 2.02 wt %, Na_2O from 0.10 to 0.28 wt %, K_2O from 0.32 to 0.58 wt % and SO_3 is ranging from 0.11 to 0.24 wt %. The average composition of the studied baggase ash suggest that this ash on average contain $\text{SiO}_2 = 87.87$ wt%, $\text{Al}_2\text{O}_3 = 2.47$, $\text{Fe}_2\text{O}_3 = 4.05$ wt%, $\text{CaO} = 2.84$ wt%, $\text{MgO} = 1.10$ wt%, $\text{Na}_2\text{O} = 0.17$ %, $\text{K}_2\text{O} = 0.44$ % and $\text{SO}_3 = 0.16$ %. The variation in composition may be due to the difference in areas and soil composition, from where the sugarcane has been obtained.

Table 4.26 Analysis of Baggase Ash using of Thermogravemetric Analyzer.

Sampling station	Sample code	Moisture (%)	Ash (%)	Loss on Ignition (%)
Premier Sugar Mill Mardan (PSM)	S ₁	2.25	85.58	14.45
	S ₂	2.35	85.21	14.80
	S ₃	2.36	85.95	14.20
Khazana Sugar Mill Peshawar(KSM)	S ₄	2.95	88.47	11.60
	S ₅	2.76	88.62	11.40
	S ₆	3.02	88.75	11.52
Frontier Sugar Mill Thakt-Bhai (Mardan) (FSM)	S ₇	3.56	85.85	14.25
	S ₈	3.68	85.66	14.44
	S ₉	3.46	86.14	14.38
Average		2.93	86.69	13.45

Table 4.27 Analysis of Baggase Ash through Carbon-Sulphur Detector

Sampling Station	Sample numbers	Sulfur (%)	Carbon (%)
Premier Sugar Mill Mardan (PSM)	S₁	0.22	15
	S₂	0.21	16
	S₃	0.21	18
Khazana Sugar Mill Peshawar(KSM)	S₄	0.17	24
	S₅	0.18	23
	S₆	0.17	23
Frontier Sugar Mill Thakt-Bhai (Mardan) (FSM)	S₇	0.23	15
	S₈	0.24	16
	S₉	0.23	18
Average		0.21	18.67

Table 4.28 Analysis of Baggase Ash through Bomb Calorimeter

SAMPLING STATION	Sample numbers	Calorific Value (kcal/kg)
Premier Sugar Mill Mardan (PSM)	S₁	50
	S₂	50
	S₃	50
Khazana Sugar Mill Peshawar(KSM)	S₄	48
	S₅	49
	S₆	48
Frontier Sugar Mill Thakt-Bhai (Mardan) (FSM)	S₇	50
	S₈	49
	S₉	50
Average		49.33

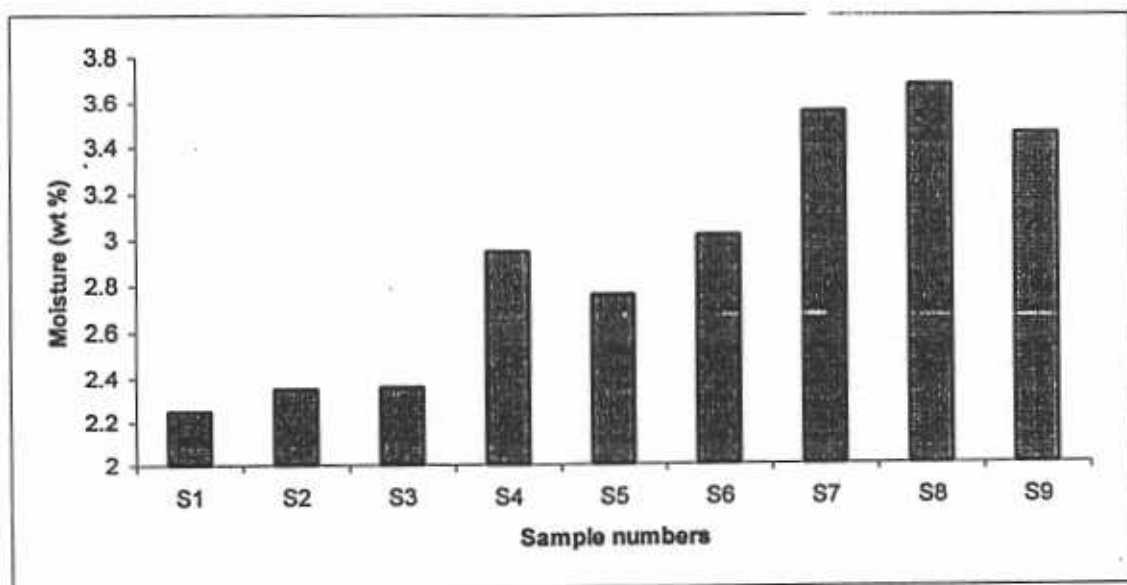


Figure 4.38 Moisture content in baggase ash.

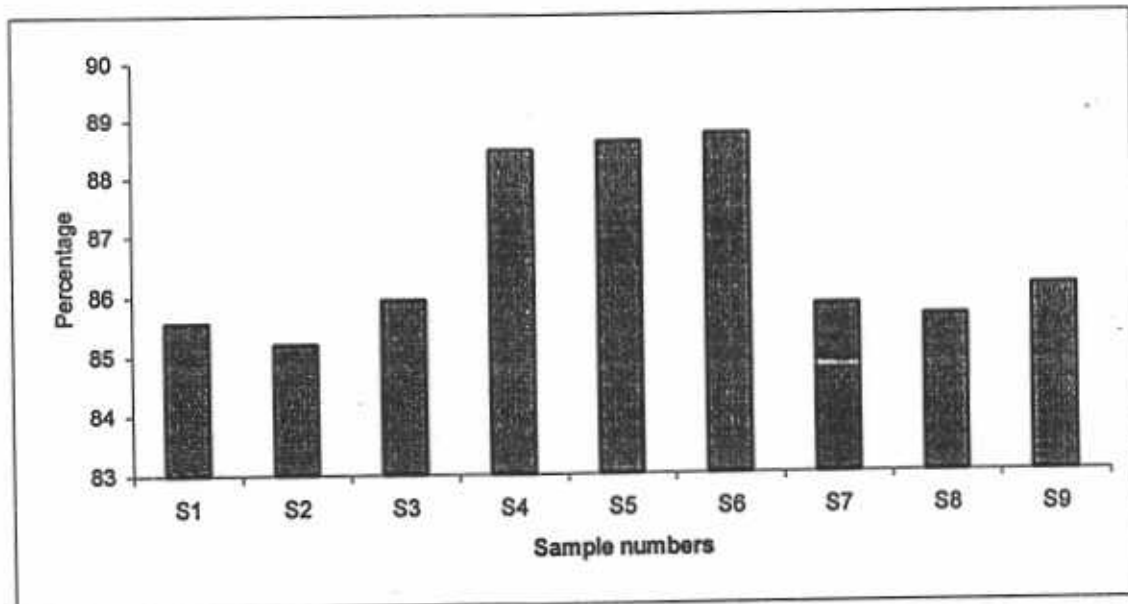


Figure 4.38 (b) Ash content in baggase ash

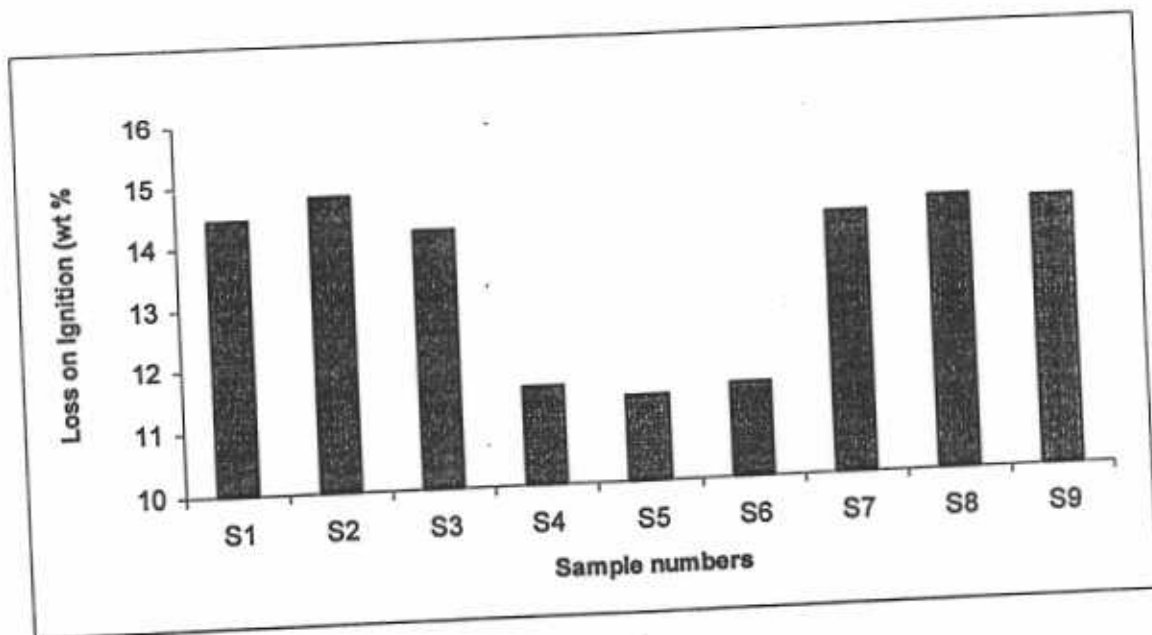


Figure 4.38 (c) Loss on ignition of baggase ash.

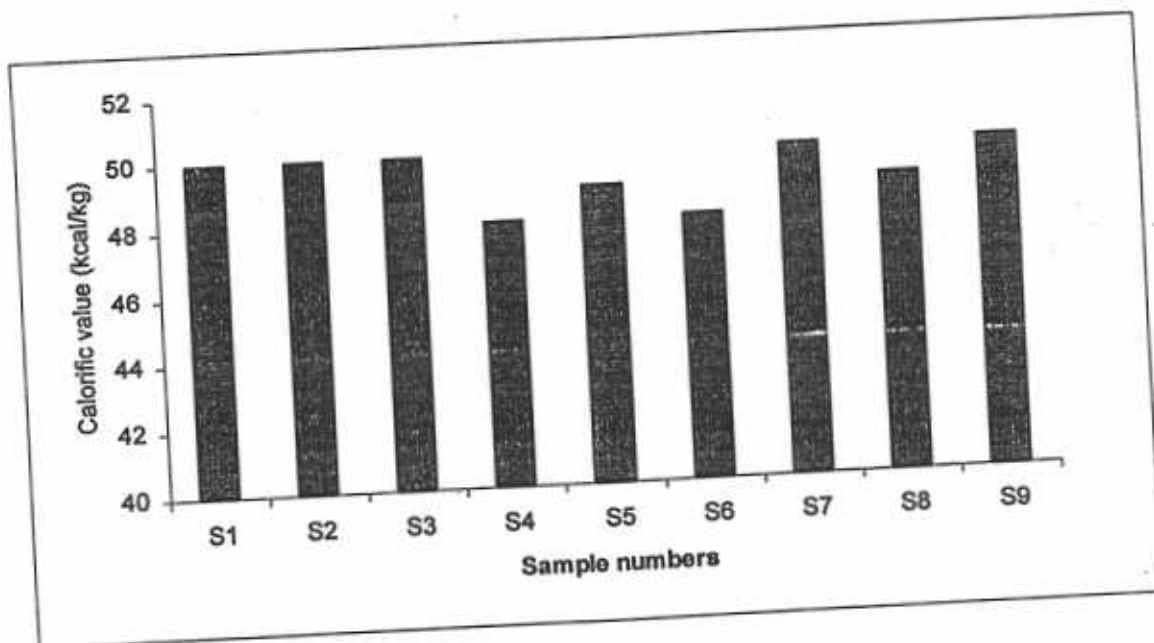


Figure 4.39 Calorific value of baggase ash (kcal/kg).

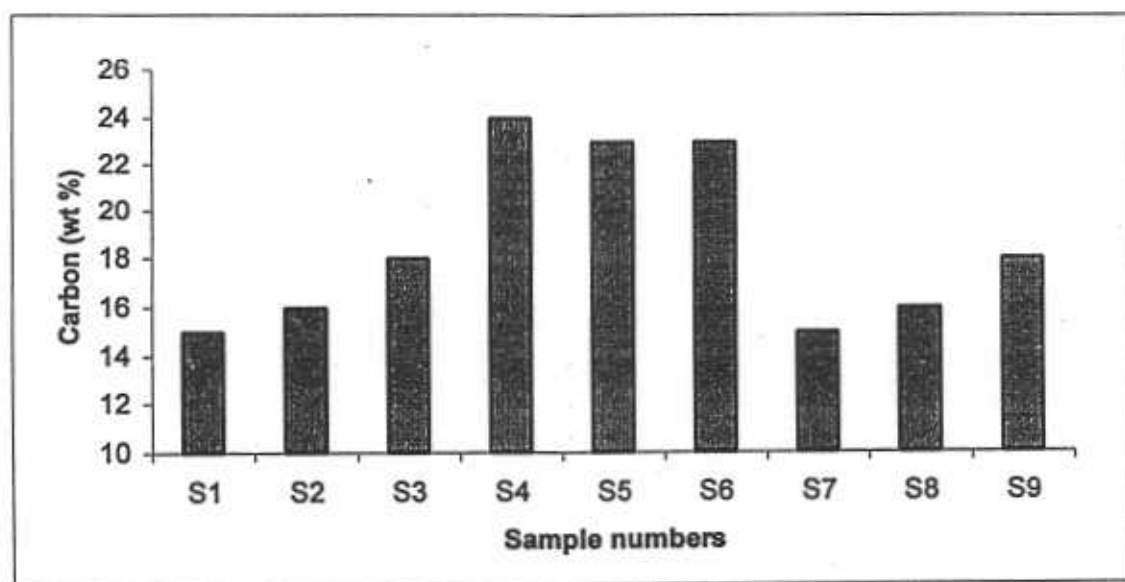


Figure 4.40 (a) Carbon content in baggase ash.

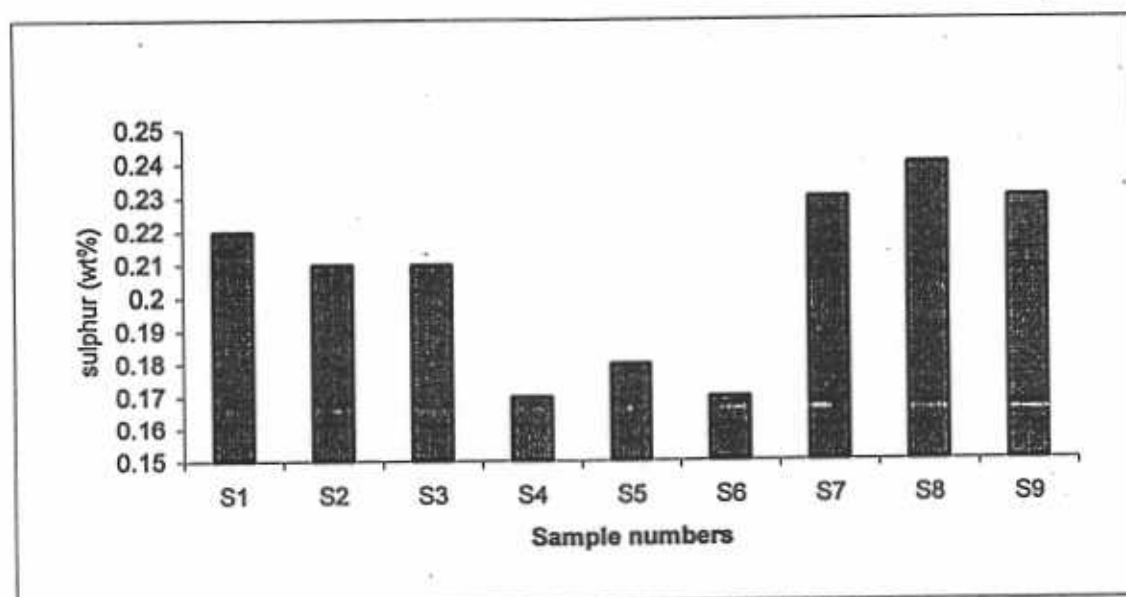


Figure 4.40 (b) Sulfur content in baggase ash.

Table 4.29 Chemical Analysis of Baggage Ash collected from Sugar Mills

Analyte	Wt %									Average
	PSM			KSM			FSM			
	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	
SiO ₂	87.4	87.23	88.65	90.09	89.89	88.36	85.65	86.25	87.32	87.87
Al ₂ O ₃	3.6	3.45	3.65	1.77	1.84	1.72	2.15	1.99	2.02	2.47
Fe ₂ O ₃	4.9	5.02	4.26	2.65	2.71	2.82	4.82	4.75	4.56	4.05
CaO	2.56	2.49	2.64	2.68	2.75	2.65	3.39	3.25	3.35	2.86
MgO	0.69	0.71	0.63	0.66	0.72	0.62	1.98	2.02	1.87	1.10
Na ₂ O	0.15	0.14	0.154	0.28	0.27	0.25	0.11	0.11	0.1	0.17
K ₂ O	0.47	0.47	0.45	0.32	0.35	0.32	0.58	0.57	0.41	0.44
SO ₃	0.11	0.12	0.11	0.16	0.15	0.12	0.23	0.21	0.20	0.16
Total	99.88	99.63	100.54	98.61	98.68	96.86	98.91	99.15	99.83	99.12

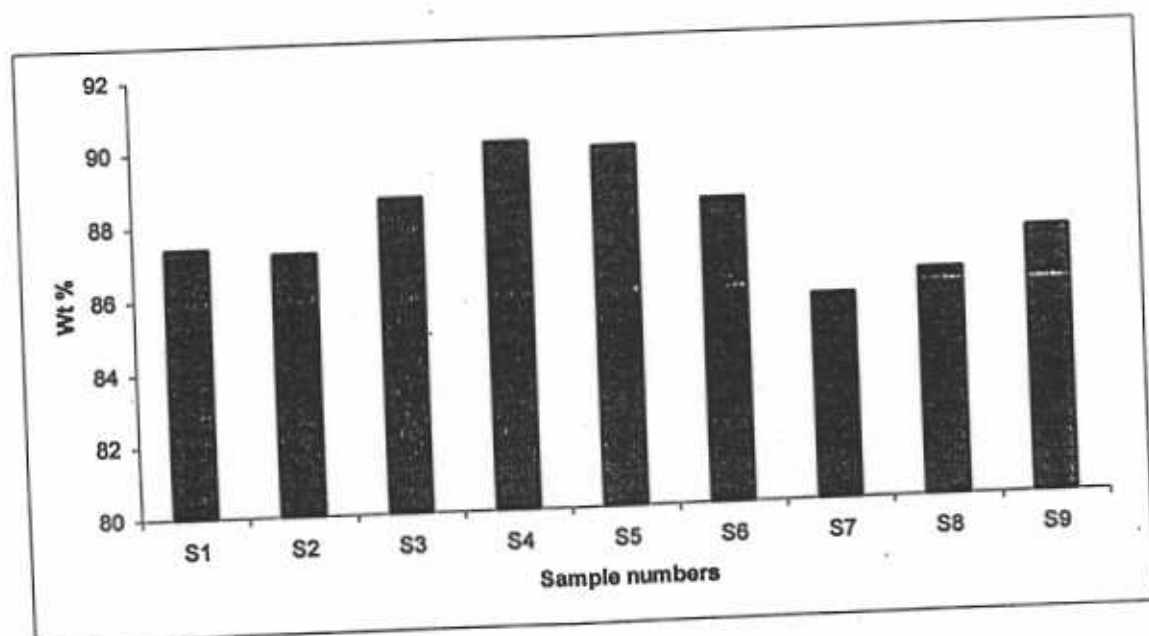


Figure 4.41 (a) Variation of silicon dioxide (SiO_2) in baggase ash.

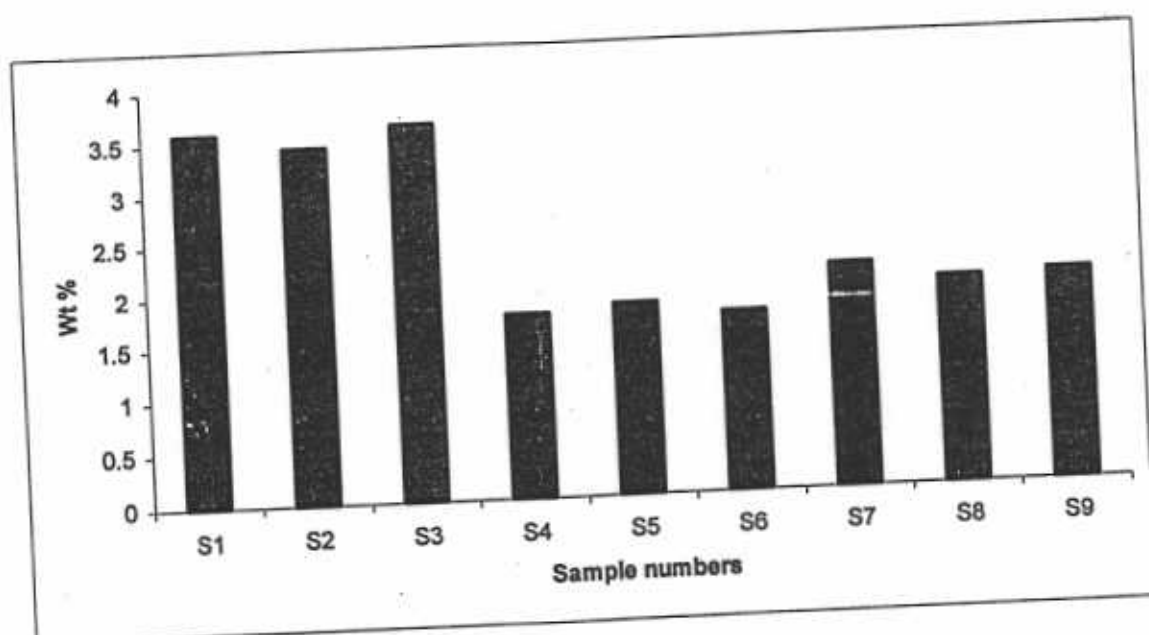


Figure 4.41 (b) Variation of aluminum oxide (Al_2O_3) in baggase ash.

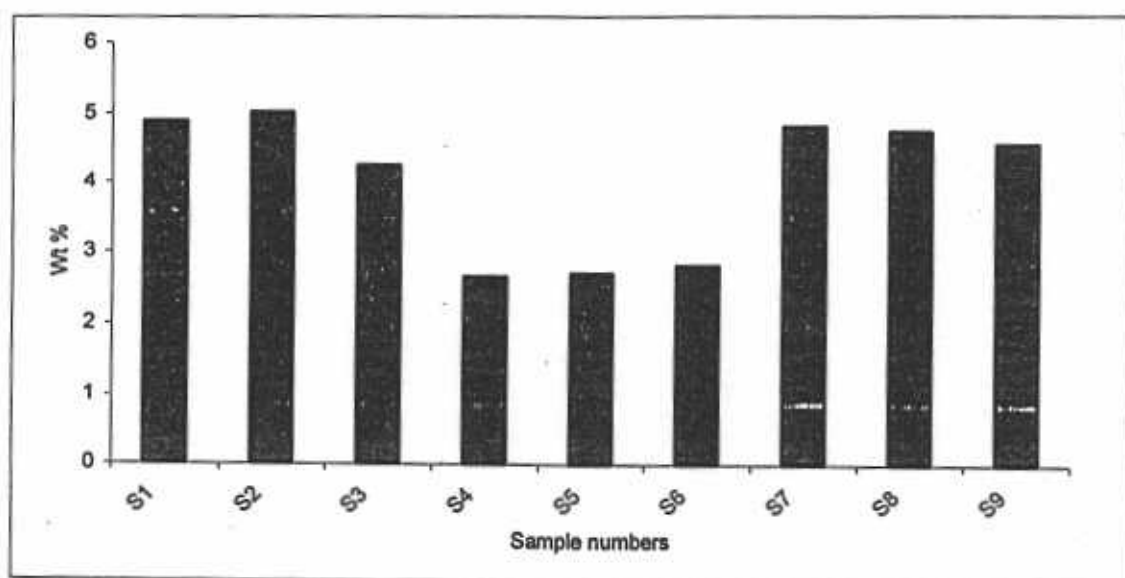


Figure 4.41 (c) Variation of iron oxide (Fe_2O_3) in baggase ash.

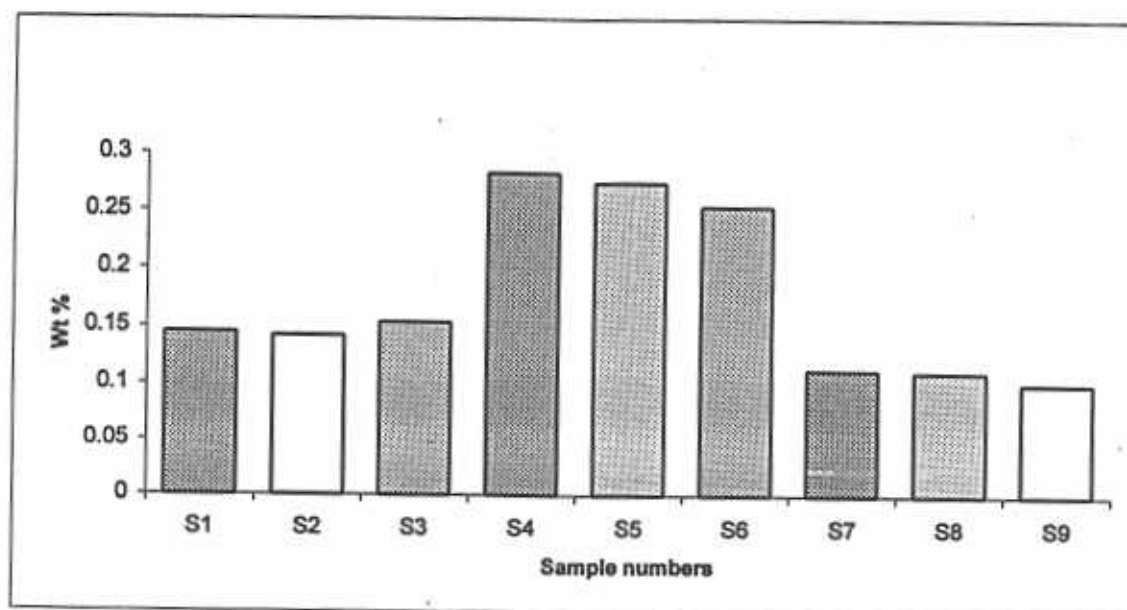


Figure 4.41 (d) Variation of calcium oxide (CaO) in baggase ash.

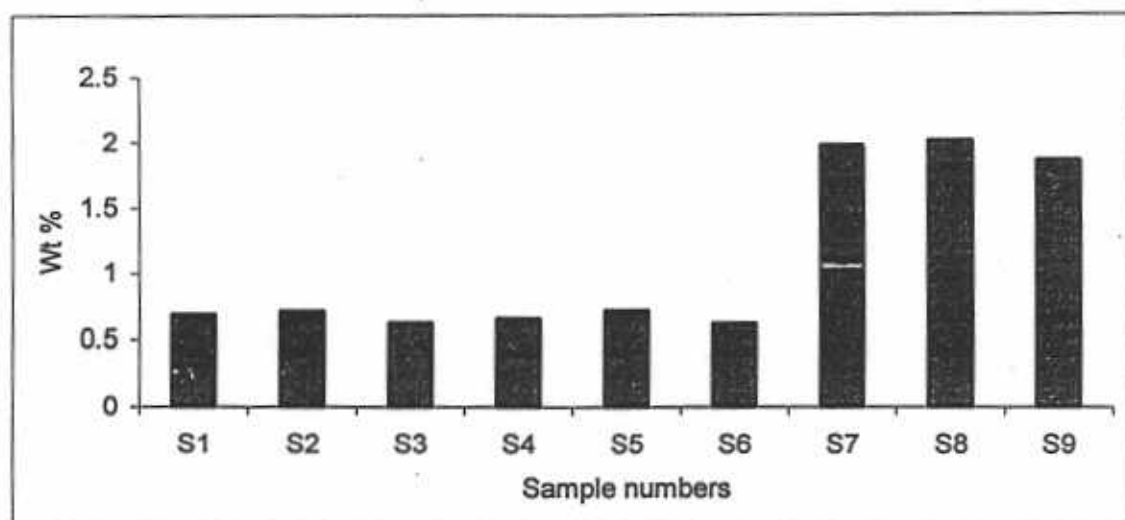


Figure 4.41 (e) Variation of magnesium oxide (MgO) in baggase ash.

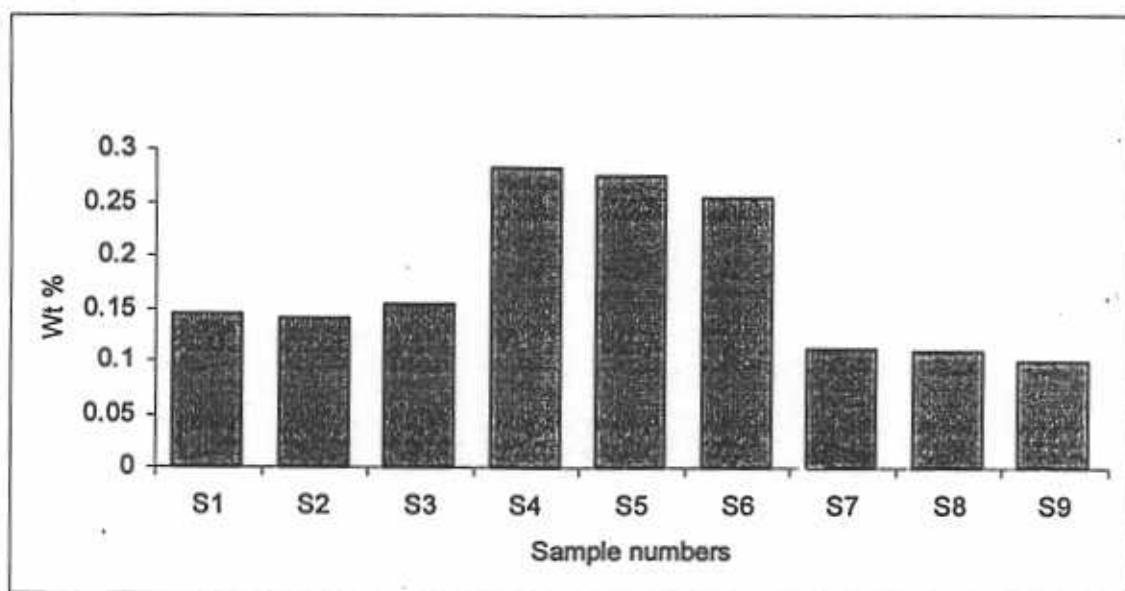


Figure 4.41 (f) Variation of sodium oxides (Na₂O) in baggase ash.

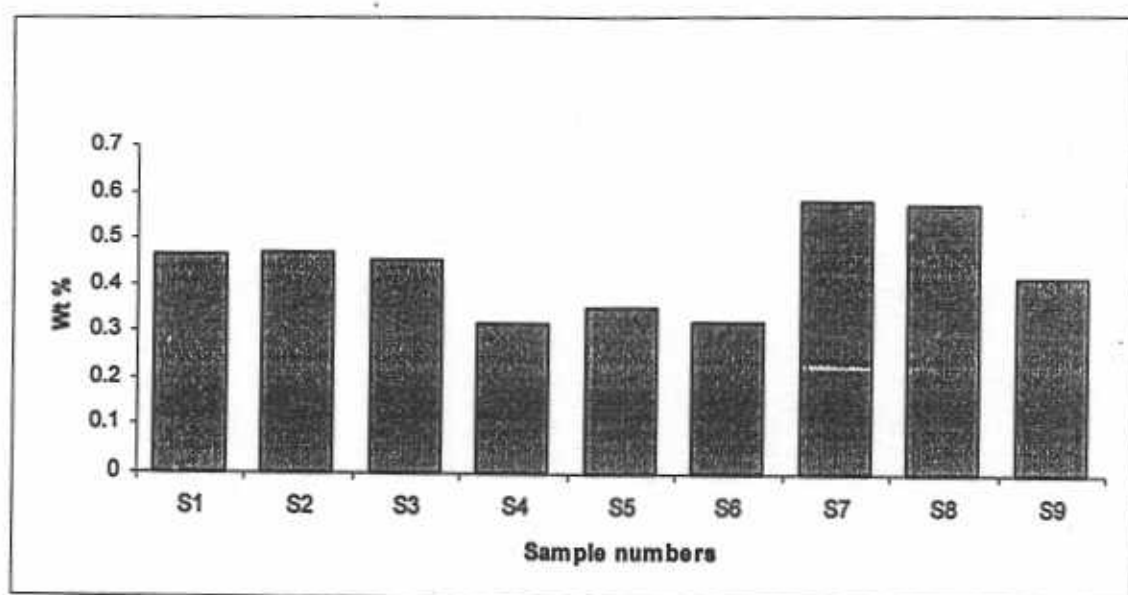


Figure 4.41 (g) Variation of potassium oxides (K_2O) in baggase ash.

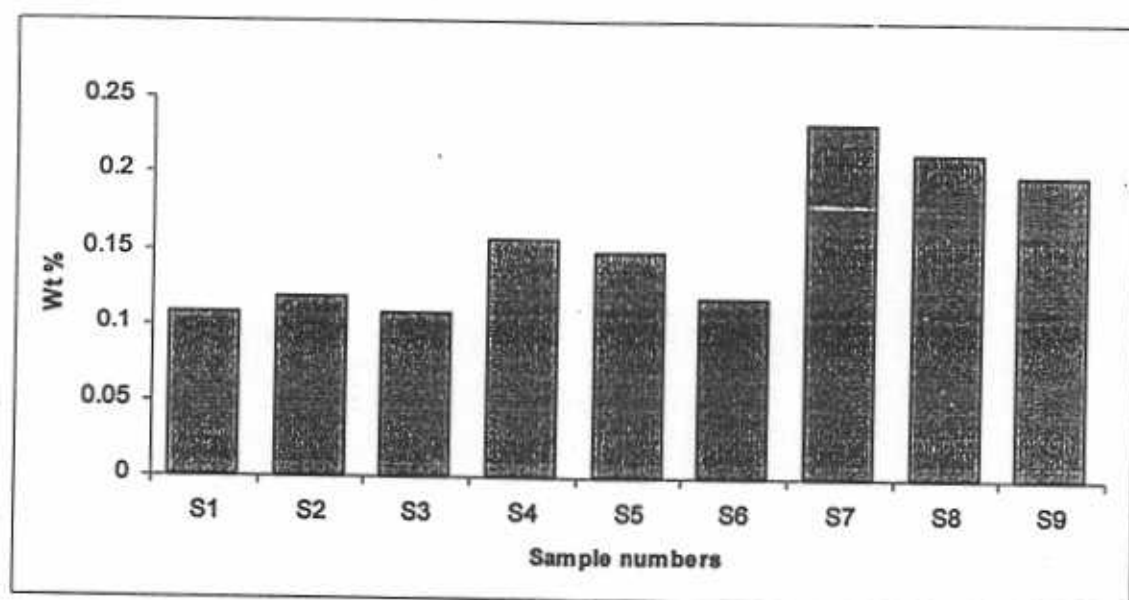


Figure 4.41 (h) Variation of sulphuric anhydride (SO_3) in baggase ash.

4.8 ADDITION OF BAGGASE ASH WITH NORMAL LIME RAW MIX

4.8.1 Effect of Baggase Ash on the Chemical Composition of the Normal Raw Mix and Clinker

The chemical composition of baggase ash is entirely different from that of cement raw mix, so when it is mixed with the raw mix, it changes its composition.

The chemical composition of normal raw mix for high strength portland cement and baggase ash are given in Table 4.30 and 4.31. Baggase ash was added with normal cement raw mix in different percentages ranging from 1-5% and thus different raw mixes for high strength Portland cement were prepared and are given in Table 4.32. It is clear from the Tables 4.28 and 4.29 that baggase ash contains silica, alumina and iron oxides in greater percentages and calcium oxide in smaller percentage as compared to the normal raw mix used for the manufacturing of cement, so when it was blended with the normal raw mix, it increased the percentage of silica, alumina and iron and decreased the calcium oxide content in the resulting raw mix. These raw mixes were converted into clinker. The chemical analysis along with clinker moduli and potential are given in Table 4.33. The clinkers thus formed were converted into cement and different parameters of the cements were studied and compared with the standards.

Table 4.30 Chemical Composition of a Normal Raw Mix

Analyte	Wt %
SiO ₂	14.60
Al ₂ O ₃	3.83
Fe ₂ O ₃	2.28
CaO	42.55
MgO	0.98
Na ₂ O	0.18
K ₂ O	0.46
SO ₃	0.10
Moduli	
MA	1.68
MS	2.39
LSF	0.91

Table 4.31 Chemical Composition of Bagasse Ash used in Clinkerization

Analyte	Wt %
SiO ₂	87.40
Al ₂ O ₃	3.60
Fe ₂ O ₃	4.90
CaO	2.56
MgO	0.69
Na ₂ O	0.15
K ₂ O	0.47
SO ₃	0.11

Table 4.32 Effect of Baggase Ash on the Chemical Composition of Normal Raw Mix

Analyte	Baggase ash (Wt %)					
	0	1	2	3	4	5
SiO ₂	14.60	15.33	16.06	16.78	17.51	18.24
Al ₂ O ₃	3.83	3.83	3.83	3.82	3.82	3.82
Fe ₂ O ₃	2.28	2.31	2.33	2.36	2.39	2.41
CaO	42.55	42.15	41.75	41.35	40.95	40.55
MgO	0.98	0.98	0.97	0.97	0.97	0.97
Na ₂ O	0.18	0.18	0.18	0.18	0.18	0.18
K ₂ O	0.46	0.46	0.46	0.46	0.46	0.46
SO ₃	0.10	0.10	0.10	0.10	0.10	0.10
Moduli						
MA	1.68	1.66	1.64	1.62	1.60	1.58
MS	2.39	2.50	2.61	2.71	2.82	2.93
LSF	0.91	0.86	0.82	0.78	0.74	0.71

Table 4.33 Effect of Baggage Ash on the Chemical Composition of Normal Clinker.

Analyte	Baggage ash (Wt %)					
	0	1	2	3	4	5
SiO ₂	22.63	23.76	24.89	26.01	27.14	28.27
Al ₂ O ₃	5.94	5.93	5.93	5.93	5.92	5.92
Fe ₂ O ₃	3.53	3.57	3.61	3.66	3.70	3.74
CaO	65.95	65.33	64.71	64.04	63.47	62.85
MgO	1.52	1.51	1.51	1.51	1.50	1.50
Na ₂ O	0.28	0.28	0.28	0.28	0.28	0.28
K ₂ O	0.71	0.71	0.71	0.71	0.73	0.71
SO ₃	0.15	0.15	0.15	0.15	0.16	0.16
Moduli						
MA	1.68	1.66	1.64	1.62	1.60	1.58
MS	2.39	2.50	2.61	2.71	2.82	2.93
LSF	0.91	0.86	0.82	0.78	0.74	0.71
Clinker potential						
C ₃ S	51.13	39.99	28.86	17.73	6.59	-4.54
C ₂ S	26.31	37.94	49.58	61.21	72.85	84.48
C ₃ A	9.76	9.68	9.60	9.53	9.45	9.37
C ₄ AF	10.75	10.88	11.00	11.13	11.25	11.37
LP (1450C)	27.43	27.51	27.59	27.66	27.74	27.82
BF	17.55	18.61	19.66	20.71	21.76	22.80

4.8.2 Effect of Baggage Ash on the Moduli and Clinker Potential of normal Raw Mix Clinker

As the composition of normal raw mix and clinker changed with the addition of baggage ash, the moduli of the resulting clinker also changed significantly. These changes in the moduli are graphically shown in Figure 4.42. From the Figure it is clear that alumina modulus (MA) of the normal raw mix decreased from 1.68 to 1.58 with the addition of baggage ash, silica modulus (MS) increased from 2.39 to 2.93 and lime saturation factor (LSF) also decreased from 0.91 to 0.71 with the addition of 5% baggage ash.

The addition of baggage ash to the normal cement raw mix decreases the alumina modulus (MA) due to greater amount of alumina in the baggage ash. The usual range of MA is 1.3 - 2.5. If it becomes greater than 2.5, viscous slag and high early strength occur and if it becomes smaller than 1.3 then fluid slags, low early strength and low heat of hydration occur. From the figure 4.42(a) it is clear that the addition of baggage ash does not take the MA out of range.

The usual range of MS is 2 - 3. If the MS becomes, less than 2, burning become very easy but excessive liquid phase and low strength cement is obtained. If the MS goes up to 3, then the high strength cement is obtained but the burning become very difficult, if it goes above 3, then no clinkerization take place at all. This is clear from the results that baggage ash does not take the MS out of range, though the burning will become hard.

The usual range of LSF is 0.90 - 0.98 even if it reaches 0.8, it creates no problem in cement manufacturing process and cement strength, but it should not be less than 0.8. 1% baggage ash decreases the LSF from 0.91 to 0.86 and 5% baggage ash decreases the LSF upto 0.71, which is too much out of the acceptable range. This shows that baggage ash should not be added to the normal raw mix more than 1%. However for this purpose high lime raw mix was used.

The effect of baggage ash on the clinker potential is graphically shown in Figure 3.43. The figure shows that with the addition of 5% baggage ash, tricalcium silicate (C_3S) decreased from 51.13 to -4.54, dicalcium silicate (C_2S) increased from 26.31 to 84.48, tricalcium aluminate (C_3A) decreased from 9.76 to 9.37 and tetracalcium aluminoferrite (C_4AF) increased from 10.75 to 11.37 (Figure 3.43)

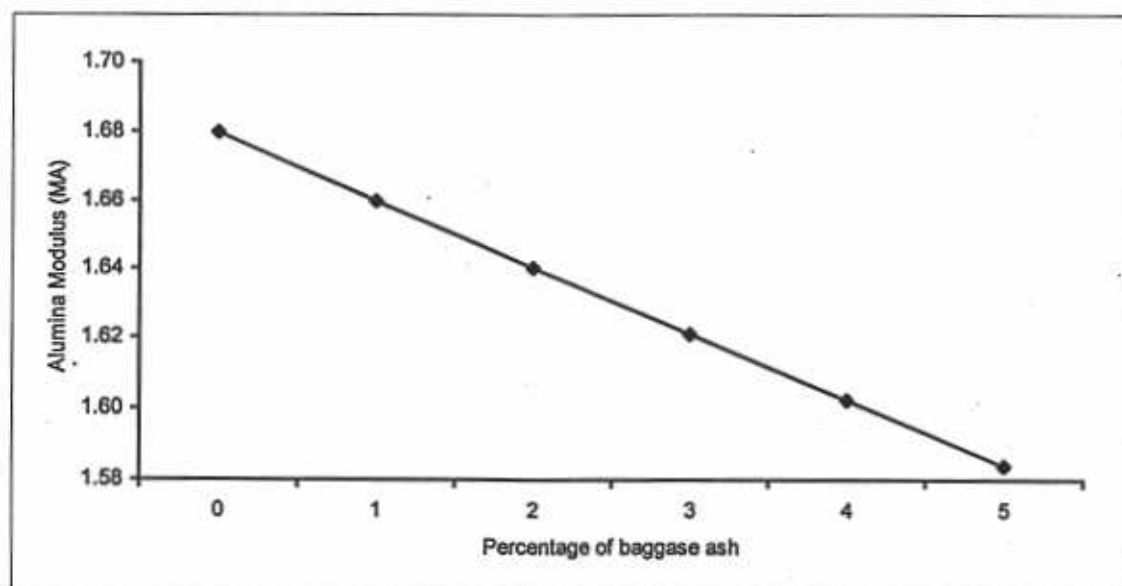


Figure. 4.42 (a) Effect of baggase ash on alumina modulus of normal raw mix clinker.

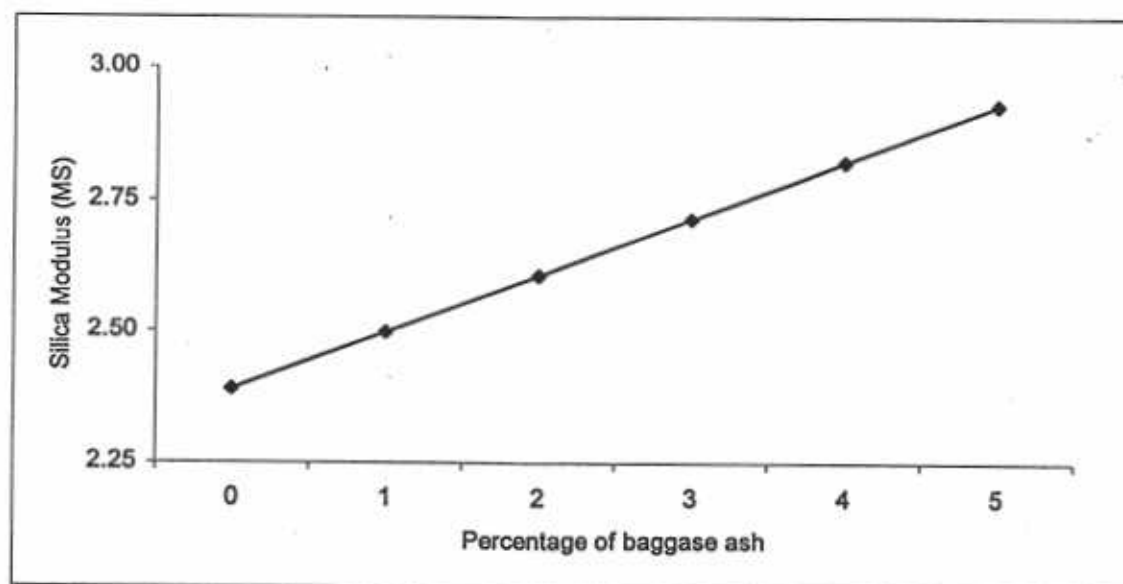


Figure 4.42 (b) Effect of baggase ash on silica modulus of normal raw mix clinker.

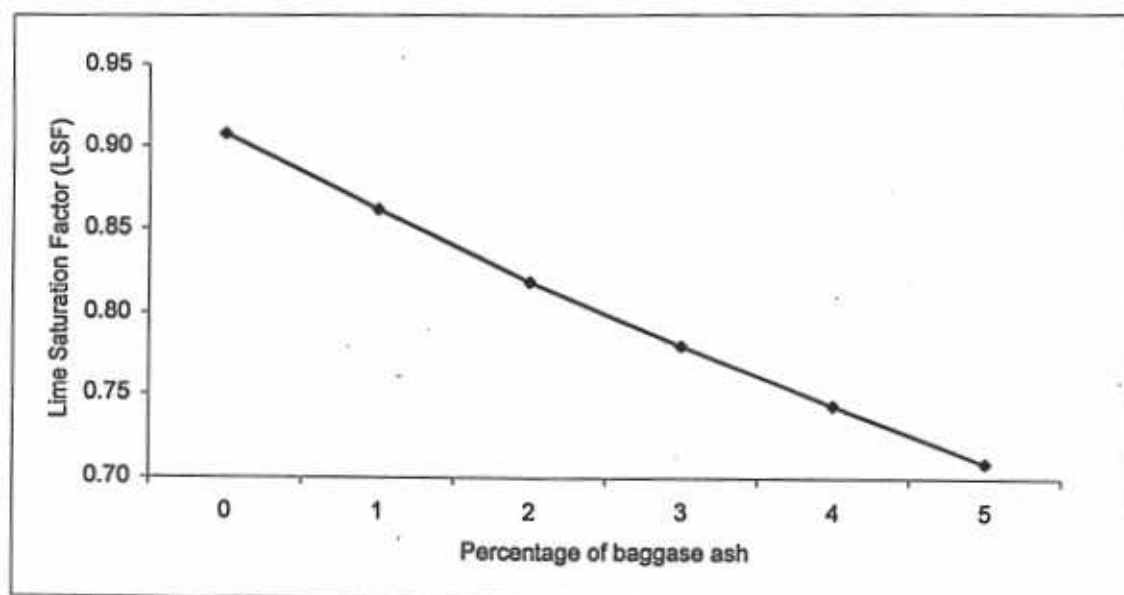


Figure 4.42 (c) Effect of baggase ash on lime saturation factor of normal raw mix clinker.

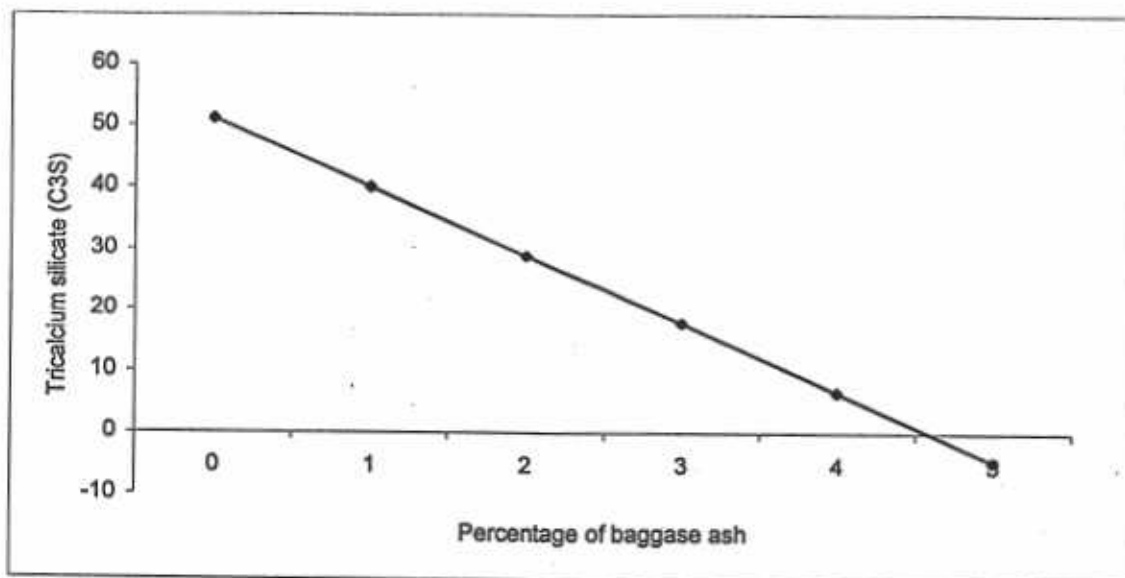


Figure 4.43 (a) Effect of baggase ash on tricalcium silicate of normal raw mix clinker.

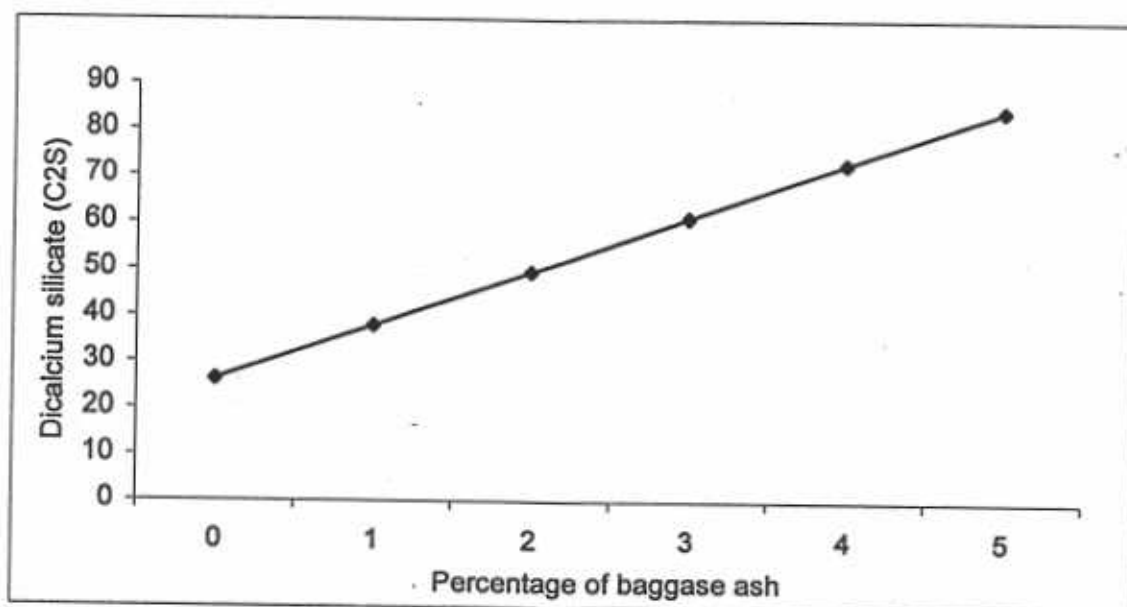


Figure 4.43 (b) Effect of baggase ash on dicalcium silicate of normal raw mix clinker.

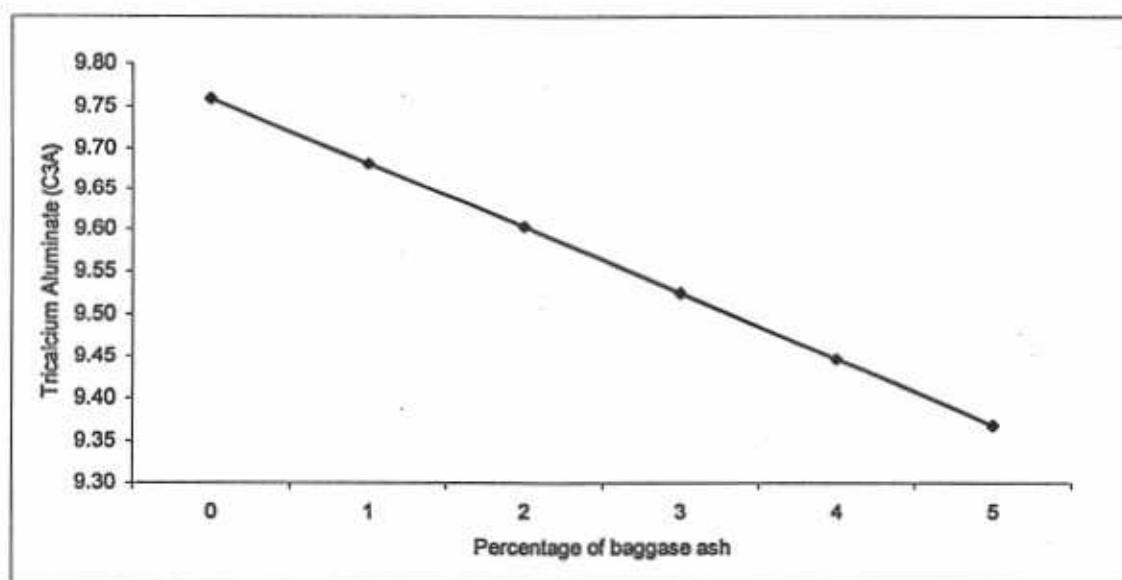


Figure 4.43 (c) Effect of baggase ash on tricalcium aluminate of normal raw mix clinker.

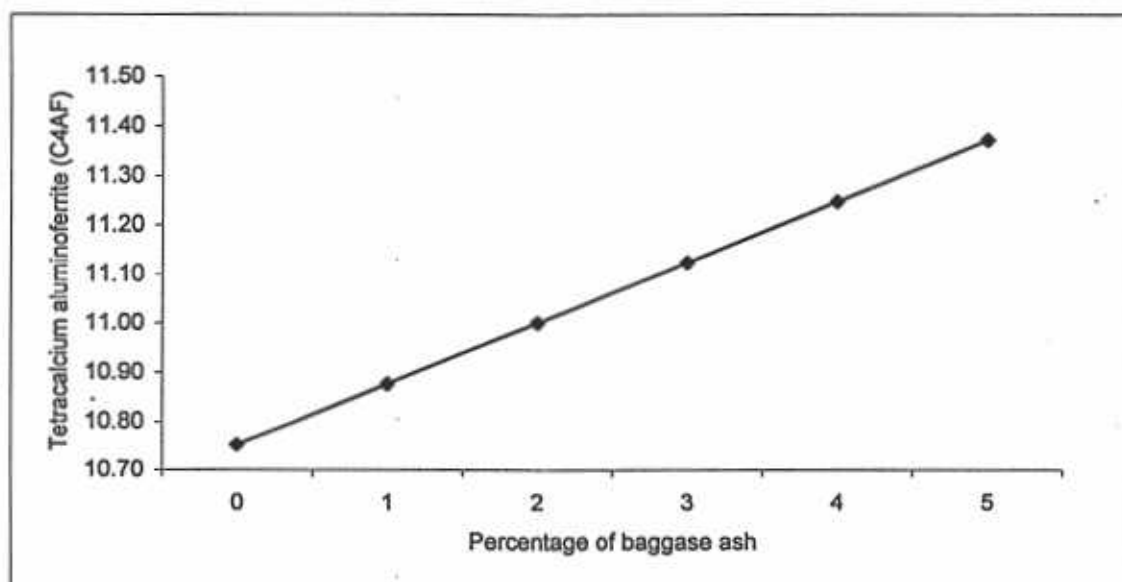


Figure 4.43 (d) Effect of baggase ash on tetracalcium aluminoferrite of normal raw mix clinker.

4.8.3 Effect of Baggase Ash on the Compressive Strength of Cement of the normal Raw Mix

Considerable effects of baggase ash on the compressive strength of the cement have been observed. The effect of baggase ash on the compressive strength of the cement is shown in Table 4.34 and graphically shown in Figure 4.44 which shows that three days compressive strength of the cement gradually decreases as the percentage of the baggase ash increases. Without the addition of baggase ash the 3 days strength of the high strength Portland cement is 4750 psi while with 1% baggase ash it reduced to 3980 psi, and with 2 % ash to 3250 psi which is less than the standard for 3 days compressive strength which is 3336 psi. (Table 4.34). With the addition of further baggase ash, compressive strength reduces significantly. 5% ash reduces the compressive strength up to 1980 psi, which is significantly smaller than the standard.

The 7 days compressive strength of the high strength Portland cement obtained from normal raw mix with out baggase ash is 5100 psi. With 1% baggase ash the compressive strength of seven days reduced to 4800 psi, which is in good agreement with the standard (4690 psi). Further addition of baggase ash took the strength out of range. With 5% baggase ash, the strength reduced to 2750 psi.

28 days strength of the high strength Portland cement without the addition of baggase ash was recorded as 6875 psi. When 1% baggase ash was added to the normal raw mix, it reduced the strength up to 6570 psi. The standard for 28-days strength of high strength Portland cement is 5960 psi, (Table 4.12) so addition of 1% baggase ash does not take the strength out of range. However above 1 %, the strength goes out of range. When 5% baggase ash was added to the normal raw mix, the strength reduced to 3145 psi.

As a conclusion we can say that 1% baggase ash can be added to the normal raw mix, which does not make the strength of cement out of range. Further addition of baggase ash can be possible by using high lime raw mix. This will reduce the amount of clay and increase the amount of limestone in the raw mix. The increase in limestone and decrease in clay will be compensated by baggase ash due to its high silica content.

Table 4.34 Effect of Baggage Ash on the Compressive Strength of Cement of the Normal Raw Mix

Percentage baggage ash	Compressive strength (PSI)		
	3 Days	7 Days	28 Days
0	4750	5100	6875
1	3980	4860	6570
2	3250	4610	5825
3	2640	3570	4815
4	2120	3220	3850
5	1980	2750	3145
Standard	3336	4690	5960

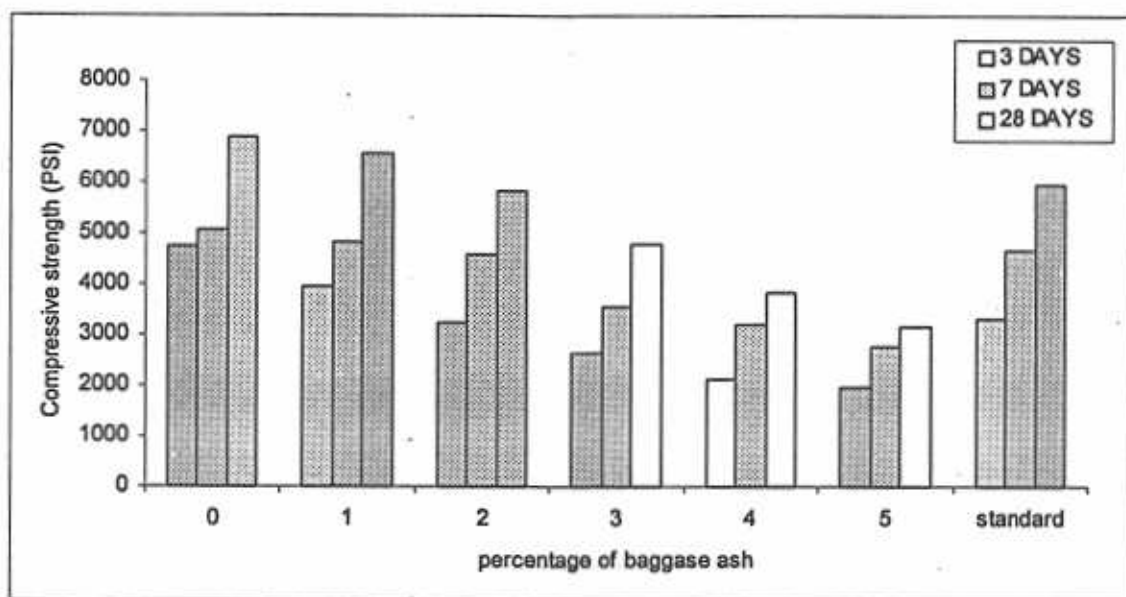


Figure 4.44 Effect of baggage ash on the compressive strength of the normal cement.

4.9 ADDITION OF BAGGASE ASH WITH HIGH LIME RAW MIX

Baggase ash is acting as a raw material for manufacturing of high strength Portland cement. If it is mixed with the normal lime saturation factor raw mix, it can not be added above 1%. Baggase ash also contains unburnt carbon which is acting as alternate fuel for clinkerization. So such raw mixes were designed in which maximum possible amount of baggase ash was utilized and the parameters of the resulting clinker and cement remained within the range of standards. For this purpose high lime saturation factor raw mix was designed shown in Table 4.35.

Table 4.35 Chemical Composition of High lime Raw Mix

Analyte	Wt %
SiO ₂	12.66
Al ₂ O ₃	3.58
Fe ₂ O ₃	2.20
CaO	43.60
MgO	1.00
Na ₂ O	0.20
K ₂ O	0.50
SO ₃	0.10
Moduli	
MA	1.63
MS	2.19
LSF	1.06

4.9.1 Effect of Baggage Ash on the Chemical Composition of the High Lime Raw Mix

The addition of baggage ash to the normal raw mix was not possible above 1%, which disturbed the parameters of the clinker. So different raw mixes with high LSF and low MS were designed. The most suitable raw mix, which was designed for mixing with baggage ash, is given in Table 4.35.

Different raw mixes with different percentages of baggage ash (ranging from 1% to 7% baggage ash) were prepared. The chemical composition of all the raw mixes is shown in Table 4.36. From the Table it is clear that with the increase in the percentage of baggage ash, the percentage of silica, alumina and iron increases, calcium and magnesium oxides decreases while sodium, potassium and sulphuric anhydride remain almost the same. The raw mixes with different percentages were converted into clinker, the chemical composition of which along with the moduli and clinker potential are reported in Table 4.37.

Table 4.36 Effect of Baggage Ash on the Chemical Composition of High Lime Raw Mix

Analyte	Baggage ash added (Wt %)							
	0	1	2	3	4	5	6	7
SiO ₂	12.66	13.41	14.15	14.90	15.65	16.40	17.14	17.89
Al ₂ O ₃	3.58	3.58	3.58	3.58	3.59	3.59	3.59	3.60
Fe ₂ O ₃	2.20	2.23	2.25	2.28	2.31	2.33	2.36	2.39
CaO	43.60	43.19	42.78	42.37	41.96	41.55	41.14	40.73
MgO	1.00	1.00	0.99	0.99	0.99	0.98	0.98	0.98
Na ₂ O	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
K ₂ O	0.50	0.50	0.50	0.50	0.50	0.49	0.50	0.50
SO ₃	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Moduli								
MA	1.63	1.61	1.60	1.57	1.55	1.53	1.52	1.50
MS	2.19	2.31	2.43	2.54	2.66	2.77	2.88	3.00
LSF	1.06	1.00	0.94	0.89	0.85	0.80	0.77	0.73

Table 4.37 Effect of Baggage Ash on the Chemical Composition of High Lime Clinker

Analyte	Baggage ash added (Wt %)							
	0	1	2	3	4	5	6	7
SiO ₂	19.62	20.78	21.94	23.10	24.26	25.41	26.57	27.73
Al ₂ O ₃	5.55	5.55	5.55	5.55	5.55	5.55	5.55	5.55
Fe ₂ O ₃	3.41	3.45	3.49	3.54	3.58	3.62	3.69	3.69
CaO	67.58	66.94	66.31	65.67	65.04	64.40	63.69	63.06
MgO	1.55	1.55	1.54	1.54	1.53	1.53	1.5	1.49
Na ₂ O	0.31	0.31	0.31	0.31	0.31	0.31	0.28	0.28
K ₂ O	0.77	0.77	0.77	0.77	0.73	0.77	0.7	0.7
SO ₃	0.15	0.15	0.15	0.15	0.16	0.16	0.16	0.16
Moduli								
MA	1.63	1.61	1.59	1.57	1.55	1.53	1.50	1.50
MS	2.19	2.31	2.43	2.54	2.66	2.77	2.88	3.00
LSF	1.06	1.00	0.94	0.89	0.85	0.80	0.76	0.73
Clinker Potential								
C ₃ S	83.39	71.93	60.47	49.02	37.56	26.10	14.33	2.95
C ₂ S	-6.65	5.32	17.28	29.24	41.21	53.17	65.37	77.28
C ₃ A	8.94	8.87	8.80	8.73	8.66	8.59	8.46	8.46
C ₄ AF	10.38	10.50	10.63	10.76	10.89	11.01	11.22	11.22
LP (1450C°)	26.03	26.11	26.21	26.30	26.39	26.48	27.59	27.58
CaO _(free)	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26
BF	15.61	16.75	17.88	19.01	20.13	21.24	22.35	23.45

4.9.2 Effect of Baggage Ash on the Moduli and Clinker Potentials of High Lime Clinker

The Moduli of the clinker are very much affected with the addition of baggage ash because it changed the composition of all the elements of the raw mix and the resulting clinker. The effect of baggage ash on the moduli and clinker potential of the clinker are graphically shown in Figure 4.45 – 4.46

The normal range of the MA is 1.3 - 2.5, so the addition of baggage ash though reduced the MA but still it remains within the range of the Standards. The range of MS is 2-3, which increased with the addition of baggage ash. The increase in MS make the burning hard, when MS exceeds 3, no clinkerization takes place at all. Similarly the usual range of lime saturation factor (LSF) is 0.9 - 0.98, but if it comes upto 0.8, still it creates no problems in cement manufacturing process and cement strength, but it should not go below 0.8. From the Table 4.36 it is clear that baggage ash upto 5% can be blended with the raw mix, but further addition take the clinker moduli and potentials out of range.

Figure 4.45 shows the effect of baggage ash on the alumina modulus (MA), silica modulus MS and lime saturation factor LSF. With 7% baggage ash, MA decreased from 1.63 to 1.50. MS increased from 2.19 to 3.00, while LSF decreased from 1.06 to 0.73.

The effect of baggage on the clinker potential is indicated in Figure 4.46. It is obvious from the figure that with 7% baggage ash tricalcium silicate (C_3S) decreased significantly i.e. from 83.39 to 2.95, dicalcium silicate (C_2S) increased from -6.65 to 77.28, tricalcium aluminate (C_3A) decreased from 8.94 to 8.46 and tetracalcium alumino ferrite (C_4AF) increased from 10.38 to 11.22 (Figure 4.46)

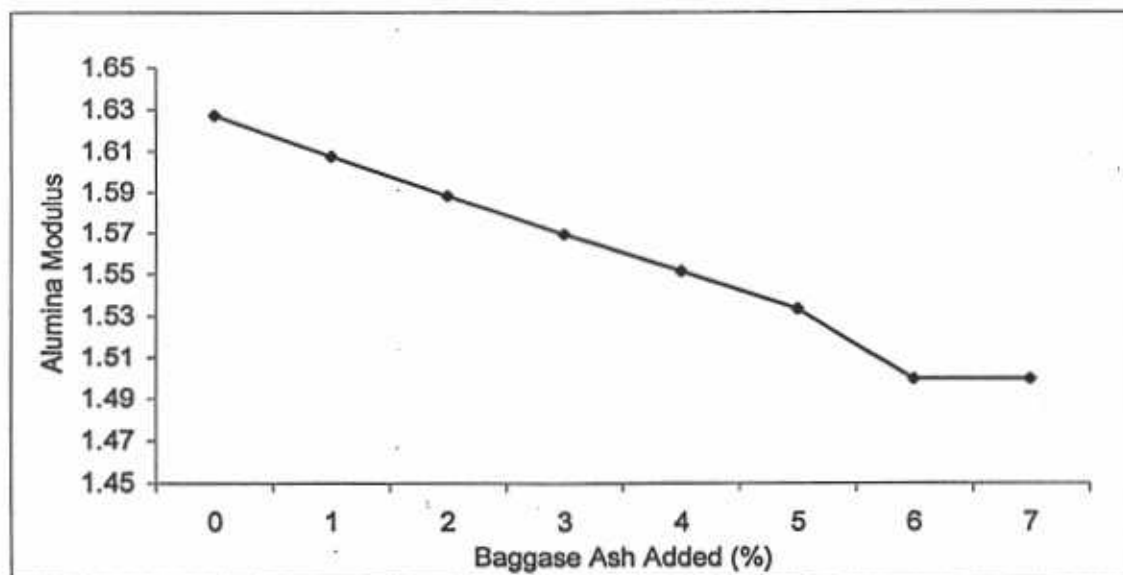


Figure 4.45 (a) Effect of baggase ash on alumina modulus (MA).

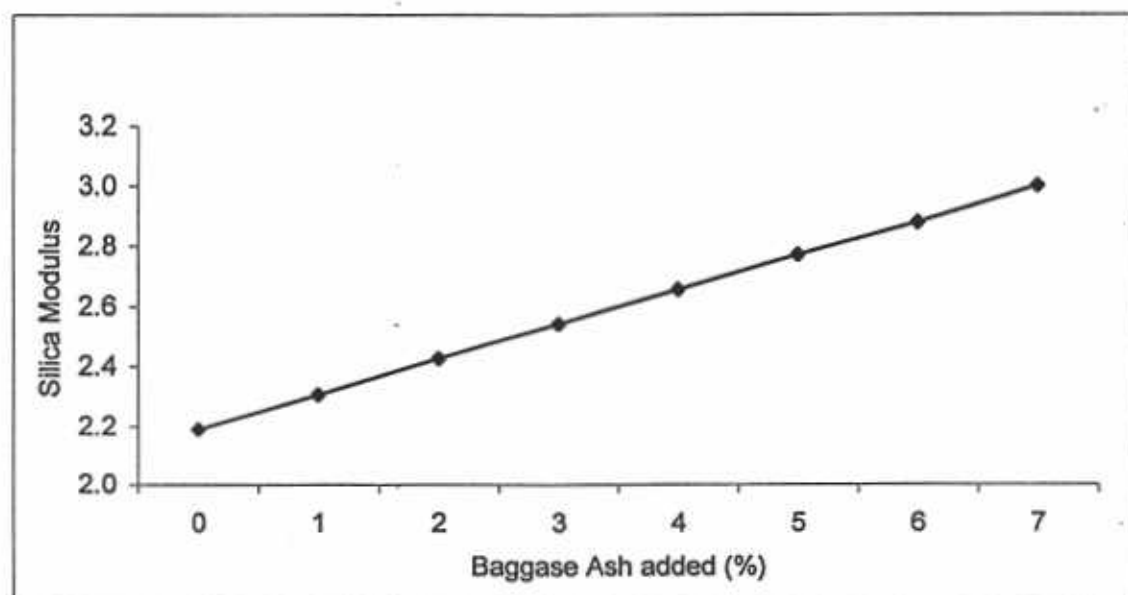


Figure 4.45 (b) Effect of baggase ash on silica modulus (MS).

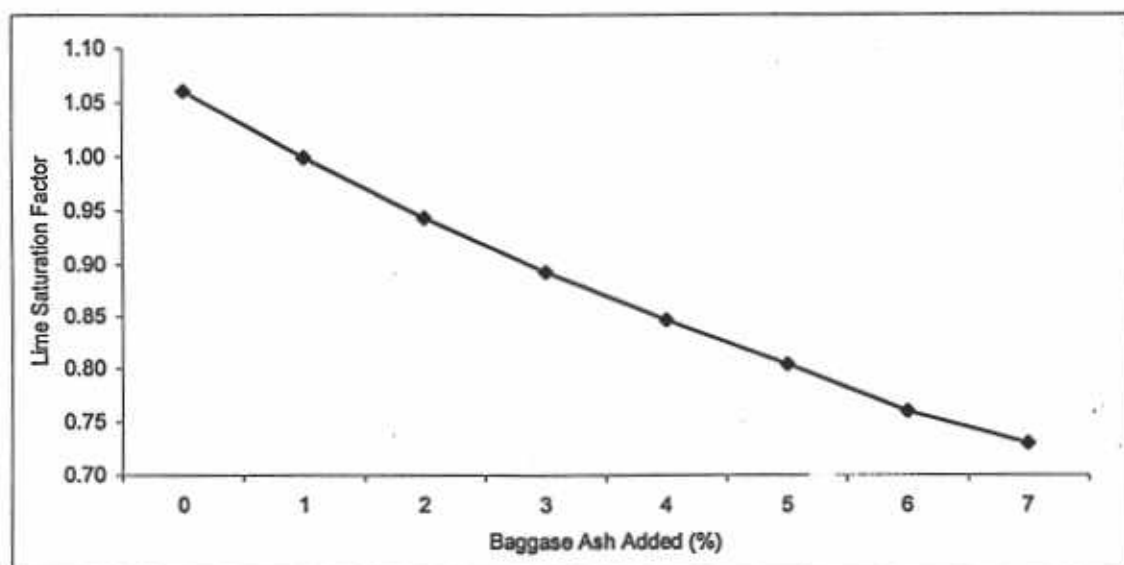


Figure 4.45 (c) Effect of baggase ash on lime saturation factor (LSF).

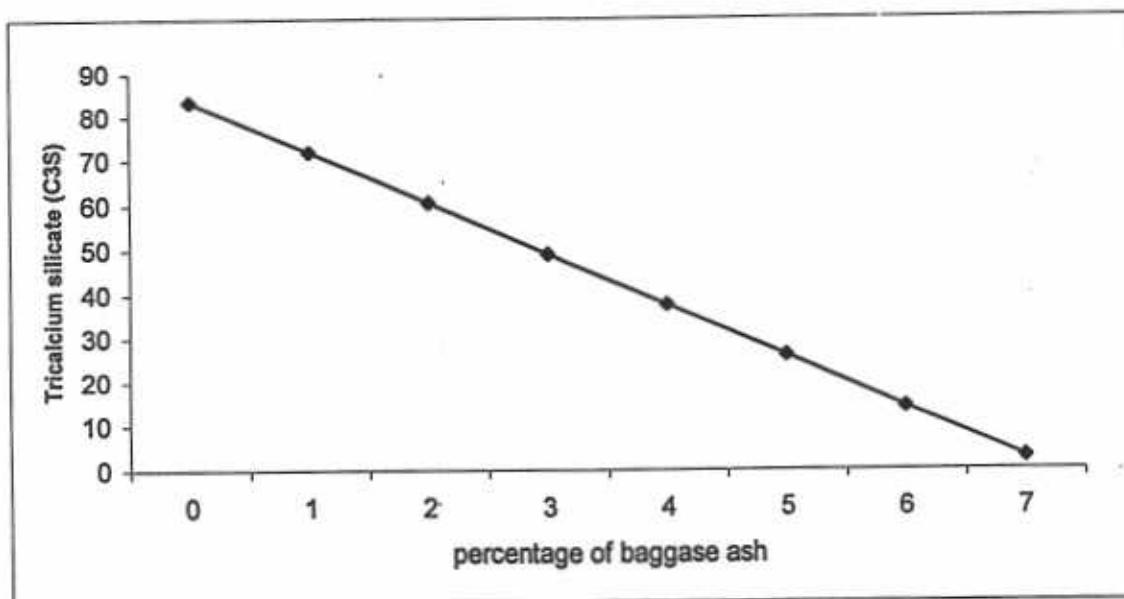


Figure 4.46 (a) Effect of baggase ash on tricalcium silicate.

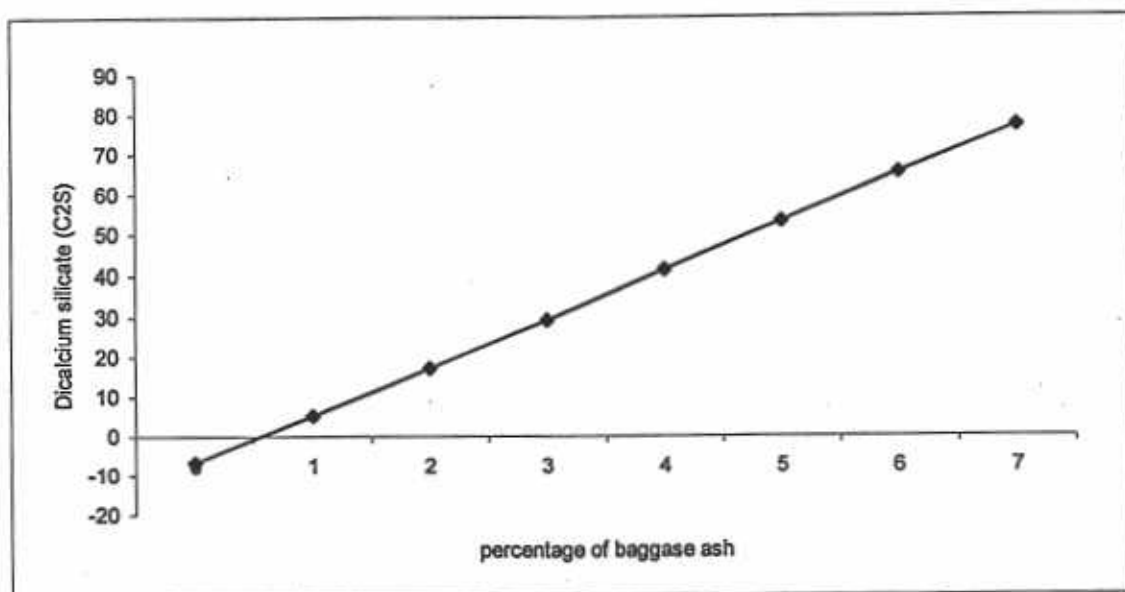


Figure 4.46 (b) Effect of baggase ash on dicalcium silicate.

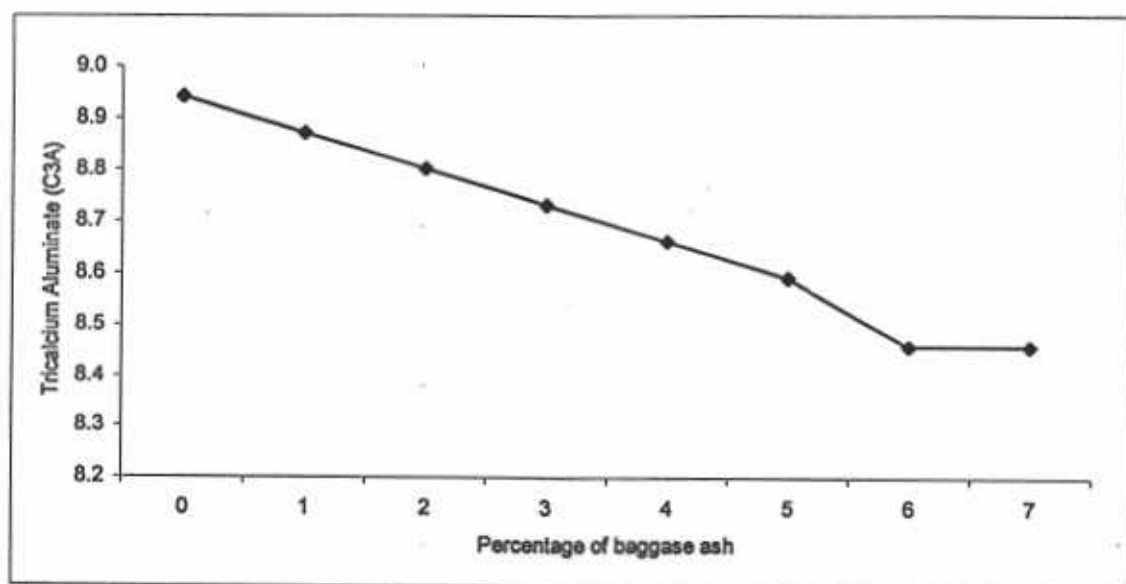


Figure 4.46 (c) Effect of baggase ash on tricalcium aluminate.

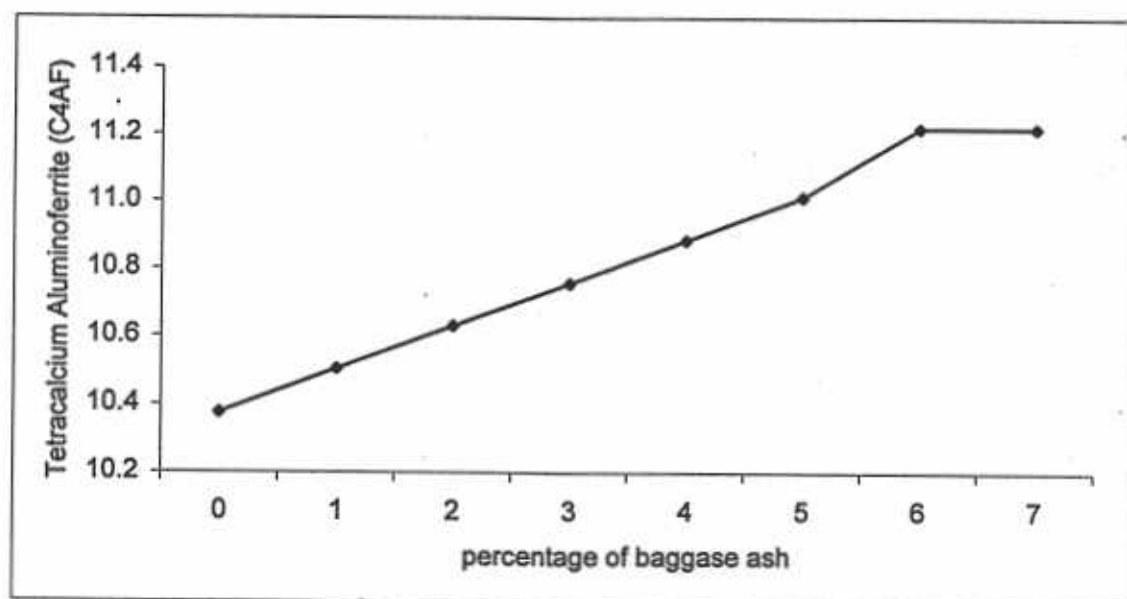


Figure 4.46 (d) Effect of baggase ash on tetracalcium aluminoferrite.

4.9.3 Effect of Baggage Ash on the Compressive Strength of the High Raw Mix Cement

The effect of baggage ash on the compressive strength of high strength Portland cement is indicated in Table 4.38 and graphically shown in Figure 4.47. From the table and figure it can be noted that as the percentage of baggage ash increases in the raw mix, the compressive strength of cement decreases.

With 5% baggage ash the compressive strength for 3, 7 and 28 days was found to be 3469, 4760 and 6157 psi, while the standards are 3336, 4690 and 5960 psi respectively. As a conclusion, this can be said that addition of 5% baggage ash does not affect the quality of cement and the compressive strength remains within the Standard limits. Further addition of ash decreases the compressive strength which go out of the Standard limits.

Table 4.38 Effect of Baggase Ash on the Compressive Strength of High Lime Cement

Percentage of baggase ash	Compressive strength (PSI)		
	3 Days	7 Days	28 Days
0	5675	6864	8470
1	4570	4980	6475
2	4435	4576	6285
3	4250	4655	6480
4	3980	4875	6258
5	3469	4760	6157
6	3248	3890	5317
7	2750	3218	4890

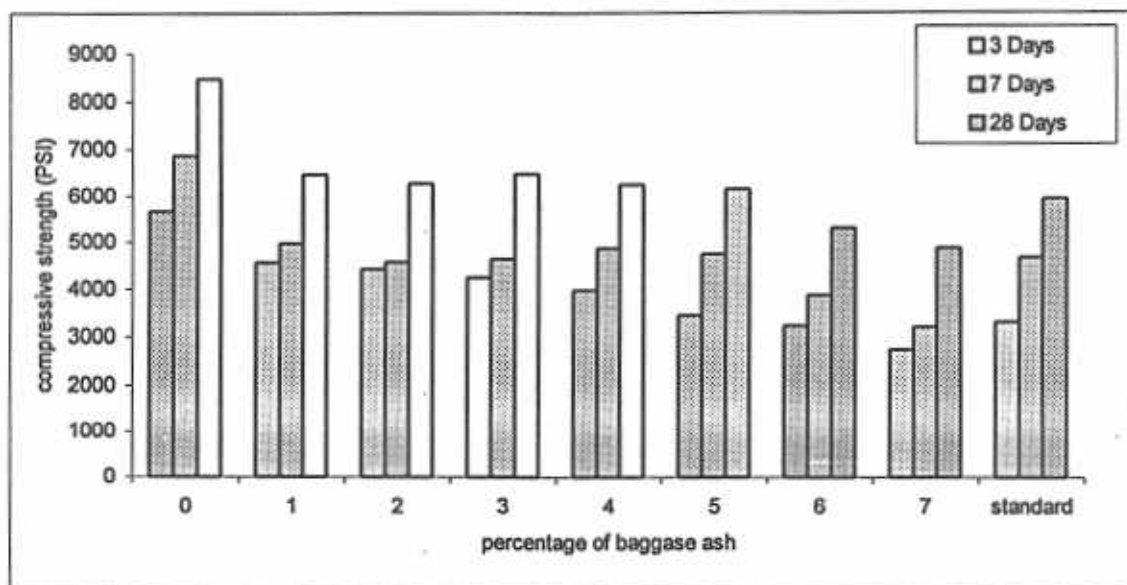


Figure 4.47 Effect of baggase ash on compressive strength of high lime cement.

4.10 HEAT OF CLINKERIZATION AND ITS DEPENDENCE UPON BAGGASE ASH

Heat of clinkerization is the sum of heat required to carry out all the chemical reactions during the clinker formation. This may be theoretically calculated as the algebraic sum of all the endothermic and exothermic reactions taking place in clinkerization process. Heat of clinkerization depends upon the chemical composition of raw mix used for the cement.

Heat of clinkerization can be calculated [106] in the units of kcal / kg in which chemical formulae represent mass percentages of the oxides in the clinker produced.

$$H_{\text{total}} = 2.22 \text{ Al}_2\text{O}_3 + 6.48 \text{ MgO} + 7.66 \text{ CaO} - (5.11 \text{ SiO}_2 + 0.59 \text{ Fe}_2\text{O}_3) = \text{kcal / kg}$$

Heat of clinkerization can also be calculated in the units of Btu / ton

$$H_{\text{total}} = 14795 \text{ Al}_2\text{O}_3 + 23326.7 \text{ MgO} + 27524.07 \text{ CaO} - (18416.58 \text{ SiO}_2 + 2123.88 \text{ Fe}_2\text{O}_3) = \text{Btu / ton}$$

The result obtained represents only that amount of heat that must be imparted to the feed to turn it into one ton of clinker. It does not include heat losses in the system nor does it account for the heat that is recoverable from the hot clinker after

the clinkering reaction is completed. The result, however, does take in account the exothermic reaction at clinkering temperature.

The calculated heat of clinkerization is different from the experimental one. The difference is due to the heat losses during the process of clinker formation in cement plants. Some of the heat is recycled but most of it is lost. The major heat losses in cement plants is from the rotary kiln which emit heat in the form of infrared radiations and is absorbed by the atmosphere. The second source of heat loss is the cooling of clinker in the clinker cooler, though some of which is recycled in the plant.

4.11 EFFECT OF BAGGASE ASH ON HEAT OF CLINKERIZATION

The heat of clinkerization of normal and high lime saturation factor clinker, with and without baggase ash, were calculated using above formula [106]. The results are reported in Table 4.39-4.40 and graphically shown in Figure 4.48-4.49.

From the Figure 4.48 it is obvious that heat of clinkerization of normal lime saturation factor without baggase is 410.0 kcal/kg. With 1,2,3,4 and 5% baggase ash, heat of clinkerization reduced to 399.9, 389.3, 378.8, 368.2 and 357.6 kcal/kg respectively. As we can not add more than 1% baggase ash with normal lime saturation raw mix (section 4.8.3). So the minimum possible heat of clinkerization for normal lime saturation factor, with baggase ash is 399.9 kcal/kg

With high lime saturation factor raw mix, the heat of clinkerization with out baggase ash is 437.7 kcal/kg. With 1, 2, 3, 4, 5, 6 and 7% baggase ash, heat of clinkerization reduced to 426.9, 416.0, 405.2, 394.4, 383.5, 372.0 and 361.1 kcal/kg respectively (Figure 4.49) the maximum amount of baggase ash, which can be blended with high lime saturation factor raw mix is 5% (section 4.9.3). So the minimum possible heat of clinkerization for high lime saturation factor raw mix, with baggase ash is 383.5 kcal/kg

Table 4.39 Heat of Clinkerization calculated for one kg of Clinker (Normal LSF Raw Mix)

Percentage of baggase ash added with raw mix	kcal/kg
0.0	410.0
1.0	399.9
2.0	389.3
3.0	378.8
4.0	368.2
5.0	357.6

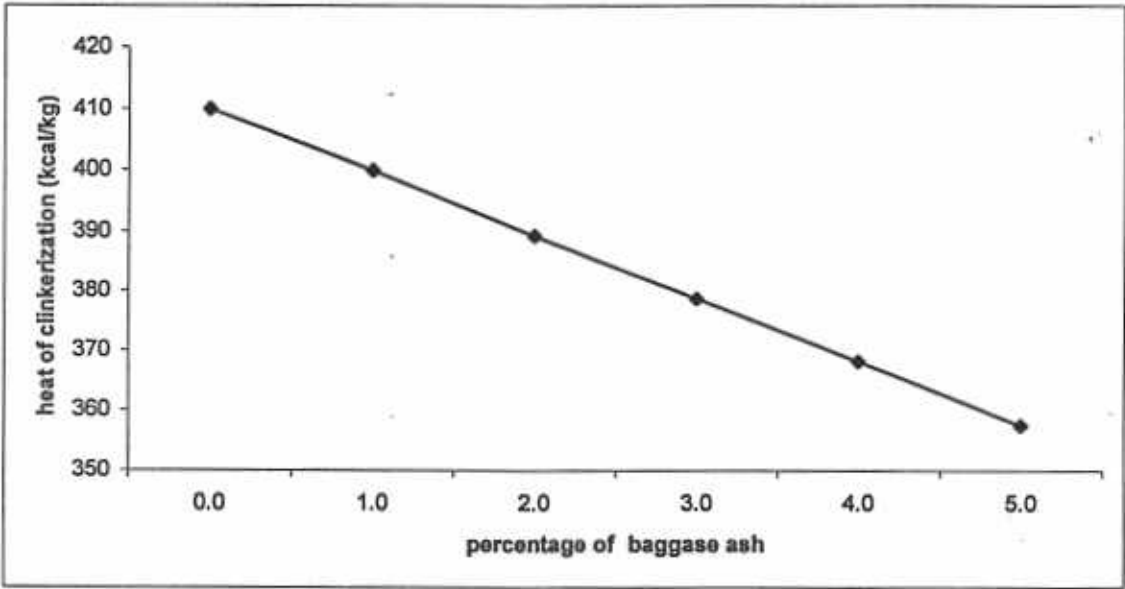


Figure 4.48 Energy required for clinkerization from normal raw mix (Kcal/ kg).

Table 4.40 Heat of Clinkerization calculated for one kg of Clinker (High LSF Raw Mix)

Percentage of baggase ash added with raw mix	kcal/kg
0.0	437.7
1.0	426.9
2.0	416.0
3.0	405.2
4.0	394.4
5.0	383.5
6.0	372.0
7.0	361.1

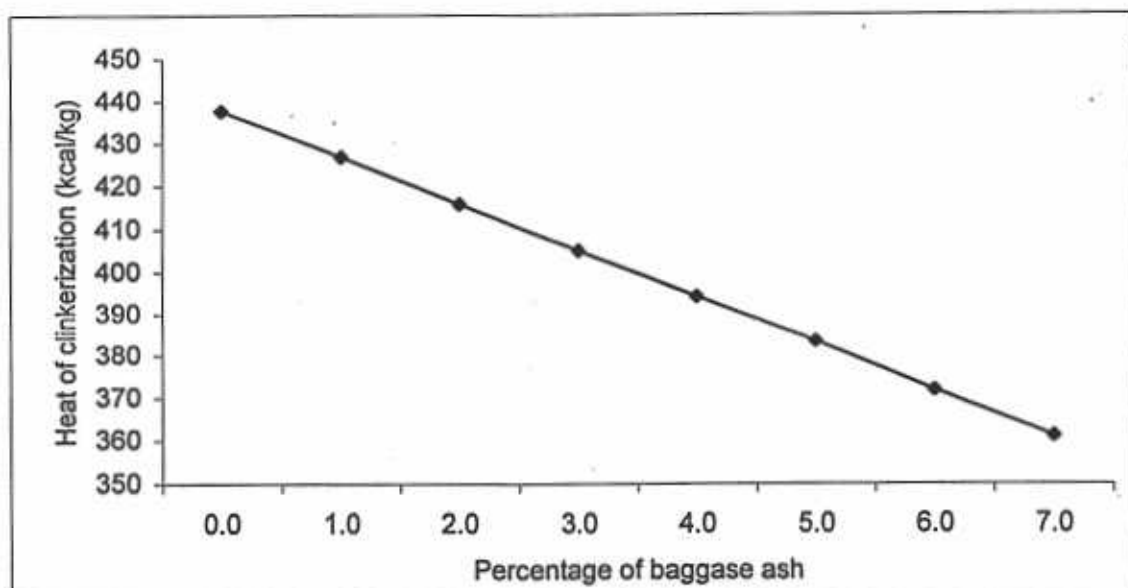


Figure 4.49 Energy required for clinkerization from high raw mix (kcal/ kg).

4.12 ENERGY SAVING DUE TO BAGGASE ASH IN CLINKERIZATION

The heat of clinkerization for normal clinker without baggase ash is 410 kcal/kg (Table 4.39)

The optimum quantity of baggase ash used in clinkerization is 5%.

Heat of clinkerization for raw mix having 5% baggase ash (Table 4.40) is 383.5 kcal / kg

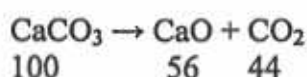
The decrease in the heat of clinkerization is $410 - 383.5 = 26.5$ kcal / kg

$$\text{Energy saving (percentage)} = \frac{26.5 \times 100}{410} = 6.46 \%$$

Thus the energy saving due to the use of 5% baggase ash is 6.46 %

4.13 EFFECT OF BAGGASE ASH ON CARBON DIOXIDE EMISSION

Raw material for cement contains calcium carbonate (CaCO_3) and magnesium carbonate (MgCO_3), both produce carbon dioxide on calcination as follow;



According to the above balanced chemical equation,

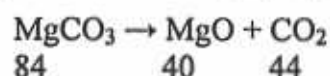
For every 56 g of CaO produced the corresponding amount of CO_2 is 44 g

The normal raw mix of high strength Portland cement contains 42.55 % CaO (Table 4.30)

Thus for 42.55 g CaO, the corresponding CO_2 produced

$$= \frac{44 \times 42.55}{56} = 33.43 \text{ g} \text{ ----- (1)}$$

Similarly the production of CO_2 by MgCO_3 is given as follow,



According to the above balanced chemical equation,

For every 40 g MgO the corresponding amount of CO_2 produced is 44 g

The normal raw mix of high strength Portland cement contains 0.98 % MgO (Table 4.30)

Thus for 0.98 g MgO, the corresponding amount of CO₂ produced

$$= \frac{44 \times 0.98}{40} = 1.08 \text{ g} \text{-----} (2)$$

Total CO₂ produced by 100 g of raw mix = 33.43 + 1.08 = 34.51g----- (3)

When 5 % baggase ash is added to the 95 % raw mix then CO₂ produced by

$$100\text{g raw mix} = \frac{34.51 \times 95}{100} = 32.78 \text{ g} \text{-----} (4)$$

Emission of CO₂ without baggase ash = 34.51 %

Emission of CO₂ with 5% baggase ash = 32.78 %

Reduction in the production of CO₂ is 34.51 - 32.78 = 1.73 %----- (5)

Thus as a conclusion when 5 % baggase ash is blended with a raw mix, it reduce the emission of CO₂ to the environment up to 1.73 %. So the use of baggase ash helps in reducing the environmental pollution.

The use of baggase ash in cement manufacturing, apart from energy saving and reducing the environmental pollution, also replaces clay up to approximately 5%, which does not have any significant economical or otherwise impact. If baggase ash is used in cement manufacturing process, in cement plant, the production capacity of the plant will be increased.

4.14 ADDITION OF BAGGASE ASH WITH CEMENT

The chemical composition of cement and baggase ash used for blending is shown in Table 4.41. Cement used for this purpose was ordinary Portland cement meeting the Pakistan Standard Specification. Table 4.42 and Figure 4.50 show the effect of baggase ash on the strength development of blended cement pastes. The replacement of Portland cement with 20 - 30% baggase ash decreased the strength of cement pastes significantly. The higher is the ash replacement; the lower is the compressive strength.

Figure. 4.50 show the effect of baggase ash on the compressive strength of high strength Portland cement. Compressive strength of high strength Portland cement

decreased with the addition of baggase ash. With the addition of 5% baggase ash, the three, seven and twenty eight days compressive strength decreased from 3980, 5430 and 6988 psi to 3350, 4700 and 5990 psi while the standards are 3336, 4690, 5960 psi respectively. It is clear from the figure that with the addition of further baggase ash, compressive strength falls below the standards values.

Table 4.41 Chemical Composition of Cement and Baggase Ash for Blending

Analyte	Percent composition	
	Cement	Baggase ash
SiO ₂	21.55	87.40
Al ₂ O ₃	5.69	3.60
Fe ₂ O ₃	3.39	4.90
CaO	64.25	2.56
MgO	0.85	0.69
Na ₂ O	0.33	0.15
K ₂ O	0.59	0.47
SO ₃	2.47	0.11

Table 4.42 Effect of baggase ash on Compressive Strength of Cement

Percentage of baggase ash added	Compressive strength (PSI)		
	3 days	7 days	28 days
0	3980	5430	6988
5	3350	4700	5990
10	2750	3750	4890
15	2300	3150	4400
20	1940	2650	4000
25	1400	2200	3700
30	800	1800	3200

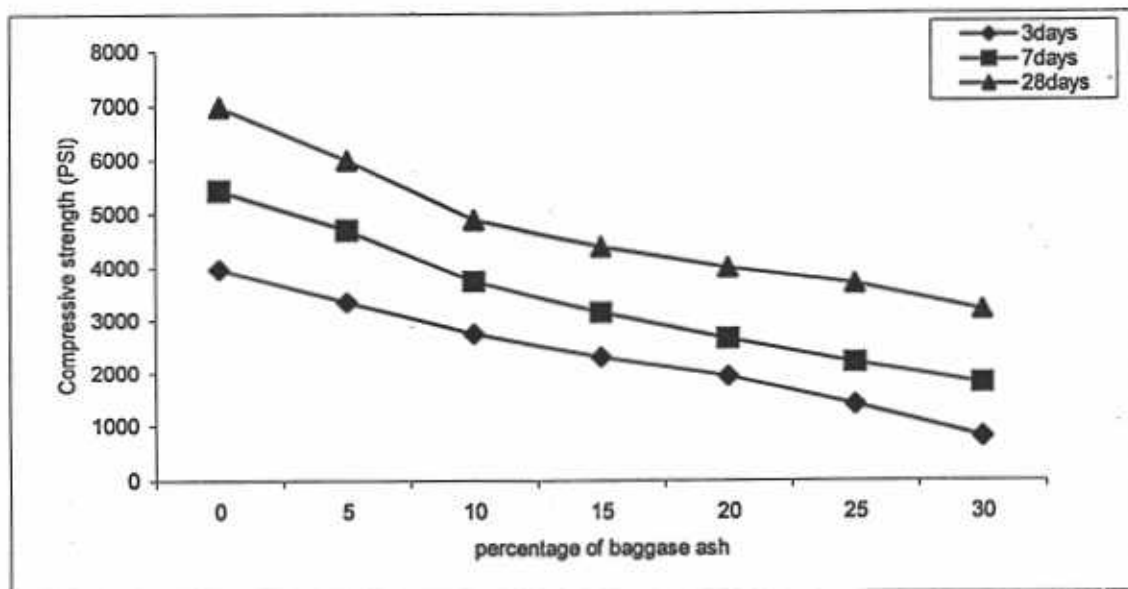


Figure 4.50 Effect of baggase ash on compressive strength of cement.

4.15 USE OF $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ AS CHEMICAL ACTIVATOR TO ENHANCE POZZOLONIC REACTIVITY OF BAGGASE ASH

There are three methods for the activation of pozzolonic reactivity [107] like prolonged grinding (mechanical method), elevated temperature curing of cement pastes containing a pozzolan (thermal method) and the use of chemical activators such as Na_2SO_4 and CaCl_2 (chemical method). Out of these methods chemical method has been used in the present work.

The effect of CaCl_2 on the strength development of the blended cement containing 10 % Ash + 90 % cement is shown in Table 4.43 and Figure 4.51. It is clear from the figure that compressive strength of ordinary Portland cement was increased with the increase in calcium chloride concentration upto 4%, above which the compressive strength was decreased again. With 4% addition of CaCl_2 , the compressive strength was increased approximately upto 20 % at three days, 26 % at seven days and 18 % at twenty eight days. Further increase in the amount of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ decreased the strength of cement significantly.

It can be concluded from the Table 4.43 and Figure. 4.51 that 4 % $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is the optimum concentration of activator for obtaining maximum compressive strength of blended cement mortar. Thus for further study of compressive strength, 4% solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was used for different blends of cement and baggase ash, the results of this study are shown in Table 4.44 and Figure. 4.52. From the Figure, it is obvious that as the percentage of baggase ash increases, the compressive strength of the cement motar decreases. With 15 % baggase ash, the compressive strength was observed to be 3500, 4800 and 6500 psi at three days, seven days and twenty eight day respectively, which meet the Pakistan Standard Specification. With 20 % baggase ash, compressive strength at three days, seven days and twenty eight day was observed to be 3204, 4540 and 5850 psi which is less than 3336, 4690 and 5960 psi respectively according to Pakistan Standard Specification, which shows that 15% baggase ash is the maximum amount which can be blended with mortar above which, the compressive strength of cement decrease significantly.

Table 4.43 Effect of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Dosage on Strength Development of Cement Paste containing 10 % ash + 90 % Cement

Percentage of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution	Compressive strength (PSI)		
	3 days	7 days	28 days
1	3100	4183	5500
2	3350	4505	5900
3	3450	4988	6320
4	3600	5030	6900
5	2420	3200	5200
6	2000	2500	3600

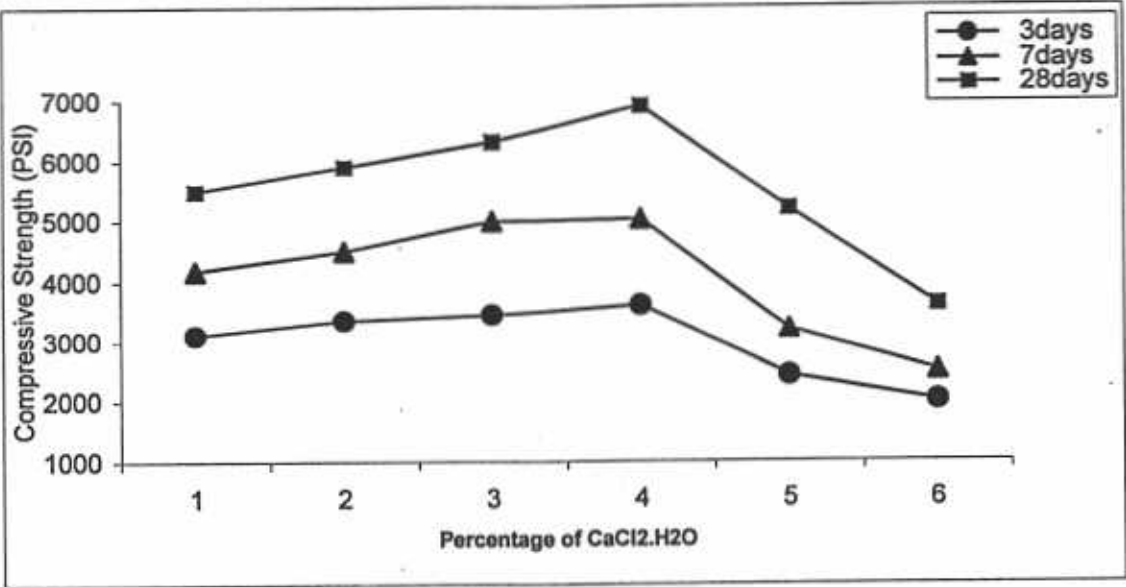


Figure 4.51 Effect of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ dosage on strength development of cement paste containing 10 % ash + 90 % cement.

Table 4.44 **Effect of Cement replacement with Baggage Ash on Strength Development of Blended Cement Pastes using 4 % $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$**

Percentage of baggage ash added	Compressive strength (PSI)		
	3 days	7 days	28 days
0	4750	5800	7420
5	4500	5500	7260
10	3600	5030	6900
15	3500	4800	6500
20	3204	4540	5850
25	2200	2800	4420
30	1550	2200	4000

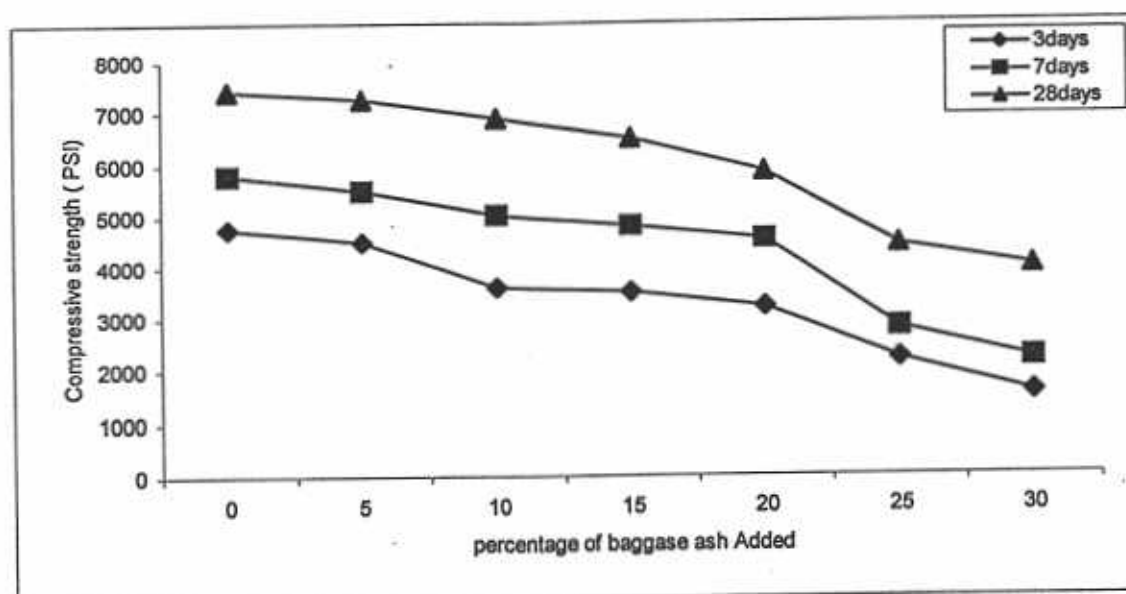
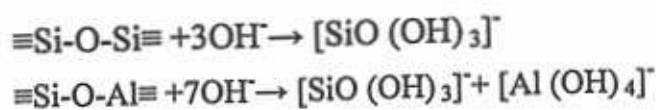


Figure 4.52 **Effect of cement replacement with baggage ash on strength development of blended cement pastes using 4 % $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$**

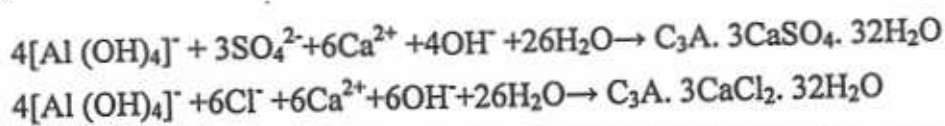
4.16 MECHANISM OF CHEMICAL ACTIVATION BY $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ has been widely used as an accelerator for Portland cement concrete. However, inspite of great effort, the detailed action mechanism of CaCl_2 on the hydration of cement is still obscure [108] various explanations have been offered from time to time, none of them would be able to explain all the effects of CaCl_2 in solid.

After mixing the ash-mixed Portland cement with CaCl_2 solution, cement grains hydrate first and the solution reaches a high pH value very quickly. The presence of CaCl_2 accelerates the hydration of cement but reduces the pH of the solution. Under the attack of OH^- in such a high pH solution, network modifiers, such as Ca^{2+} , K^+ , Na^+ , etc, in the pozzolan are dissolved into the solution very quickly. Silicate or aluminosilicate network formers in the pozzolan are also depolymerized and dissolved into the solution. However, a larger fraction of network modifiers are dissolved into the solution than network formers due to the lower bond energy of network modifiers. Depolymerised monosilicate and aluminate species enter the solution, as follows,



The drop of pH retards and reduces the dissolution of the fly ash particles. Compared with the control paste, the solution in the CaCl_2 activated pastes has a higher concentration Ca^{2+} but a lower concentration of dissolved monosilicate and aluminate species, which results in the formation of $\text{C}_3\text{A} \cdot 3\text{CaCl}_2 \cdot 32\text{H}_2\text{O}$ very quickly in addition to the formation of $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ due to the gypsum present in cement,



Since $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ and $\text{C}_3\text{A} \cdot 3\text{CaCl}_2 \cdot 32\text{H}_2\text{O}$ have the same type of crystal structure, they can coexist in a solid solution $\text{C}_3\text{A} \cdot 3(\text{CaSO}_4, \text{CaCl}_2) \cdot 32\text{H}_2\text{O}$. Depending on $(\text{SO}_4^{2-}, \text{Cl}^-)/[\text{Al}(\text{OH})_4]^-$ ratio in the solution, $\text{C}_3\text{A} \cdot 3(\text{CaSO}_4, \text{CaCl}_2)$.

$32\text{H}_2\text{O}$ will convert to $\text{C}_3\text{A} \cdot (\text{CaSO}_4, \text{CaCl}_2) \cdot 12\text{H}_2\text{O}$ if the ratio is lower than a certain value.

Since one mol of Al_2O_3 requires three mols of lime to form $\text{C}_3\text{A} \cdot 3 (\text{CaSO}_4, \text{CaCl}_2) \cdot 32\text{H}_2\text{O}$ or $\text{C}_3\text{A} \cdot (\text{CaSO}_4, \text{CaCl}_2) \cdot 12\text{H}_2\text{O}$, more lime is consumed than for the formation of C-S-H (Calcium silicate hydrate), the formation of $\text{C}_3\text{A} \cdot 3 (\text{CaSO}_4, \text{CaCl}_2) \cdot 32\text{H}_2\text{O}$ or $\text{C}_3\text{A} \cdot (\text{CaSO}_4, \text{CaCl}_2) \cdot 12\text{H}_2\text{O}$ consumes dissolved monosilicate and aluminate species quickly, and the dissolution of fly ash and the precipitation of hydration products can continue at a high rate. The formation $\text{C}_3\text{A} \cdot 3 (\text{CaSO}_4, \text{CaCl}_2) \cdot 32\text{H}_2\text{O}$ or $\text{C}_3\text{A} \cdot (\text{CaSO}_4, \text{CaCl}_2) \cdot 12\text{H}_2\text{O}$ increases the solid volume much more than C-S-H even more than $\text{C}_3\text{A} \cdot \text{Ca}(\text{OH})_2 \cdot 12\text{H}_2\text{O}$. It can be expected that the CaCl_2 activated pastes will give a denser structure and a higher strength than the control pastes. Extensive examinations on lime ash or lime natural pozzolan systems activated with up to 5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ could not identify the formation of $\text{C}_3\text{A} \cdot 3\text{CaCl}_2 \cdot 32\text{H}_2\text{O}$. However, $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ can be identified in lime ash or lime natural pozzolan systems activated with 4% Na_2SO_4 . It seems that $\text{C}_3\text{A} \cdot 3\text{CaCl}_2 \cdot 32\text{H}_2\text{O}$ is more difficult to form than $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ in those lime-pozzolan systems. The optimum CaCl_2 dosage is dependent on the available reactive Al_2O_3 from cement and ash.

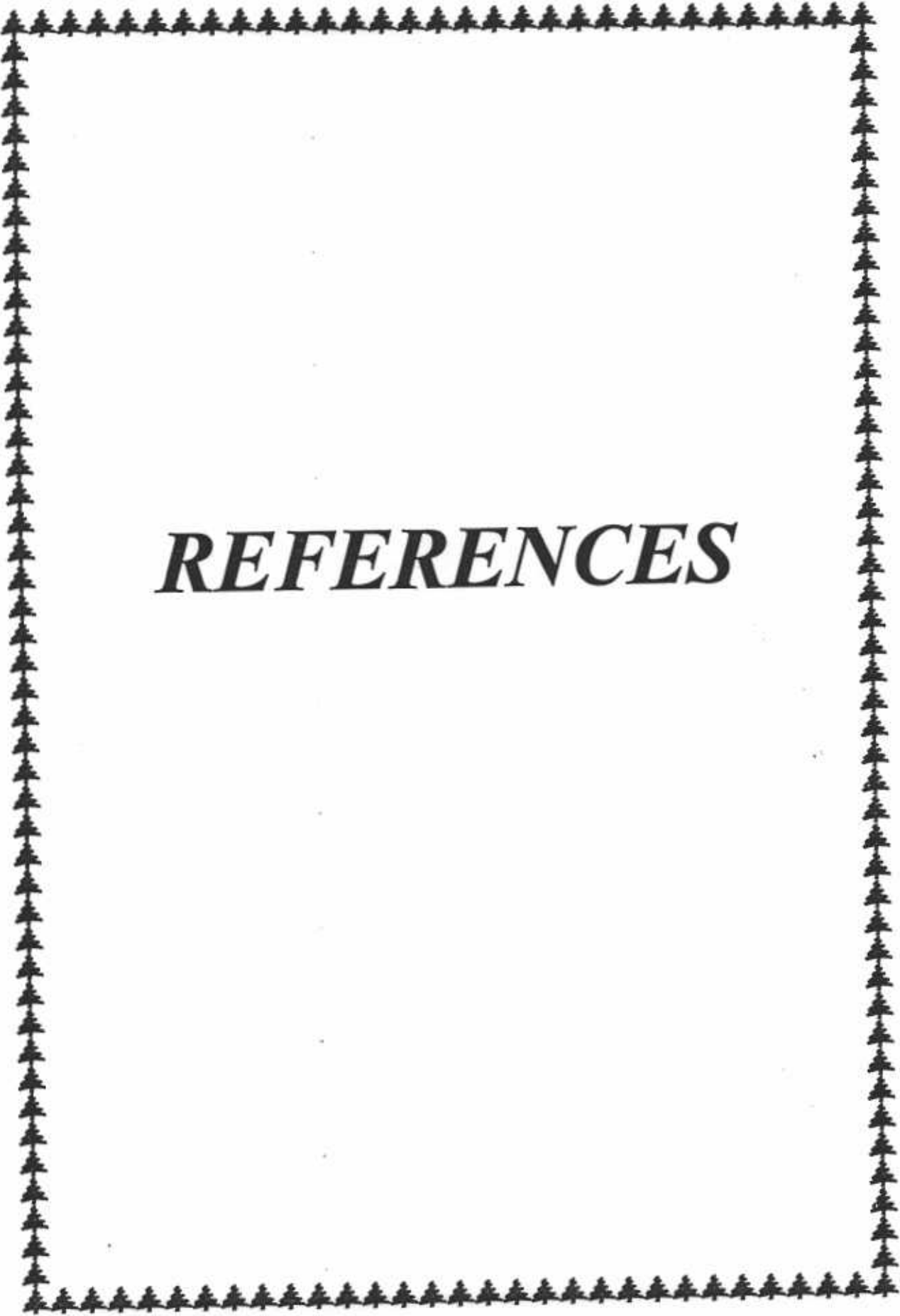
CONCLUSION

The raw material found in the study area (Darukhula and adjoining areas of Nizampur) has promising potential for standard quality cement each for high strength Portland cement, sulphate resisting cement and white cement. The cement samples prepared from the raw material were tested for physical and chemical parameters and found to meet the British and Pakistan Standard Specifications

Baggase ash which is the waste product of sugar mills, and creates a number of environmental problems, has been found to contain all other ingredients which are necessary for cement due to which it has been utilized in the preparation of high strength Portland cement as a raw material, and replaced about 5% of clay from the cement raw material. Moreover it has been found to contain 15-25% unburnt carbon, a calorific value of 15 kcal/kg, due to which it saved the fuel in cement production upto 6.46%, and reduced the emission of carbon dioxide to the environment upto about 1.73 %.

Baggase ash has also been used in cement blends to replace cement, upto 5% without affecting the quality of cement. Moreover the use of chemical activator (CaCl_2) has further increased the cement replacement in mortar upto 15%.

As a conclusion, this can be said that baggase ash can be used either as a part of the raw mix in the raw mix designing for high strength portland cement manufacturing, to increase the cement production and save some fuel and ultimately reduce the cost of production, or in cement mortar, to reduce the use of cement in cement mortars.



REFERENCES

REFERENCES

1. Davey, N. Building materials in antiquity. A history of building materials. Phoenix House, London, 1960.
2. Hewlett, P.C. Lea's chemistry of cement and concrete. 4th ed, Arnold London, 1998.
3. Cement Association of Canada, 2004.
4. Barry, T.; Glasser, F.P. Calculation of Portland cement clinkering reactions. Adv. Cem. Res. At press. 1999.
5. Bye, G.C. Portland cement composition, production and properties, 2nd ed, Thomas Telford limited London. 1999.
6. Mémoire sur une découverte dans l'art de bâtir, faite par le Sr. Lorient, Paris, 1774.
7. De la Faye. Recherches sur la préparation que les Romains donnoient à la chaux dont ils se servoient pour leurs constructions, et sur la composition et l'emploi de leurs mortiers, Paris 1777.
8. Faujas de Saint-fond, Recherches sur la pouzzolane, sur la théorie de la chaux, et sur la cause de la dureté du mortier, Grenoble and Paris, 1778.
9. Rondelet, L. Art de Bâtir, Paris, 1805.
10. Viollet-le-Duc, E.E. Dict. Raisonné de l'Architecture Française, 1863, Vol. 6: 402.
11. Rogers, J.C.; Trans. St. Albans. Hertfordshire Architectural and Archaeological Society 1933, 76, 99.
12. Belidor. Architecture Hydraulique. Vol. 2: Paris, 1788.
13. Lea, F.M. The chemistry of cement and concrete. 3rd ed, Edward Arnold London. 1980.
14. DAVIS, A.C. A hundred years of Portland cement, London, 1924.
15. Lesley, R.W. History of the Portland cement industry in the U.S.A. International Trade Press, Chicago, 1924.

16. Gonnerman, H.F. Development of cement performance tests and requirements
Bull. Res. Dept. U.S. Portland cements. Association. 1958, No.93.
17. Skempton, A.W. Portland cement 1843-1887, trans. Newcomen Soc. 1962, 35,
117.
18. Bury, C.R.; Davies, E.R.H. *J. Chem. Soc.* 1932.
19. *J. Am. Chem. Soc.* 1932, 54, 2372.
20. Demediuk, T.; Cole, W.F.; Hueber, H.V. *Aust. J. Chem.* 1955, 215.
21. Barry, Y.I.; Glasser, F.P. Calculations of Portland cement clinkering reactions,
Adv. Cem. Res. at press, 1980.
22. Twenhofel, W.H. Principles of sedimentation, 1950.
23. Clausen, C.F. Cement materials, industrials and rocks. seeley W. Mudd series,
New York, 1960.
24. Erhard, H.S.; Scheuer, A. Burning technology and thermal economy. 1993.
25. Glasser, F.P. The burning of Portland cement. *Lea's chemistry of cement and
concrete.* 4th ed. Arnold. London. 1998.
26. Eitel, W. *Silicate Science*, Vol. 5, 133, Academic Press, New York and London
1966.
27. Jander, W.; Hoffman, E.; *Anorg. Z. allg. Chem.* 1934, 218, 211.
28. Jander, W.; Petri, J. *Electro Chem.* 1938, 44, 748.
29. Weyer, I.; *anorg. Z. allg. Chem.*, 1932, 209, 409.
30. Dekeyser, W.L. *Bull. Soc. chem. Belg.* 1955, 64, 395.
31. Kurdowski, W. *Silic. Ind.* 1965, 30, 500.
32. Weyer, I. *Cement.* 1931, 20, 560.
33. De Keyser, W.L. *Bull. Soc. Chem. Beg.* 1951, 60, 516.
34. De Keyser, W.L. *Bull. Soc. Chem. Beg.* 1955, 64, 395.
35. Curilli, V. *Ricerca scient.* 1947, 17, 439.
36. Van Bemst, A. *Silic. Inc.* 1961, 26, 290.

37. Ludwig, U.; Muller-Hesse, H.; Schweite, H. E. *Zement-Kalk Gips* 1960, 13, 449.
38. Becker, F.; Schramli, W. *Cem. Lime mf.* 1969, 42, 91.
39. Amafuji, M.; Tsumagari, A. *Sym. Tokyo*, 1968.
40. Weber, P. *Zement -Kalk-Gips, Heat transfer in Rotary Kilns. Special issue No. 9.* 1963.
41. Coughlin, J. P. *J. Am. Chem. Soc.* 1956, 78, 5479.
42. Newman, E.S. *J. Res. Nat. Bur. Stand.* 1959, 61, 75.
43. Yokokawa, T.; Kleppa, O.J. *J. Phys. Chem.* 1964, 68, 3264.
44. Bonnickson, K. R. *J. phys. Chem.* 1955, 59, 220.
45. Coughlin, J. P.; Brien, C.J. *J. phys. Chem.* 1957, 60, 767.
46. Walker, B. E., Grand, J. A., Miller, R.R. *J. phys. Chem.* 1956, 60, 231.
47. Johansen, V. *Cement production and cement quality. Material science of concrete.* American Ceramic Society. Westerville, Ohio, 1989.
48. Tayler, H.F. *Cement chemistry.* 2nd ed, Thomas Telford publishing, London 1997.
49. Lerch, W.; Bogue, R.H. *J. phys. Chem.* 1927, 31.
50. Grutzeck, M.W.; Roy, D. M.; *Nature, Lond.* 1969.
51. Funk, H.; Fahlke, B.; *Anorg, Z. Allg. Chem.* 1964, 334.
52. Long, J. V. P.; Mc Connell, J. D. C. *ibid*, 1959, 32.
53. Funk, H.; Greenberg, S.A.; chang, T.N. *J. phys. Chem.* 1965, 69.
54. Feldman, R. F.; Ramachandran, V.S. *J. Am. ceram. Soc.* 1966, 49.
55. Murakami, K.; Tanaka, H.; Nakura, Y. *Chem. Ind.* 1969.
56. Carlson, E.T. *J. Res. natn. Bur. Stand. Bldg, Sci.* 1966.
57. Schwiete, H. E.; Iwai, T. *Zement-alk-Kalk-Gips.* 1964, 17.
58. Mielenz, R.C.; Witte, P.; Glantz, O. *J. spec. Tech. Publ. Am. Soc. Test. Mater.* 1949, No. 99.
59. Potter, C. J. *J. Soc. Chem. Ind., Lond.* 1909, 28.

60. ASTM Special technical publication, 1950, 99.
61. Hoon, R. C. *Indian Concr. J.* 1952, 26.
62. Davis, R.E.; Carlson, R. W.; Kelly, J. W.; Davis, H.E. *proc. Am. Concr. Inst.* 1937, 33.
63. Abdun-Nur, E. A. *Bull. Highw. Res. Bd.* 1961, 184.
64. Kokubu, M. *Sym., Tokyo*, 1968.
65. Bhatti, J.I.; Gajda, J.; Miller, F.M. Use of high-carbon fly ash in cement manufacture. *cement Americas*, May 1, 2001.
66. Bhatti, J.I.; Gajda, J.; Miller, F.M. Use of high-carbon Illinois fly ash in cement manufacturing demonstration phase ICCI project number: 99-1/2.1A-1 November 1, 1999, through October 31, 2000.
67. Bhatti, J.I.; Gajda, J.; Miller, F.M. High carbon fly ash in cement manufacturing. A commercial demonstration, 27th International technical conference on coal utilization & fuel systems, sheraton sand key, clearwater, florida, march 3-7, 2002.
68. Tripodi, R.A.; Cheremisinoff, P.N. Coal ash disposal. Solid waste impacts, technomic publishing company, Inc., Westport, and CT. 1980.
69. Valenti, Michael. Using fly ash for construction, mechanical engineering, 1995, Vol. 117, 5, 82-86.
70. Al-Amoudi, OSB.; Maslehuddin, M.; Asi, I.M. Performance and Correlation of the Properties of Fly Ash Cement Concrete. *Cement Concrete and Aggregate*, 1996, vol.18. Issue.2.
71. Carette, G. G.; Malhotra, V.M. Early ash strength development of concrete on incorporating fly ash and condensed silica fume, American Concrete Institute, Detroit Publication 1983, 79, vol. 2.
72. British Standards Institution. Specifications for pozzolanic pulverized fuel ash cement, BSI, Milton keynes, BS 6610.1995.

73. Saraswathy, V.; Muralidharan, S.; Thangavel, K.; Srinivasan, S. Activated fly ash cements: tolerable limit of replacement for durable steel reinforced concrete. *Advances in Cement Research* 14, 2002.
74. Thomas, MDA.; Shehata, M.H.; Shashiprakash, S.G. The use of fly ash in concrete. Classification by composition. *Journal of Testing and Evaluation*, 1999, Vol. 21.
75. Carette, G.G.; Malhotra, V.M. Early age strength development of concrete incorporating fly ash and condensed silica fume. American Concrete institute Detroit, 1983.
76. Goni, S.; Guerrerl, A.; De Luxan, M.P.; Macias, A. Dehydration of pozzolonic products hydro thermally synthesized from fly ashes, Microstructure evolution. *Materials Research Bulletin*, 2000.
77. Guerrero, A.; Goni, S.; Macias, A. Durability of new fly ash belite cements mortar in sulphated and chloride medium, *cement and concrete research*, 2000.
78. Kameshwara rao, B., arvind kumar Jain. The role of fly ash in minimizing cement content in concrete. Proceedings of national seminar on cement content and parameters for durability of concrete, organized by Maharashtra India, 1998, 2.
79. Berry, E.E.; Malhotra, V. M. Fly ash in concrete, a critical review, *J. ACI*, proc. 1982.
80. Muralidharan, S.; Saraswathy, V.; Thangavel, K.; Srinivasan, S. Competitive role of inhibitive and aggressive ions in the corrosion of steel in concrete. *Journal of Applied Electrochemistry*, 2000.
81. Mangat, P.S.; Molloy, B.T. Influence of PFA, slag and Micro silica on chloride induced corrosion of reinforcement in concrete. *Cement and concrete research*, 1991.
82. Bai, J.; Sabir, B.B.; Wild, S.; Kinuthia, J.M. Strength development in concrete incorporating PFA and metakaoli, *Magazine of concrete research*, 2000.
83. Ampadu K.O.; Toril, K.; Kawamura, M. Beneficial effect of fly ash on chloride diffusivity of hardened cement paste. *cement and concrete research*, 1999.

84. Saltam, M. Influence of fly ash on chloride diffusion in concrete in Swamy. R. N. (ed.), Sheffield Academic Press Sheffield, 1994, 2.
85. Bhehara, J. P.; Sarangi, B.; Nayak, B. D.; Ray, H.S. Investigation on the development of blended cements using activated fly ash. Indian concrete Journal, 2000.
86. Smith, Anne. Controlled low strength material aberdeen's concrete construction, 1991, vol. 36, No. 5.
87. Carette, G.G.; Malhotra, V.M.; Berard, C.; Debenedictis, V.; Plumat, M. Development of heat curing cycles for Portland cement-fly ash concrete for the precast industry. Proceedings of second international conference on Fly ash, silica fume, slag, and natural pozzolanas in Concrete. American concrete institute SP-91, 1986.
88. Bouzoubaa, N.; Zhang, M.N.; Malhotra, V.M. The effect of grinding on the physical properties of fly ashes and a Portland cement clinker. Cement and concrete research 1997.
89. Shi, C.; Day, R.L.; Qian, J. Characterization and utilization of agriculture, coal combustion and municipal solid waste incineration residues as pozzolanic materials in cement and Concrete, in state of the art 2000. Cement and Concrete Research, 31, 2001.
90. Caijun, Shi.; Jushi, Qian. Activated blended cement containing high volume coal fly ash. Advances in Cement Research, CJS Technology Inc., Chongqing University. 2000, 13, No. 4.
91. Bouzouba, N.; Zhang, M.N.; Malhotra, V.M. The effect of grinding on the physical properties of fly ashes and a Portland cement clinker. Cement and Concrete Research, 1997, 27, No.12.
92. Bouzouba, N.; Zhang, M. N. ; Malhotra, V. M. Chemical activators. Part II: reaction mechanisms. Cement and Concrete Research, 2000, No. 4.
93. Nehdi, M.; Khan, A.A. Cementitious composites containing recycled tire rubber an overview of engineering properties and potential applications, cement concrete and aggregate 2001, Vol. 23, Issue. 1.

94. Holcim cement plant proposal to burn tires as fuel, Holcim cement plant trident, montana state. 2003.
95. Waste treatment and recycling equipment ebara corporation 1-6-27, Konan, Minato-ku, Tokyo, Japan, 2001, 108 - 8480.
96. Miyata, T. Technical Report. Nikkan. Kogyo. Shimbun. September. 2001.
97. Miller, FM., Conway, T. Use of ground granulated blast furnace slag for reduction of expansion due to delayed ettringite formation , Cement Concrete and Aggregate 2003, Vol. 25, Issue. 2.
98. Wang, R.; Trettin, V.; Rudert, R. Umlauf recrystallization of granulated blast furnace slag and the significance for the hydraulic Reactivity. Institute for Building and material chemistry, Siegen University., Wilhelm Dyckerhoff Institute for building material technology. Advances in Cement Research, 2003.
99. Liu, Z.; Tang, M.; Cui, X. Expansion of cement containing crystalline magnesia with and with out fly ash and slag, Cement Concrete and Aggregate, 1998, Vol. 20, Issue.1.
100. Technologies for conserving the Global Environment. Taiheiyo cement corporation 2001.
101. Chen, G., Lee, H., Young, K.L., Yue, P.L., Wong, A., Yao, Y., Choi, K.K. Glass recycling in cement production and innovative approach. Department chemical engineering, University of science and technology, Kowloon, Hong Kong, waste management, Vol. 22, No.7 2002.
102. Waste treatment and recycling equipment, Ebara Corporation, 1-27, Konan, Minato-ku, Tokyo, Japan, 2003.
103. Miyata, T. Technical report Nikkan. Kogyo. Shimbun. September, 2001.
104. Bernard, ES. The Omani artificial pozzolans (Sarooj), Cement, Concrete and Aggregate, 2001, Vol.23 Issue.1.
105. Jeffery, P.G. Chemical methods of rock analysis. 3rd ed, laboratory of Govt. chemist, London, UK. 1986.

106. Jons, E.; Hundebol, S. Production of heat of reaction of cement raw meal. ZKG International, 1995, 48, No. 9.
107. SHI C.; DAY, R.L. Pozzolanic reactions in the presence of chemical activators part II: reaction mechanisms. Cement and concrete research, 2000, 30, No. 4, 607-613,.
108. Caijun. Shi.; Robert, Day. Comparison of different methods for enhancing reactivity of pozzolans. Department of civil engineering, University of Calgary, Calberta, Canada, 2001.