Utilization of Blast Furnace Slag as a Raw Material for the Manufacture of Portland Cement Clinker

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

Master of Technology
In
Ceramic Engineering

Submitted by

Debabrata Dutta

Department of Ceramic Engineering
National Institute of Technology
Rourkela
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Under the supervision of

Prof. J.Bera

Department of Ceramic Engineering
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CERTIFICATE

This is to certify that the thesis entitled, "**Utilization of blast furnace slag as a raw material for the manufacture of portland cement clinker.**", submitted by **Debabrata Dutta** in partial fulfillment of the requirements for the award of Master of Technology Degree in **Ceramic Engineering** at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under our supervision and guidance.

To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

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Date:

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Abstract

Presently, there is an increased emphasis on the use of blended cement like slag cement, fly ash cement etc. This reduces the energy requirement for cement production or reduces the CO_2 release in the environment as the portland cement clinker is produced utilizing calcium carbonate based raw material. The replacement of calcium carbonate by alternative raw material like slag may again reduce the energy consumption. In the present investigation, blast furnace slag has been utilized as a cement raw material for the production of portland cement clinker. Clinker thus produced has been characterized to see the effect of slag utilization. A normal portland cement clinker has also been prepared to compare the properties. The clinkerisation process was quicker in case of slag containing raw mix. The free lime content of that clinker was also low compared to normal clinker. The amount of C_3S phase formation was higher in slag containing clinker. Similarly, the hydration rate and compressive strength of cement produced utilizing slag clinker was higher compared to normal portland cement. All these results indicate that slag could be utilize to reduce the calcium carbonate content of cement raw mix efficiently to produce better, cheap and environmental friendly cement.

Keywords: clinker, slag, clinkerisation

LIST OF ABBREVIATIONS:

Cement Chemists' Notations

A = Al_2O_3

C = CaO

F = Fe_2O_3

H = H_2O

M = MgO

S = SiO_2

$\hat{S}$ = SO_3

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Introduction

CHAPTER 1

INTRODUCTION

1.1: Introduction

Rising levels of ‘greenhouse’ gas in the environment, and the associated increase in temperature of the atmosphere, are potentially able to alter the ability of the planet to support present life forms [1, 2]. Carbon di-oxide is the most important greenhouse gas. On the world wide scale, action is being taken to limit the fossil fuels uses which release CO_2 on combustion [1, 3]. It has been estimated that the average rise in temperature of the environment should reach between 1.9 and 5.3°C in the next 100 years [1]. The EU is seeking to limit CO_2 emissions and has recommended (September 1991) that member states adopt a new energy and fuel tax, thereby restricting CO_2 emissions to 1990 levels [1, 4, 5].

The cement production industry has been identified as one of the most important users of carbon-based fuels as a source of heat energy and also as an industry in which the technology exists for large savings in this respect [1, 6]. More importantly, decarbonation of limestone constitutes as initial step in traditional cement production, thereby releasing CO_2 to the atmosphere. Portland cement production involves the sintering of raw feed (composed of limestone and clay) at about 1450°C and then grinding the cooled clinker with 5 % gypsum. A typical fuel energy requirement for efficient production may approach 3000kJ/ kg cement, of which 2000kJ/kg is used in drying the feed and carrying out the chemical reactions, while 1000kJ/kg is assumed by energy losses (radiation, evaporation, grinding, etc). The theoretical heat energy requirement to form Portland cement clinker is calculated to depend on the percentage of limestone employed, or the lime saturation factor,

$$\text{lime saturation factor} = \frac{100\%\ \mathrm{CaO} + 75\%\ \mathrm{MgO}}{2.8\%\ \mathrm{SiO_2} + 1.18\%\ \mathrm{Al_2O_3} + 0.65\%\ \mathrm{Fe_2O_3}}$$

rising from about 1570-1800 kJ/kg as the lime saturation factor is increased from 80 to 100 percent [1, 7]. The specific electrical energy consumption, which includes the power absorbed in grinding the cement, is ~110kWh/t on average, (or an additional 396 kJ/kg electrical energy, which is equivalent to ~ 990 kJ/kg fuel energy) [1].

Although energy use and release of CO_2 are closely related in the usual cement manufacturing industry, it is the release of CO_2 to the atmosphere rather than the consumption of energy which is of chief concern. Decarbonation of limestone ($CaCO_3$) results in the release of CO_2 and, since natural limestone and chalk are the only large-scale sources of calcium available to the cement industry, this CO_2 release can only reducible by changing the chemical composition of the cement. The rate of increase of cement production is much higher in the underdeveloped world, in China and India for example, than in the developed Western countries, and any attempt to limit CO_2 emissions (and Portland cement production) to the 1990 levels (as proposed) will penalize the developing world [1, 4].

Usually more than half the CO_2 released in the process of Portland cement production arises from the decarbonation of the raw feed, with a smaller fraction resulting from the burning of fuel [1].

A number of approaches to limiting the energy requirement (or reducing CO_2 release) in the production of modern construction cements have been proposed or adopted. For example [1]:

1. The introduction of energy efficient dry process cement kiln where CO_2 release reduced because of reduced thermal energy requirements.
2. By increasing hydraulic activity of cement and thus encouraging the use of leaner concrete mixes. For example, 0.25 percent fluoride (F^-), can lead to increased reactivity.
3. Dilution of highly reactive portland cement with low energy waste material like fly ash, granulated blast furnace slag etc.
4. By reducing CaO content of final cement resulting in belite (C_2S) based cement rather than alite (C_3S) based.
5. By using clinkerisation additive like sulphoaluminate, sulphoferrite leading to the lowering the clinkerisation temperature.

A reduction in the release of CO_2 to the atmosphere, in general, will accompany the reduction in the use of energy in the industry. The increased emphasis on the use of blended cements, which incorporate secondary cements developed from waste by-products, has been encouraged. Up to 75 per cent reduction in both energy requirement and CO_2 release may be expected if granulated blast furnace slag is employed as the diluent [1].

At present, most of the cement manufacturer produces portland slag cement by mixing 30-40 percent slag with portland cement clinker and gypsum. At the same time, granulated slag can be used as a raw material in the production of Portland cement clinker which again reduces the CO_2 emission as slag is an amorphous glassy material containing silica and calcium oxide in majority. This may reduce the percentage of limestone in the composition. The second advantage of using slag in the raw mix is that it may lower the clinkerising temperature, forming early liquid phase, enabling reduced energy requirement and simultaneously reduced CO_2 release.

1.2: Objective

The objective of the present investigation is to the use of granulated blast furnace slag as a raw material in the production of Portland cement clinker with specific following points:

a) To investigate the effect of slag in clinkerisation.
b) To investigate the effect of slag on the hydration behavior and strength development of cement produced utilizing clinker containing slag as a raw material.

Chapter 2

Back Ground

CHAPTER 2

BACK GROUND

2.1: Burning of cement

Burning of cement [1] means the firing of the raw materials mixture to produce the clinker having the characteristic phases, C_3S, C_2S, C_3A, and C_4AF.

2.2: Burnability

Burnability [8] of the cement raw mix indicates the amount of mass transfer of its constituents with ease or difficulty to produce the clinker phases. It is determined by amount of CaO_f after burning the raw mix for a certain time (θ) at a certain temperature (T), i.e., $CaO_f = f(\theta, T)$.

2.3: Factors affecting burnability

The following are the important parameters which affect the burnability of a raw mix.

2.3.1: Mineralogical composition

- The dissociation temperature of the individual mineral and the appearance of CaO in the most reactive state increases in the order:

Ankenite< dolomite< Calcite [9, 8]

- The reactivity of clay minerals with $CaCO_3$ increases in the order:

Muscovite< montmorillonite< chlorite< illite< kaolinite [10, 11, 8]

- The reaction of different form of silica with CaO increases in the order:

Quartz< chalcedony< opal< α-cristobalite< α-tridymite< silica of feldspars< silica of micas and amphiboles< silica of clay minerals< silica of glassy slags. [9, 8]

- Minor volatile & nonvolatile components are in the following order:[12, 8]

MgO - K – SO_3 –Na_2O- Ti – Mn – P- Sr – F – Cl – Cr

- Modifiers (fluxes and mineralizers) such as CaF_2, Na_2SiF_6, $CaSO_4.2H_2O$, $Ca_3(PO_4)_2$ etc are very often used in a very small quantity with the raw mix.

2.3.2: Chemical composition

Each component of the raw mix has individual(C, A, S and F) and combined [(Lime Saturation Factor (LSF), Silica Modulus (SM), Alumina Modulus (AM),] effects on burnability. The formula, limiting range and the preferable range of the LSF, SM & AM is shown in table 2.1.

Table 2.1: The formula, limiting range and the preferable range of the LSF, SM & AM:

Parameter	Formula[1]	Limiting range[8]	Preferable range[8]
LSF	$\frac{\%\ CaO}{2.8 \times \%\ SiO_2 + 1.2 \times \%\ Al_2O_3 + 0.65 \times \%\ Fe_2O_3}$	0.66-1.02	0.92 – 0.96
SM	$\frac{\%\ SiO_2}{\%\ Al_2O_3 + \%\ Fe_2O_3}$	1.9-3.2	2.3-2.7
AM	$\frac{\%\ Al_2O_3}{\%\ Fe_2O_3}$	1.5-2.5	1.3-1.6

2.3.3: Granulometric composition

- Fineness and particle size distributions affect the raw mix burnability. The more fine grained, decomposition and reactions are easy. The maximum permissible particle size of quartz, feldspars and calcite is to be 44µm, 63µm and 125 µm respectively. [13, 8] The normal target of fineness of raw mix is 12% residue on 170 BSS mesh and 2.6% residue on 72 BSS mesh. This target also differs from plant to plant.

- Homogenization of the raw mix affects the clinker quality, burning process and fuel consumption. The homogeneity depends on the fineness and particle size, method of mixing and efficiency of the blending system.

2.3.4: Thermal treatment

- Burning of the raw mix is generally carried out at 1450-1500°C. Excessive high burning temperature results in a great stress on the kiln and the refractory lining, more fuel consumption, reduction in cement strength [14, 8] and larger alite crystal [15, 8]. The burning temperature was determined by the following formula:

°C = $1300 + 4.51C_3S - 3.74C_3A - 12.64C_4AF$ [9]

- On increasing holding time, C_3A content may decrease, C_4AF may increase, C_2S may decrease, C_3S may increase. [8]

- Rapid burning is always favored as because fine grains of C_2S formed which accelerate the interaction of C_2S, CaO_f and liquid. [8]

- Thermal activation can be enhanced by either with mechanical (vibratory mill) or chemical (mineralizer) activation. Mechanical activation gives better results than chemical. [8]

2.3.5: Liquid phase formation

- A,F,M, minor volatile and non-volatile components generally govern the amount of liquid formed, its appearance temperature, viscosity, surface tension and ionic mobility in the clinkerisation process.[8]

2.3.6: Clinker quality

The burnability becomes worse as C_3S content increases while an increasing C_3A and C_4AF, the burnability improves.[8]

2.3.7: Coal ash

- As a fuel, when coal is used for clinker making, its ash quantity, composition and fineness affect the burnability. The effect of ash absorption on burnability is as follows:

- Increases liquid content with reduced viscosity and increase ionic mobility.
- Introduce the micro inhomogeneity due to ash-clinker reaction resulting in some reduction in the strength.

2.3.8: Kiln atmosphere

- A reducing atmosphere during burning affect the colour of the clinker by reducing iron oxide, enhancing C_3A, decreasing C_4AF, C_3S[8]. Therefore, oxidizing condition (O_2 ~ 0.5-2 vol. % in exit gas) should be maintained in the kiln.

2.4: Reaction during burning

The reaction sequence is almost identical in dry, semi-dry and a wet kiln. Different investigators after subsequent experimental observation reported the following phenomena [1, 8]:

i) The first aluminate phase 'CA' is formed at lower temperature (550-600°C) which, in turn, combines with free CaO resulting $C_{12}A_7$ and finally it converts into C_3A above 900°C.
ii) The formation of C_2AS as an intermediate phase.[8]
iii) The ultimate formation of C_4AF at higher temperature (1300-1400°C) is consecutively followed by the appearance of ferrite phase (CF and C_2F) at lower temperature (800-900°C).

Some investigations shows that [8]

i) The dissociation and decarbonation of raw mix starts at 550-600°C.
ii) The first detectable phases $CA+C_{12}A_7+C_2S$ were noticed at 700°C. The amount of these phases increases with temp up to 900-1000°C, when poorly detectable C_3S and some C_4AF/C_2F are traced.
iii) α-Fe, FeO and Fe_2O_3 along with the formation of α-wallastonite with β-C_2S are detected.
iv) The solid-state reactions are almost complete at a temperature of about 1300°C and a melt phase appears. The melt phase contains a complete melting of $C_3A + C_4AF$, and a partial melting of C_2S and CaO with incorporation of such constituents as R_2O, MgO. The formation of C_3S is activated through diffusion of C_2S and CaO in the presence of melt. The final clinker phases appear with the formation C_3A, C_4AF, C_2S, C_3S, MgO and glass after crystallization of the residual liquid.

In some other investigation, the first phases detected are CF + CA + CS which are subsequently converted into clinker phases with rise of temperature. [8]

$CA \longrightarrow C_{12}A_7 \longrightarrow C_3A$

$CF \longrightarrow C_2F \longrightarrow C_4AF$

$CS \longrightarrow C_3S_2 \longrightarrow C_2S$

In addition to the above finding, the formation of spurrite ($2C_2S.CaCO_3$) is detected at the temperature ranging from 680 - 1000°C particularly presence of halides and alkalies in the raw mix.

Gahlenite, C_2AS (or melilite with very little magnesia) was also detected which is the reacted product between kiln refractories and clinker forming materials. C_2AS is found particularly where high alumina bricks would normally be used, but akermanite and melilite would also be expected when dolomite and magnesite bricks are used.

It is also reported that the magnesio-ferrite, $MgO/FeO.Fe_2O_3$, is formed when a raw mix is burnt in a coal fired kiln reducing conditions.

2.5: Burning technology

2.5.1: Classification of kiln process depending on state of raw material

Cement kiln processes may be classified as wet or dry depending on the state of the raw material:

- **Wet process:** In this process, the feed is slurry with 30 – 40 % of water.
- **Semi-wet process:** In the semi-wet process, part of the water in the slurry is removed and a cake containing about 20 % of water is produced. Cake is fed to the kiln either directly or via a preheater.
- **Semi-dry process:** In the semi-dry process, the pulverized dry feed is pelletized into small nodules by adding 10-15 % of water and then the nodules are fed onto a traveling grate where the particles are dried and partly calcined before they enter the rotary kiln.(This process is often called the Lepol process,).[17]
- **Dry process:** In the dry process, the feed is a dry powder.

2.5.2: Classification of rotary kiln on the basis of the kiln length

Rotary kilns may be classified on the basis of the kiln length [17, 18, 8]:

- **Long kiln:** This kiln is operated with a wet or dry process. The meal is not thermally treated before enters the kiln, which has a length of typically 32-35 times of the shell diameter.
- **Short kiln:** This kiln is operated with dry or semidry process and has a length 15-17 times of the shell diameter.

2.5.3: Classification of the rotary kiln based on the degree of pyro processing of the meal

Based on the degree of pyro processing of the meal before it enters the rotary kiln may be further classified:

- **Long dry kiln:** The meal is not thermally pretreated, it enters the kiln directly & drying and calcination takes place inside the kiln. The fuel is supplied through a burner which is axially in the kiln outlet, i.e. at the solid discharge end. Heat exchanging between gas and solids is usually happened by means of internal heat exchanging devices, such as chains. For the long dry kiln, the specific heat requirement is about 4.8 MJ/ (kg clinker). [19, 8]
- **Preheater kiln:** In the dry processes with preheaters, raw mix is heated and partly calcined by hot kiln-gases. In the suspension preheater (SP), this process takes place in a series of cyclones placed on top of each other. There are two parallel strings, each consisting of four cyclones. There is close contact between the meal flowing downwards and the gas flowing upwards. The heat input requirement is about 4.0 MJ/ kg clinker [19, 8]. Also, since the meal is dried and partly calcined, the rotary kiln is shorter.
- **Precalciner kiln:** The most modern suspension preheaters are equipped with a precalciner [Fig 2.1]. The precalciner is a separate furnace usually positioned after the cyclone stage. Normally more than half of the total fuel energy input is supplied to the calciner and the meal is 90% calcined when it enters the rotary kiln and the rest of the fuel is supplied in the main burner. The high degree of precalcination means that the length of the calcining zone in the rotary kiln is reduced to a minimum and hence, the

rotary kiln can be considerably shortened. In addition, the production capacity is higher and the heat input requirement is lower, about 3.5 MJ/kg clinker [19]. This is the modern process used in cement industries.

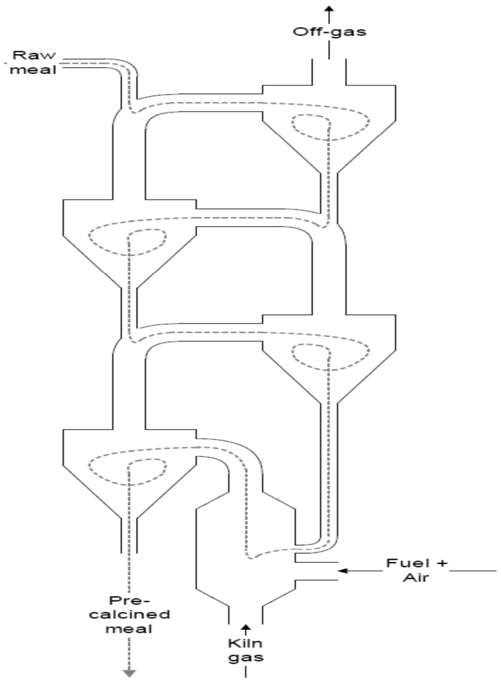


Fig 2.1: suspension precalciner

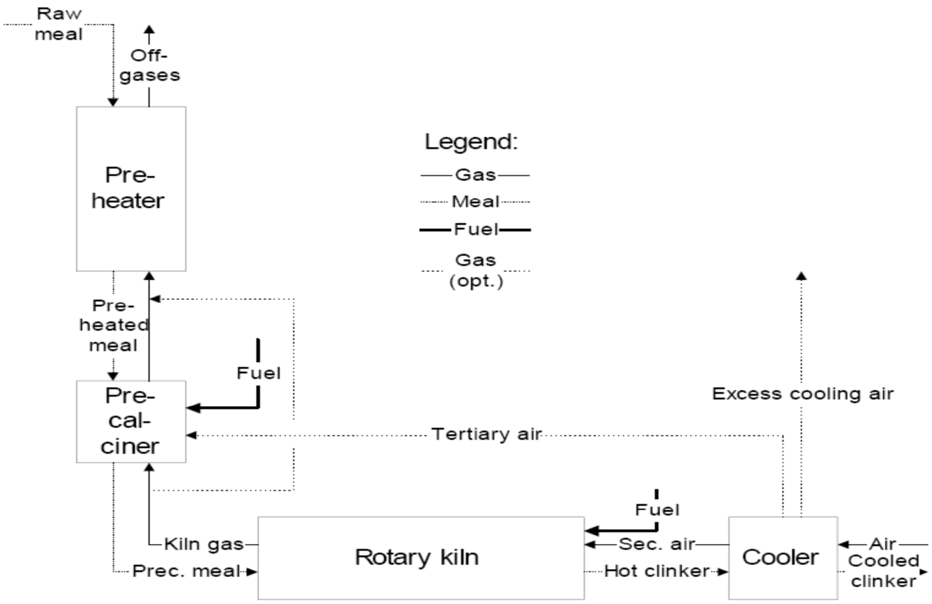


Fig 2.2: Principle drawing of rotary cement kiln with suspension preheater, precalciner and clinker cooler.

2.5.4: Precalcining cement kiln process

The Precalcining cement kiln process has been shown in Fig 2.2. The raw meal is injected into the gas flow at the top of the cyclone stages in the preheater. In the cyclone tower, the meal is dried and the clay minerals dehydrate and decompose. In this preheating process, the meal temperature is typically increased to about 700°C, while the temperature of the counter flowing gas is reduced from about 900 to about 350°C.

In the precalciner, the meal is calcined at a temperature of about 900°C. The solids residence time in the preheater and precalciner is about 2 minutes.

After coming at the lower cyclone stage (which is sometimes regarded as being part of the precalciner), the precalcined meal enters the rotary kiln. In the kiln, the meal is first completely calcined, then the clinker formation reactions take place. The combination of the slight inclination (typically 3°) and the revolution of the kiln cause the solid material to be transported slowly through it. Typically, the residence time in the rotary kiln is 30 minutes. After reaching at a maximum temperature of approximately 1450-1500°C, the clinker is discharged from the kiln and cooled in the clinker cooler, the residence time in the cooler being about 15 minutes. The purpose of the cooler is both to recover heat from the hot clinker and to cool the clinker to a suitable level of temperature.

The cooling air is generally divided into three: one part, the secondary air, is used as combustion air in the primary burning zone, in the rotary kiln. Another part, called the tertiary air, is drawn from the cooler to the precalciner through a separate duct - the tertiary air duct and used as combustion air in the secondary burning zone, in the precalciner. The last part of the cooling air, which may be called excess cooling air, is drawn out of the cooler and release to the surroundings. The temperature of the excess cooling air discharged from the cooler is typically 200-300°C.

The energy required for the process in the rotary kiln is supplied by burning various types of fuel (primary fuel) in the main burner (primary burner). Today, pulverized coal and petroleum coke (pet coke) are the fuels most commonly used. However, oil and gas as well as liquid and solid waste fuels are the most commonly used fuels. The air supplied through the main burner is called primary air. With indirect firing, it contributes about 10% to the total combustion air required in the primary burning zone. The secondary air, which is preheated in the cooler to about 900°C, constituents the major part of the combustion air.

The energy required for the precalcining process is mainly provided by combustion in the precalciner; typically 50-60% of the total fuel input is fed to the calciner. In kiln systems with separate tertiary air duct, air separate (AS) systems, tertiary air preheated to about 800°C in the cooler is used for the precalciner combustion process. However, in systems without tertiary air duct, air through (AT) systems, the precalciner combustion air is drawn through the kiln. [20, 8]

In the AT systems, the off gas from the kiln is led through the calciner. This is usually also the case in AS systems. The in line calciner (ILC) can be used where only one stream of preheater and precalciner is used. However, in some AS systems the kiln gas bypasses the calciner, and the tertiary air is the only gas entering the calciner. Then, if the off gas from the precalciner is not subsequently mixed with the kiln gases, the term separate-line calciner (SLC) is used. If mixing occurs, the term semi-SLC (SLC-S) is used.[21, 8]

In the cyclone tower, the meal is conveyed by the hot gas from one cyclone to another. In the cyclones, typically 80% of the solid phase is separated from the gas. The gas phase, containing the remaining solids, flows to the cyclone stage above. Usually, double-cyclones are used in the uppermost cyclone stage on each string, giving higher cyclone efficiency, typically 95%.

2.5.5: Refractory used in rotary kiln:

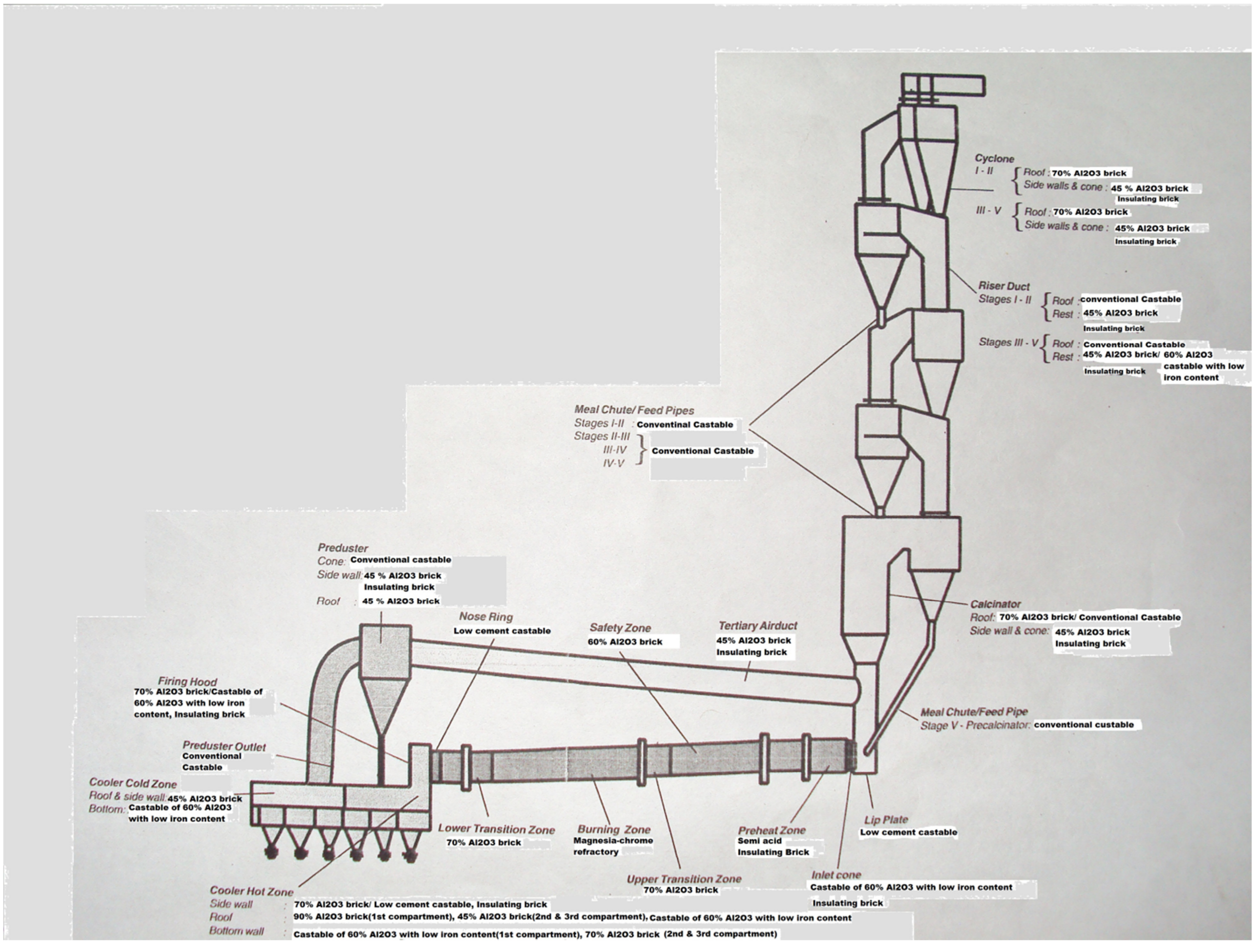


Fig 2.3: Refractories used for cement rotary kiln, preheater and precalciner

Refractories used in different zones are shown in fig 2.3.

2.5.6: Clinker cooler

There are five main types of clinker coolers [18, 8]:

1) **The rotary cooler**, which is a cooling drum located underneath the rotary kiln,
2) **The satellite cooler**, which consists of several cooling drums attached to the circumference of the discharge end of the rotary kiln,
3) **The grate cooler**, in which the clinker is transported by moving grates while being cooled by cross and counter flowing air

4) **The shaft cooler**, where the clinker is cooled while being fluidized by counter flowing air.
5) **Cross bar cooler**, in which air distribution plate is equipped with a Mechanical flow Regulator (MFR) which regulates the airflow via a self-adjusting orifice.[23, 8]

2.6: Hydration of cement

Cement contains mainly four phases, C_3S, C_2S, C_3A, C_4AF. The hydration of cement means the hydration of these phases.

2.6.1: Hydration of C_3S

Tricalcium silicate (C_3S) is the main cementitious component in Portland cement. This phase hydrates steadily with an evaluation of 500 J/gm [8] heat of hydration. The majority of this phase hydrates within 28 days[8]. The hydration reaction is represented by the following equation: [8]

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH$$

The C-S-H is very poor crystalline and non-stoichiometric phase. C-S-H phase is the main binder in the hardened Portland cement paste and also main contributor of compressive strength development at least up to 7 days.[8]

2.6.2: Hydration of C_2S

Dicalcium silicate (C_2S) is another main silicate phase present in the Portland cement. The heat of hydration of this phase is 250J/gm [8]. The hydration reaction occurs mainly after 28 days. The hydration reaction is as follows:

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH$$

2.6.3: Hydration of C_3A

Tricalcium aluminate(C_3A) normally present in portland cement of less amount(~ 5-15 %). The heat of hydration of this phase is 1340J/gm. and it reacts very quickly with water. The hydration reaction is as follows:

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

$$C_4AH_{13} + 3C\hat{S}H_2 + 14H \longrightarrow C_3A.3C\hat{S}.H_{32}\text{(Ettringite)} + CH$$

$$C_3A.3C\hat{S}.H_{32} + 2C_4AH_{13} \longrightarrow 3[C_3A.C\hat{S}.H_{12}]\ \text{(monosulphate)} + 2CH + 20H$$

Both the monosulphate and C_4AH_{13} are hexagonal plate type phases.

2.6.4: Hydration of C_4AF

Calcium aluminoferrite (C_4AF or $C_2A_{0.5}F_{0.5}$) is the solid solution within the C_2A-C_2F system. These phases react with water very slower rate than the C_3A phase and contribute very less amount of strength of portland cement. The heat of hydration of this phase is 420J/gm. The hydration reactions are as follows:

$$C_2A_{0.5}F_{0.5} + CH + 3C\hat{S}H_2 + 25H \longrightarrow C_3A_{0.5}F_{0.5}.3C\hat{S}.H_{32}$$

$$C_2A_{0.5}F_{0.5} + CH + 11H \longrightarrow C_4A_{0.5}F_{0.5}H_{13}$$

$$C_3A_{0.5}F_{0.5}.3C\hat{S}.H_{32} + C_4A_{0.5}F_{0.5}H_{13} \longrightarrow 3[C_3A_{0.5}Fe_{0.5}C\hat{S}.H_{12}] + 2CH + 20H$$

$C_3A_{0.5}F_{0.5}.3C\hat{S}.H_{32}$ is iron substituted ettringite phase. $C_4A_{0.5}F_{0.5}H_{13}$ is the iron substituted C_4AH_{13} phase and $C_3A_{0.5}Fe_{0.5}C\hat{S}.H_{12}$ is the iron substituted monosulphate phase. The iron substituted C_4AH_{13}, ettringite and monosulphate are structurally very similar with the in C_3A hydration phases.

Chapter 3

Experimental

CHAPTER 3

EXPERIMENTAL

3.1: Raw materials for producing clinker

The P.C. clinker was prepared in industrial rotary kiln. Normal P.C. clinker was prepared to compare the properties of clinker containing slag in raw mix. Following raw materials were used for the clinker preparation.

3.1.1: Slag

The granulated slag was taken from Rourkela Steel Plant (India). The slag was characterized for its chemical composition as per Indian Standard IS: 4032-1985. The slag was also characterized for its phase composition analysis using powder X-Ray diffraction.

3.1.2: Limestone

The limestone was taken from Shiva cement mines. Limestone was characterized for its chemical constituents as per the Indian standard. It was also characterized for its phase composition analysis using powder X-Ray diffraction.

3.1.3: Clay

Clay was taken from local mines situated at Kutra, Orissa (India). The clay was also characterized for its chemical constituents as per Indian standard and phase composition analysis using X-Ray diffraction.

3.1.4: Laterite

Laterite was also taken from local mines. Laterite was characterized for its chemical constituents as per Indian standard and also for its phase composition analysis using X-Ray diffraction.

3.1.5: Coal

Coal fines, used as a fuel, was taken from SHIVA sponge iron plant. During clinkerisation coal ashes are incorporated into the cement composition. For that reason, the proximate analysis of coal, chemical and phase analysis of coal ash are required for proper batch composition designing.

3.1.6: Chemical analysis of raw materials

All the raw materials were analyzed for chemical composition as per IS: 4032-1985

Loss on ignition (L.O.I.) was first determined by heating 1gm sample at 950°C for 1 hour. Percentage weight loss is reported as % L.O.I.

% L.O.I. = loss in weight X 100.

0.5 gm. sample was taken into a platinum crucible. The fusion mixture (NaOH + Na_2CO_3 mixture about 2 gm.) was mixed with the sample and homogenized. Then the crucible was heated slowly in oven for 15 mins and kept inside the furnace at 950°C for 1 hour. In every 10 mins, the crucible was slowly rotated so that molten contents spreaded over the side of the crucible and solidified as a thin shell on the interior portion. The crucible was taken out from the furnace and quenched in 30 ml 1:1 HCl inside 500 ml beaker. All the mass was dissolved into the HCl with stirred. After removing the all mass, the crucible was washed well. Then a watch glass kept upon the beaker with partly covered and placed over the hotplate to evaporate all the solution. 2-3 wire gauges were kept in between beaker and the hotplate to prevent the boiling. After complete disappearance of the chloride, the beaker was removed from the hot plate and 20-30 ml of 1:1 HCl was added to it. The solution was boiled for some time and then filtered through whatman no 42 filter paper. 8-10 times washing was given using hot distilled water. The residue (Residue 1) was used for silica quantification and the filtrate (Filtrate 1) was used for further oxide determination.

Residue1: (for silica)

The filter paper containing residue was transferred in a cleaned nickel crucible and ignited at 950°C for 1 hour in a furnace. After burning the weight was taken and the percentage of silica was determined by the following equation:

Percentage of silica = wt. of ash X factor

Filtrate 1:

The filtrate was taken in 250 ml volumetric flask and water was added to it to make up the volume. 100 ml of solution was taken in a 250 ml beaker and 10 cc of saturated bromine water was added to it to convert the entire Fe++ ion into Fe+++ ion. Then 3-4 gm. of solid NH_4Cl was added to it to prevent the precipitation of hydroxides by lowering the concentration of OH. ions. 2-3 drops of methyl red indicator was added and then drop by drop 1:1 NH_4OH solution was added till the solution became yellow i.e., till the complete precipitation of R_2O_3. Excess ammonia was removed by boiling. Then the precipitate was allowed to settle and filtered through whatman filter paper no 41 and 5-6 times washing was done using hot NH_4NO_3 and then 5-6 times washing was done by cold distilled water. The residue (Residue 2) obtained was used for R2O3 determination and filtrate (Filtrate 2) was used for CaO, MgO determination.

Residue 2 (For R_2O_3)

Filter paper containing residue was transferred in a cleaned nickel crucible and ignited it at 950°C for 1 hour in a furnace. After the burning the weight was taken and the percentage of R_2O_3 was determined by the following formula:

Percentage R_2O_3 = wt. of ash x factor

Filtrate 2:

Filtrate was taken in 250 ml beaker and HCl solution was added drop by drop for making it acidic and boiled. NH_4OH was added drop by drop till the red colour disappeared. Then 50 ml of 5 % hot ammonium oxalate was added to it. The Ca-oxalate precipitate obtained was boiled for 10 minutes. Then the solution was filtered through whatman no 41 and washing was given by hot distilled water of 5/6 times. The residue (Residue 3) obtained was used for CaO determination and filtrate (Filtrate 3) was used for MgO determination.

Residue 3(For CaO)

The filter paper containing residue was transferred to that original beaker and dissolved in 100 ml 10% H_2SO_4 in warmed condition and ultimately titrated against std. $KMnO_4$ solution. The percentage of CaO was determined by the following equation:

Percentage CaO = titrate value x strength of $KMnO_4$ x factor

Filtrate 3: (For MgO)

The filtrate was collected in 250 ml volumetric flask and made up the volume with water. 100 ml of solution was taken in a porcelain dish and 3-5 ml of triethanol amine was added and also 20-30 ml pH Buffer 10. Then the solution was stirred vigorously and a pinch of Eriochrome Black – T indicator was added till the solution became light violet. The solution was then titrated with N/50 EDTA solution till a blue colour appeared. The percentage of MgO was determined by the following equation:

Percentage MgO = Burette reading x 0.403 x factor

Determination of Fe_2O_3

10 ml was taken from filtrate 1 into a conical flask. 20 ml of 1:1 HCl was added to it and allowed to boil for 4-5 minutes. Then $SnCl_2$ solution was added drop by drop upto the disappearance of yellow colour indicating the conversion of all the ferric ions into ferrous ions. Then the solution was allowed to cool. After complete cooling, 10ml of $HgCl_2$ and 10 ml of acid mixture (H_2SO_4 + H_3PO_4) was added to it and titrated against $K_2Cr_2O_7$ solution using barium Di-Phenyl amine Sulphonate(BDS) as an indicator till the violet colour came. The percentage of Fe_2O_3 was determined by using the following equation:

Percentage of Fe_2O_3 = Titrate value x Strength of $K_2Cr_2O_7$ x factor.

3.1.6.1: Chemical composition of raw materials

The cement clinker was produced with and without slag as a raw material for comparison. The clinker production was carried out in actual cement rotary kiln in SHIVA cement Ltd, kutra. The plant has a regular continuous production of normal clinker (without slag). That clinker and associated raw materials used for the production of that were collected from a particular date of production in the month of August. Those raw materials were analyzed separately and results are stated in Table 3.1. For the production of clinker by using slag (slag clinker), the respective raw materials were sampled from the stock yard during the month of October and they were analyzed separately and the results are shown in Table 3.2.

Table: 3.1: chemical composition of the raw material used for production of normal clinker

Percentage of Constituents	Lime Stone	Clay	Laterite	Coal Ash
L.O.I.	40.1	6.86	7.54	--------------
SiO_2	6.4	66.84	35.14	58.12
Al_2O_3	1.12	14.10	10.36	24.9
Fe_2O_3	0.7	8.20	43.22	12.48
CaO	48.78	1.69	1.32	2.1
MgO	2.10	1.32	0.84	1.1
Others	0.8	0.99	1.58	1.3

Table: 3.2: chemical composition of the raw material used for production of slag clinker

Percentage of Constituents	Lime Stone	Clay	Laterite	Slag	Coal Ash
L.O.I.	40.2	7.2	5.23	0.1	----------
SiO_2	6.32	71.31	45.1	34.1	60.0
Al_2O_3	1.08	11.10	10.19	22.4	25.0
Fe_2O_3	0.8	5.5	36.2	0.8	12.0
CaO	48.5	1.9	1.1	32.1	1.0
MgO	1.4	1.6	1	9.5	1
Others	0.9	1.39	1.18	1	0.6

3.1.7: Phase analysis of raw materials

Phases were determined by XRD analysis using Philips Panalytical XRD instrument with Ni filter and CuKα radiation (30 kV and 35 mA). The sample was scanned in the 2θ range 10 – 70 °. The scan rate was 1°/min. phases present in the sample has been identified by the Philips X'Pert High Score software, where search match facility is available. The XRD pattern for slag is shown in Fig 3.1.

The Figure shows the amorphous phase of the based on silica glassy material. There is a very broad peak around 28° 2θ corresponding silica tetrahedron amorphous material.

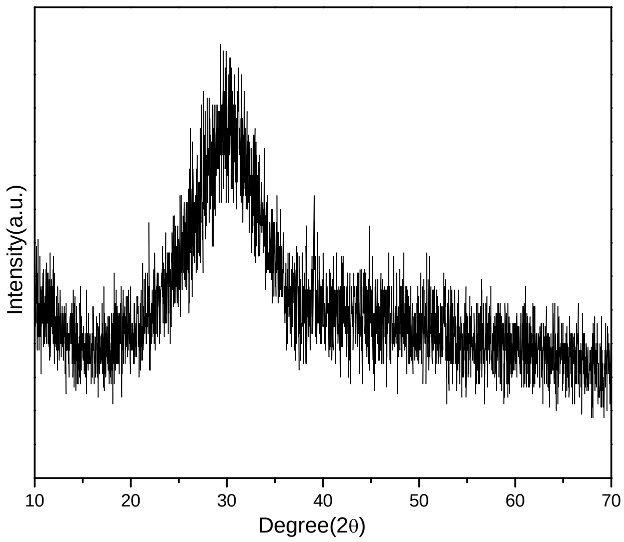


Fig 3.1: XRD pattern for the slag.

Fig 3.2 and 3.3 shows the XRD pattern of the limestones those used for producing normal clinker and slag clinker respectively. The Figure show the presence of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), quartz (SiO_2) and illite in the limestones. So, the analysis indicates that the limestone contain mainly silica and clay impurities. Also, it contains some dolomite which usually found in limestone.

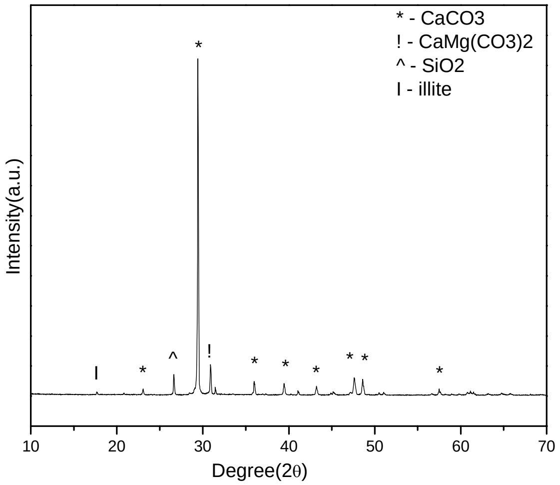


Fig 3.2: XRD pattern for the limestone used for normal clinker

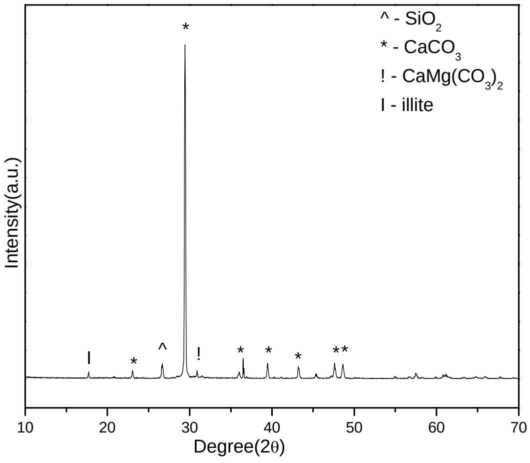


Fig 3.3: XRD pattern for the limestone used for slag clinker

Fig 3.4 and 3.5 shows the XRD pattern of the clay used for two types of clinkers. Both the figures show the presence of quartz as a major material. Besides quartz there are some other clay type material like muscovite. A small amount of dolomite impurity was present in the clay used for slag clinker. The chemical analysis of clay shows (Table 3.1 and Table 3.2) about 70 % silica and 12 % Al_2O_3. So, XRD results also indicate the presence of very high amount of silica sand in the clay material. This clay may be considered as very very impure.

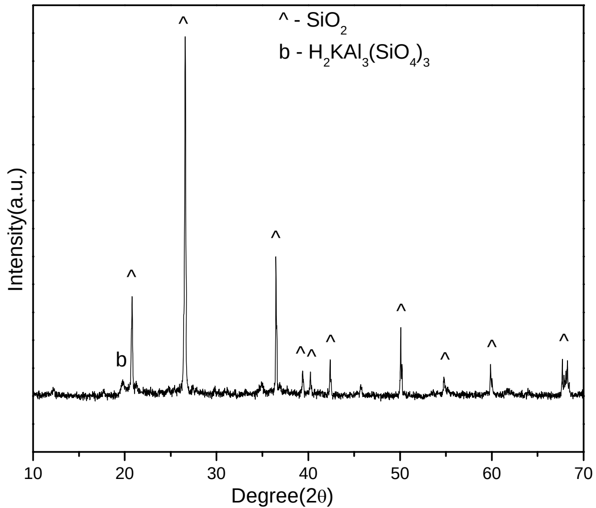


Fig 3.4: XRD pattern for the clay used for normal clinker.

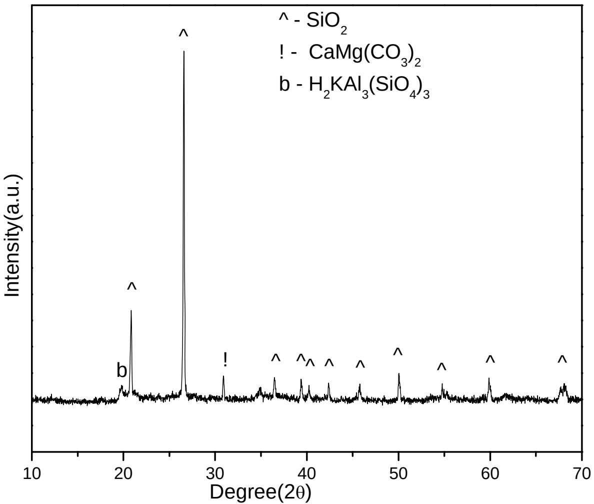
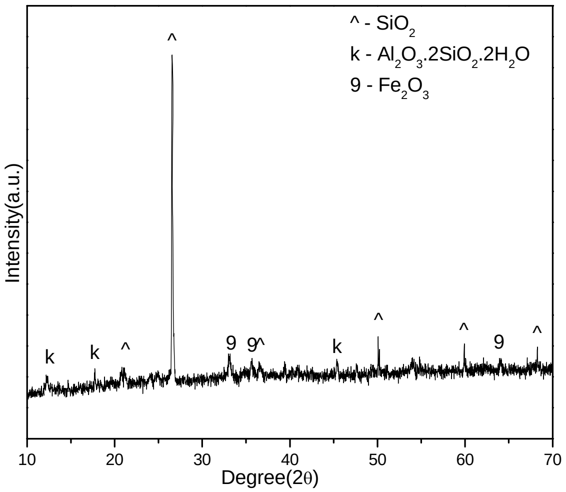


Fig 3.5: XRD pattern for the clay used for slag clinker.

Fig 3.6 and 3.7 show the XRD pattern of the laterite used for producing normal clinker and slag clinker respectively. Both the figures show the laterite contains a major silica impurity besides iron oxide. Some amount of kaolinite clay impurity is also associated with the mineral.



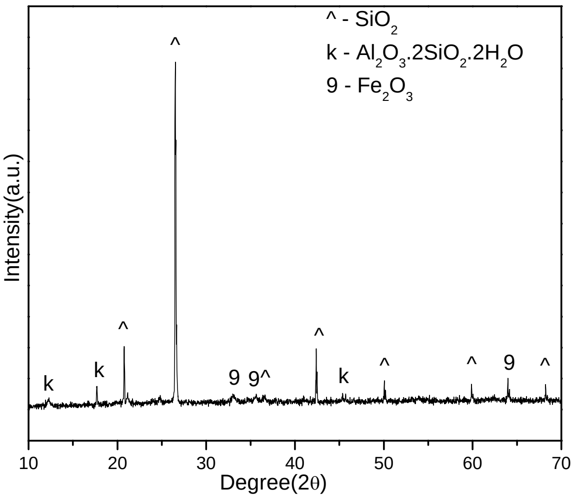
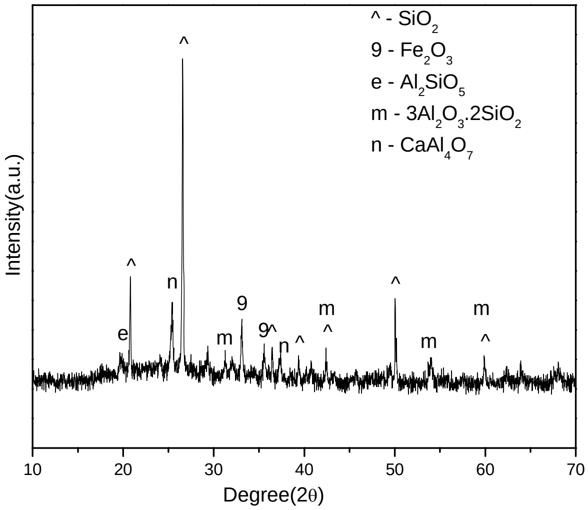


Fig 3.6: XRD pattern for the laterite used for normal clinker

Fig 3.7: XRD pattern for the laterite used for slag clinker

Fig 3.8 and 3.9 show the XRD pattern of the coal ash used for producing normal clinker and slag clinker respectively. Both the figures show the major phases are quartz, mullite, calcium aluminum oxide and iron oxide. Quartz associated with the ash may be due to the presence of silica sand impurity in coal fines.



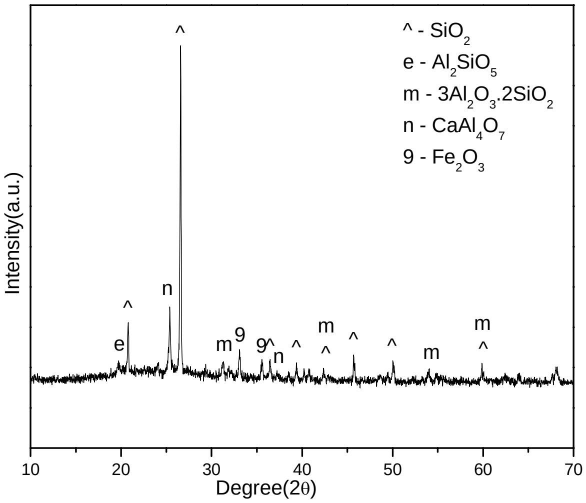


Fig 3.8: XRD pattern for the coal ash used for normal clinker

Fig 3.9: XRD pattern for the coal ash used for slag clinker

3.1.8: Proximate analysis of coal

The Proximate analysis of the coal sample has been carried out in the following procedure:

1.5 gm. of received coal sample was taken in a glass plate and put into the dryer at 110°C for 1.5 hrs. After that, the glass plate was kept in a dissector for cooling and then the weight was taken. The inherent moisture was determined by the following formula:

Percentage of moisture = weight difference X factor.

The dried coal powder was taken in a silica crucible. A lid was put over the crucible and kept in a furnace for 7 minutes at 900°C, then cooled in a dissector and weight was taken. The percentage of volatile matter was determined by the following formula:

Percentage of volatile matter = weight difference x factor.

Then the sample was heated in a furnace at 815°C for 3 hrs., cooled in dissector and weight was taken. The percentage of ash was determined by the following formula:

Percentage of ash = weight difference x factor.

The fixed carbon present in the coal sample was determined by the following formula:

Percentage of fixed carbon = 100 – [% ash + % volatile matter + % moisture]

The proximate analysis of the coal sample is shown in Table3.3.

Table: 3.3: Proximate analysis of coal

Coal used for	Moisture	Volatile Matter	Ash	Fixed Carbon
Normal clinker	3.5	27.1	30	39.4
Slag clinker	3.1	26.2	32	38.7

3.2: Raw mix design

The raw mix was designed based upon the chemical analysis of the raw materials. The lime saturation factor (L.S.F.) ~ 0.9, silica modulus (S.M.) ~ 2.3 and alumina modulus (A.M.) ~ 1.3 were used for the raw mix design. The formula of the L.S.F., S.M. and A.M. are given below:

L.S.F. = $CaO/ [(2.8 \times SiO_2) + (1.2 \times Al_2O_3) + (0.65 \times Fe_2O_3)]$

S.M. = $SiO_2 / [Al_2O_3 + Fe_2O_3]$

A.M. = Al_2O_3/Fe_2O_3

3.2.1: Raw mix design for the normal clinker production

The raw mix design for the clinker production without slag in the raw mix was determined by the following procedure:

Assumed $Fe_2O_3 = n$

Then by putting the value in the A.M. formula, we got,

$Al_2O_3 = 1.3n$ and

Then after putting the value in the S.M. formula, we got,

$SiO_2 = (1 + 1.3) \times 2.3n = 5.29n$.

By putting the value in the L.S.F equation:

$$CaO/ [(2.8 \times 5.29n) + (1.2 \times 1.3n) + (0.65 \times n)] = 0.9$$

$$CaO= 0.9(14.81 + 1.56 + 0.65)\, n = 15.32n$$

Again, MgO = 4.0%, others = 1.5 %.

Now, $CaO + SiO_2 + Al_2O_3 + Fe_2O_3 + MgO + \text{others} = 100$

$$15.32n + 5.29n + 1.3n + n + 4.0 + 1.5 = 100$$

$$n = 4.12$$

Which conclude that the clinker should have the following percentage of chemical constituents as shown in Table 3.4.

Table 3.4: The required percentage of chemical constituents for normal clinker:

Chemical constituents	Amount in percentage (%)
CaO	63.11
SiO_2	21.79
Al_2O_3	5.36
Fe_2O_3	4.12
MgO	4
Others	1.5

The Table 3.4 shows the required percentage of chemical constituents for normal clinker considering the coal ash contribution to the clinker.

Coal contains 30% ash with a heating value = 4500 kcal/kg

Now, the basis was for producing 1 kg of clinker, 900 kcal heat was required.

So, for producing 100 kg of clinker, the amount of ash was (900 x 100 / 4500) kg = 20 kg.

So, 20 % coal has to be used for producing clinker.

Now the ash absorption = (20 x 30 / 100) % = 6.0 %.

And raw mix absorption = (100 – 6.0) % = 94 %

Assume a %, b %, c% and d % of CaO, SiO_2, Fe_2O_3 and Al_2O_3 was present in the raw mix respectively.

From the Table, it has been found that the ash contained 3.1%, 58.12 %, 12.48 %, 24.19 % of CaO, SiO_2, Fe_2O_3, Al_2O_3.

So, For CaO: (a x 94) + (3.1 x 6.0) = 63.11 x 100 a = 66.94

For SiO_2 : (b x 94) + (58.12 x 6.0) = 21.79 x 100

b = 19.47

For Fe_2O_3 : (c x 94) + (12.48 x 6.0) = 4.12 x 100

c = 3.59.

For Al_2O_3 : (d x 94) + (24.19 x 6.0) = 5.36 x 100

d = 4.16

So, the final percentage of chemical constituents requirement in the raw mix for normal clinker should be as presented in Table 3.5

Table 3.5: The percentage of chemical constituent of raw mix requirement for producing normal clinker:

Chemical constituents	Amount in percentage (%)
CaO	66.94
SiO_2	19.47
Al_2O_3	4.16
Fe_2O_3	3.59
MgO	4
Others	1.5

Now from the Table 3.1, the raw mix analysis was as follows:

	L.O.I.	SiO_2	Al_2O_3	Fe_2O_3	CaO
Limestone:	40.1	6.4	1.12	0.7	48.78
	0	10.68	1.87	1.17	81.44

Clay:	6.86	66.87	14.10	8.2	1.69
	0	71.16	15.14	8.8	1.82
Laterite:	7.54	35.14	10.36	43.22	1.32
	0	38.01	11.21	46.75	1.43

Assumed the raw mix contained m%, n%, p% of limestone, clay and laterite respectively.

Now, for CaO: 81.44 x m + 1.82 x n + 1.43 x p = 66.94

For SiO_2: 10.68 x m + 71.76 x n + 38.01 x p = 19.47

For Al_2O_3: 1.87 x m + 15.14 x n + 11.21 x p = 4.16

After solving this, the final proportion is shown in Table 3.6.

Table: 3.6: Raw mix weight percentage for production of normal clinker

Raw material	Weight percentage
Lime Stone	81.3
Clay	7.7
Laterite	11.0

3.2.2: Raw mix design for producing slag clinker

For the slag clinker production, the raw mix design calculation was as follows:

From the above Table 3.4, the clinker should have the following percentage of chemical constituents:

Fe_2O_3 = 4.12 %, Al_2O_3 = 5.36%, SiO_2 = 21.79%, CaO = 63.11%, MgO = 4% and others = 1.5%

Coal contains 32% ash with a heating value = 4500 kcal/kg

Now, the basis was for producing 1 kg of clinker, 900 kcal heat was required.

So, for producing 100 kg of clinker, the amount of ash was (900 x 100 / 4500) kg = 20 kg.

So, 20 % coal has to be used for producing clinker.

Now the ash absorption = (20 x 32 / 100) % = 6.4 %.

And raw mix absorption = (100 – 6.4) % = 93.6 %

Assume a %, b %, c% and d % of CaO, SiO_2, Fe_2O_3 and Al_2O_3 was present in the raw mix respectively.

From the Table 3.2, it has been found that the ash contained 1%, 60 %, 12 %, 25 % of CaO, SiO_2, Fe_2O_3, Al_2O_3.

So, For CaO: (a x 93.6) + (1 x 6.4) = 63.11 x 100

a = 67.36

For SiO_2 : (b x 93.6) + (60 x 6.4) = 21.79 x 100

b = 19.18

For Fe_2O_3 : (c x 93.6) + (12 x 6.4) = 4.12 x 100

c = 3.58.

For Al_2O_3 : (d x 93.6) + (25 x 6.4) = 5.36 x 100

d = 4.02

So, the final chemical constituents requirement in the raw mix for the slag clinker should be as presented in Table 3.7.

Table 3.7: The percentage of chemical constituent of raw mix requirement for producing slag clinker

Chemical Constituents	Amount in Percentage (%)
CaO	67.36
SiO_2	19.18
Al_2O_3	4.02
Fe_2O_3	3.58
MgO	4
Others	1.5

Now from the Table 3.7, the raw mix analysis was as follows:

	L.O.I.	SiO_2	Al_2O_3	Fe_2O_3	CaO
Limestone:	40.2	6.32	1.08	0.8	48.5
	0	10.57	1.81	1.34	81.5
Clay:	7.2	71.31	11.10	5.5	1.9
	0	76.31	11.96	5.93	2.05
Laterite:	5.23	45.10	10.19	36.20	1.1
	0	47.59	10.75	38.2	1.16
Slag:	0.1	34.1	22.4	0.8	32.1
	0	34.1	22.4	0.8	32.1

Assumed the raw mix contained m%, n%, p% and q % of limestone, clay, laterite and slag respectively.

Now, for CaO: $81.10 \times m + 2.05 \times n + 1.16 \times p + 32.1 \times q = 67.36$

For SiO_2: $10.57 \times m + 76.84 \times n + 47.59 \times p + 34.1 \times q = 19.18$

For Al_2O_3: $1.81 \times m + 11.96 \times n + 10.75 \times p + 22.4 \times q = 4.02$

$$m + n + p + q = 1$$

After solving this, the final proportion is shown in Table 3.8.

Table: 3.8: Raw mix weight percentage for production of slag clinker

Raw material	Weight percentage
Lime Stone	79.7
Clay	5.2
Laterite	12.2
Slag	2.9

3.3: Process for producing clinker

The clinker production flow chart is shown in Fig 3.10.

3.3.1: Processing of limestone

From the mines, 200- 300 mm size limestone was received. In primary crusher (impact hammer crusher), it was crushed and then it was sent to sieve shaker, where the >16 mm size limestone was separated and the fines was sent to limestone stock pile through belt conveyor. The above 16 mm size limestone then was sent to the secondary crusher (impact hammer crusher) where it was crushed and then it was sent to the same sieve shaker. Ultimately the limestone from the stock pile was sent to the raw mill hopper through the belt conveyor.

3.3.2: Processing of clay, laterite and slag

The others raw material such as clay, Laterite, slag were mixed according to the raw mix design and kept it into the additive stock pile and then it was sent to the raw mill hopper through the belt conveyor.

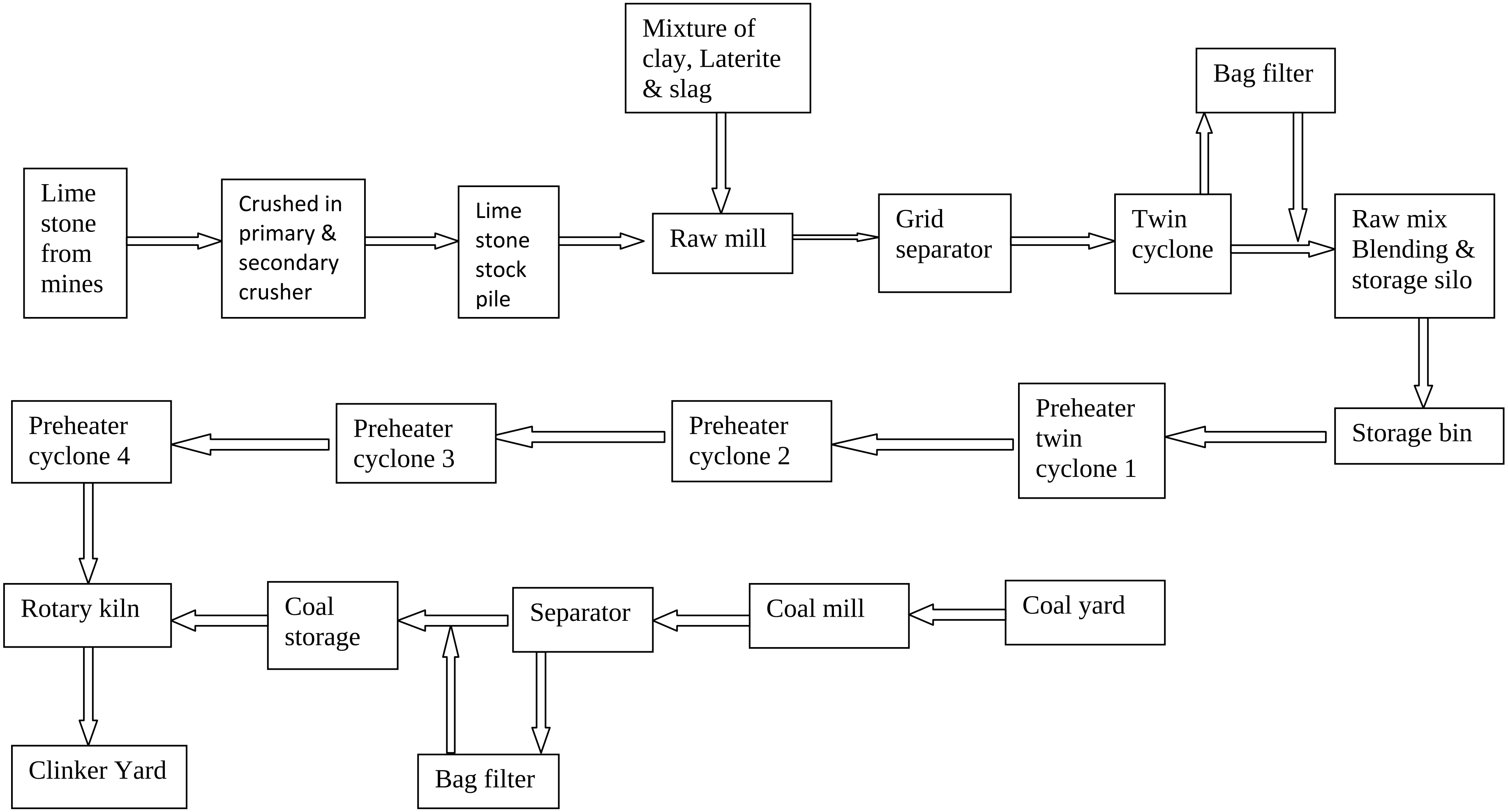


Fig3.10: Flow sheet for clinker production from the raw materials

3.3.3: Processing of raw mix

The hoppers are attached with table feeder with variable speed drive by which the raw mix variables are controlled. The limestone and the additives were fed into the raw mill where the temperature of the raw mill was maintained at 150-160°C by hot air. The materials were grounded into a fine powder in the mill. Then the fine mixture was separated into fine and coarse by the grid separator. The coarse raw mix was then recycled into the raw mill for further crushing through the air slide. The fine raw mix was sent into the twin cyclone where gas was separated from the material. The gas was then sent to the bag filter where the very fine material was separated and was fed into the vp pump. On the other hand, the material collected from the twin cyclone was fed into the vp pump through the air slide. Then the material was sent into the blending silo by compressed air, where it was blended for minimum variation in quality and then the mix was sent to the storage silo through the rotary slide valve.

3.3.4: Characterization of raw mix

3.3.4.1: Total carbonate of the raw mix

The total carbonate has been measured by using the following procedure:

0.5 gm. of sample was taken in a clean and dried 250 ml conical flask. 10 ml distilled water was added to it with stirring well and then 25 ml of 0.4N HCl was added to it. The solution was boiled for 2 minutes in a heater, the side of the conical flask was washed by distilled water and 2/3 drop of phenolphthalein indicator was added into it. Finally it was titrated against 0.1N NaOH. The amount of total carbonate was determined by the following formula:

Percentage of total carbonate = (100 – burette reading) x Factor

The total carbonate of the raw mix is shown in Table: 3.9

Table: 3.9: Total carbonate for raw mix

Raw mix	Total Carbonate (%)	
	As actual	As per design
For normal clinker	79.6	80
For slag clinker	79.5	80

The total carbonate of the raw mix according to the design was 80 %. From the above result, it indicates that the total carbonate of the raw mix was maintained.

3.3.4.2: Fineness of raw mix

The residue (in 170 mesh) was determined by the following procedure:

For residue determination, 10 gm. of sample was taken in the sieve (170 mesh). The material was washed by tap water and the residue was taken in a glass plate. Then it was dried at 110°C for 30 min. Dry weight was taken and % residue is:

Percentage of residue = weight of the residue x Factor.

The residue of raw mix in 170 mesh is shown in the Table: 3.10.

Table: 3.10: Fineness of raw mix

Raw mix	Residue in 170 mesh (%)	
	Actual value	As per design
For normal clinker	19.8	20
For slag clinker	19.6	20

The residue of the raw mix was maintained 20% according to the design. So, from the above result, it indicates that the residue of the raw mix was maintained.

3.3.4.3: Chemical constituents of the raw mix

The raw mix was also analyzed for its chemical constituents as per the procedure stated above for slag. The chemical analysis of the raw mix is shown in Table 3.11.

Table: 3.11: Percentage of Chemical constituents of raw mix

Chemical constituents	Raw mix			Raw mix with slag		
	L.O.I. basis	Zero L.O.I. basis		L.O.I. basis	Zero L.O.I. basis	
		Actual value	Designed value (Table 3.5)		Actual value	Designed value (Table3.7)
L.O.I	35.8	0	0	34.8	0	0
SiO_2	12.48	19.44	19.47	12.2	18.71	19.18
Al_2O_3	2.58	4.02	4.16	2.9	4.44	4.02
Fe_2O_3	2.5	3.89	3.59	2.2	3.37	3.58
CaO	42.71	66.52	66.94	43.5	66.71	67.36
MgO	2.14	3.33	------	2	3.06	----
Others	1.79	2.8	-------	2.4	3.71	-----

In actual case, for the normal clinker the raw mix contains 19.44% SiO_2 whereas the designed value was 19.47%. On the other hand, for the slag clinker the raw mix contains 18.71% SiO_2 whereas in design, the SiO_2 percentage was 19.18%. In case of Al_2O_3, for normal clinker and slag clinker the raw mix contains in actual case 4.02% and 4.44% respectively whereas the designed value was 4.16% and 4.02% respectively. In case of Fe_2O_3, the designed value for normal clinker and slag clinker was 3.59% and 3.58% respectively whereas in actually the amount is 3.89% and 3.37% respectively. Moreover, in case of CaO for the normal clinker and slag clinker contains in actual case 66.52% and 66.71% respectively whereas the designed value was 66.94 and 67.36%.

3.3.5: Processing of coal

The coal is crushed in a coal mill where the temperature of the coal mill was maintained at 60-70°C by hot air obtained from the kiln. Then the fine particles are separated from coarse by the separator, the fine coal is passed to the cyclone separator and the coarse coal is passed to the coal mill for further grinding. In the cyclone separator the gas was separated from the material and the material was sent to the bucket elevator. Again, in the bag filter, the fine coal was separated and material was fed into the same bucket elevator, the gas was released into the environment by the exhaust fan. From the bucket elevator, the coal was fed into the coal hopper. From the coal hopper, the coal was fed into the burner pipe and the calciner through the screw conveyor. The burner pipe was used for the firing in the rotary kiln and also for maintaining the flame direction; the primary air was used with the coal feeding in the kiln.

3.3.6: Characterization of coal

3.3.6.1: Particle size distribution of the coal:

The particle size distribution of as received coal was done by sieving and shown in Fig 3.11.

From the figure, it has been seen that the particle size distribution of as received coal sample for both sample was same.

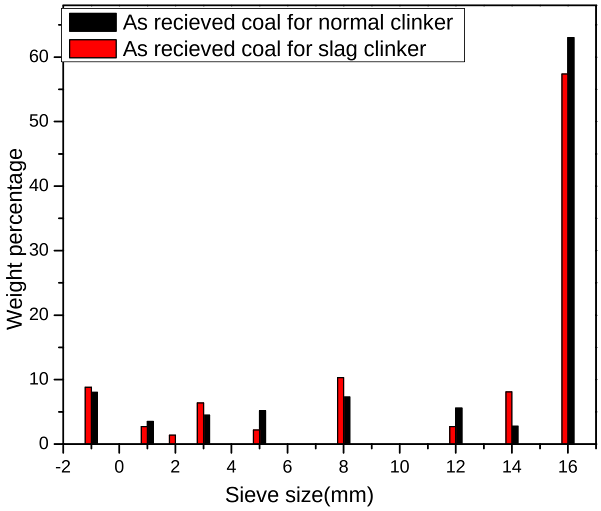


Fig 3.11: The particle size distribution of as received coal sample

3.3.7: Calcination of raw mix

From the storage silo, the raw mix was fed into the bucket elevator through the air slide. The material was then fed into the storage bin. From storage bin, the material was fed into the vp pump through the air slide and then it went to the preheater top and fed into the preheater twin cyclone 1. From the cyclone 1, the material went to the cyclone 2, then cyclone 3, then cyclone 4 and ultimately to the kiln. In the different cyclone, the raw mix was calcined by the counter current flow of the flue gas.

3.3.8: Precalcining cement kiln process

In the Precalcining kiln process, the flue gas which was coming from the rotary kiln went to the cyclone 4. In the cyclone 4, the flue gas carries the material coming from the cyclone 3 and cycloning in the cyclone chamber where the flue gas has released the temperature. From the cyclone 4, the flue gas went to the cyclone 3 and then cyclone 2 and then twin cyclone 1. After that, from cyclone 1, the flue gas went through preheater fan and then divided into 2 parts, one part went to the raw mill chamber, which was controlled by the damper, and another part went to the multiclone, where the flue gas cycloning in the chamber and released some material which was taken in preheater cyclone. After that the flue gas was divided into 3 parts controlled by the dampers. First part went to the coal mill, 2nd part went to the cement mill and 3rd part went to the bag filter, where the dust which was present in the flue gas, was collected. Then the flue gas was released in the atmosphere through the exhaust fan. Now, the material which was collected from the multiclone and the bag filter was fed into the vp pump, which then fed into the preheater cyclone.

3.3.9: Process data for producing clinker in rotary kiln

The process data for producing clinker in rotary kiln is shown in Table: 3.12 and 3.13.

Table 3.12: Temp and draft for production of normal clinker and slag clinker:

	Temp(°C)		Draft(mmWG)	
	Normal clinker	Slag clinker	Normal clinker	Slag clinker
Preheater fan	320	320	-425	-431
Cyclone 2 inlet	550	577	-230	-246
Cyclone 2 outlet	--	--	-113	-111
Cyclone 3 inlet	635	672	-160	-160
Cyclone 3 outlet	--	---	-36	-39
Cyclone 4 inlet	790	784	-70	-71
Cyclone 4 outlet	--	---	-42	-48
Kiln inlet	840	848	-11	-11
Multi clone outlet	--	---	-105	-106

Table: 3.13: Feed rate of coal and raw mix feed rate for producing normal clinker and slag clinker

	Coal feed (kg/hr)		Raw mix feed (kg/hr)
	Primary	Secondary	
Producing normal clinker	624	288	6780
Producing slag clinker	592	288	6401

The Table 3.13 shows the feed rate in producing normal clinker and slag clinker was approximately the same.

3.3.10: Pyro processing of the raw mix

In the kiln, there was a burning zone, where the raw-materials were clinkered and coming out through the planetary cooler. In planetary cooler, there was a natural cooling system. After cooling, the clinker was transported through drag chain and ultimately fed into a belt conveyor. Through belt conveyor, the clinker went to the clinker storage silo.

3.3.11: Characterization of the clinker produced in rotary kiln

3.3.11.1: Bulk density of the clinker

The bulk density was measured by the following procedure:

The clinker was passed through ½ inch and ¼ inch sieve and the clinker in ¼ inch was taken in a steel can whose volume was 1 litre and the weight was taken and the bulk density was determined by the following procedure:

Bulk density = weight of clinker in 1 litre steel can

The bulk density of clinker is reported in Table 3.14.

Table 3.14: Bulk density for normal clinker and slag clinker

Clinker	Bulk density(kg/dm^3)	Designed value(kg/dm^3)
Normal clinker	1135	1150
Slag clinker	1185	1150

The Table 3.14 shows the bulk density for the clinker without slag and clinker with slag. The bulk density for without slag and with slag was 1135 kg/dm^3 and 1185 kg/dm^3 respectively whereas the designed value was 1150kg/dm^3.

3.3.11.2: Phase evaluation of the clinker

Phases were identified by using XRD analysis.

3.3.11.3: Chemical composition of the clinker:

Clinker was characterized for its chemical constituents as per Indian standard IS: 4032-1985. The details procedure was as following:

0.5 gm. of clinker sample was taken in 100 ml beaker and about 0.7 gm. of ammonium chloride was added to it and mixing was done with the glass rod and 5ml of conc. HCl acid was added to it. Then the solution was kept on a hot plate along with wire gauge at 70 °C for about half an hour. After that it was removed from the hot plate and about 50 ml of slightly warm water was added to it and then stirred well. Then the solution was filtered through whatman 42 filter paper and 8-10 times washing was given by hot distilled water.

Residue1: (for silica)

The filter paper containing residue was transferred in a cleaned nickel crucible and ignited at 950°C for 1 hour in a furnace. After burning the weight was taken and the percentage of silica was determined by the following equation:

Percentage of silica = wt. of ash X factor.

The remaining procedure was as stated earlier.

For free lime

0.5 gram of sample was taken in a dried 100 ml conical flask and then 50 ml of ethylene glycol was added to it and the flask was then closed with a cork. The solution was vigoursly shaken and kept in oven at a constant temperature 70°C for half an hour. For every 5 minutes interval the flask was taken out and shaken vigoursly. Then the solution was filtered with whatman filter paper no 1 under vacuum and the filtrate was transferred to a 250 ml flask. After that the residue was washed with 10 ml of ethylene glycol for 3 times. Then 2-3 drops of bromo cresol green indicator was added to the filtrate and then titrated against 0.1N HCl. The end point was the straw colour.

Free lime was determined by the following formula:

%Free lime = Titre Volume x 0.56 x Factor.

3.3.12 Preparation of the raw mix for producing clinker in laboratory muffle furnace

For the preparation of the raw mix for producing clinker in laboratory muffle furnace, the coal collected from the coal silo was heated in the muffle furnace at the rate of 2°/min upto 950°C and then 2 hours holding. After cooling the coal ash was taken out from the furnace. Then 6% and 6.4% ash was mixed with raw mix for without slag and with slag respectively in a pot mill.

3.3.13: Characterization of the raw mix for producing clinker in laboratory

3.3.13.1: Thermal behavior of the raw mix

The thermal decomposition behavior of the raw mix has been also studied using Netzsch, STA 449C.The DSC-TG was determined as a function of temperature up to 1200°C under N_2 atmosphere. The heating rate was 10°C/min.

3.3.14: Production of clinker in laboratory muffle furnace

20 gm. of the both raw mix was taken in a glass slide and 4 ml of water was taken into it and mixing was done properly. After well mixing, a round ball like structure was formed and was taken inside the cleaned platinum crucible, then put into the muffle furnace at a temperature ranging from 500 upto 1500°C. In the muffle furnace, the heating rate was 2°C/min and 60 min soaking was done. After the soaking period, the material was taken out from the furnace and quenched under a high speed air. After quenching, the clinker was kept inside the plastic zip and kept inside the vacuum chamber.

3.3.15: Characterization of the clinker produced in laboratory muffle furnace

3.3.15.1: Phase evaluation of the clinker produced in laboratory

The phases were determined by X-ray diffraction by using the previously stated procedure.

3.3.15.2: Free lime determination of the clinker

The free lime was determined of the laboratory produced clinker by using the previously stated procedure.

3.4.1: Ordinary Portland cement production

200 gm. gypsum was added with the 3800 gm. clinker (produced in the rotary kiln) in a laboratory ball mill. The ball mill contained 80mm, 70mm, 40mm and 30 mm size of grinding media and the total load of 32 kg. and the grinding media were made of high chrome.

3.4.2: Characterization of the Portland cement

3.4.2.1: Specific Surface area of the cement

Specific surface was determined by Blain's apparatus (as per IS 5516:1996):

As per IS: 4031: Part2-1999, 2.8 gm. of Portland cement was weighed. Then a perforated plate and a 12.5 mm dia whatman 41 filter paper were inserted inside the cleaned permeability cell. Then the weighed quantity of cement sample was placed in the cell and a plunger was used to compact the cement after covering the cement with another filter paper circle. The conical surface of the cell was inserted into the top of the manometer using silica grease to make an air tight joint. Then, the stopcock was opened and raised the level of the manometer liquid (dibutylphthalate) to that of the highest etched line by sucking and then the stopcock was closed. Now, the manometer liquid began to flow downward. The stopwatch was started as soon as the liquid reached the second etched line and stopped it when it reached the third etched line. The time was recorded and the specific surface area was determined by the following formula:

$$\text{Specific surface area} = \text{factor} \times \sqrt{\text{time}}$$

The specific surface area was reported in the Table: 3.15

Table 3.15: The specific surface area for the $(PC)_{\text{without slag}}$ and $(PS)_{\text{with slag}}$

Cement	Specific surface area (cm2/gm.)
$(PC)_{\text{without slag}}$	4700
$(PS)_{\text{with slag}}$	4660

The Table 3.15 shows the specific surface area for the $(PC)_{\text{without slag}}$ and $(PS)_{\text{with slag}}$. The $(PC)_{\text{without slag}}$ contains more surface area than the $(PS)_{\text{with slag}}$.

3.4.2.2: Normal consistency of cement

The normal consistency (IS: 4031: Part 4 - 1988) was determined by the following procedure:

400 gm. of cement sample was taken in a tray and then 120 ml water was added to it and then it was mixed by gauging trowel for 3-5 min to make a paste. As per IS: 10086: 1962 the gauging trowel was of 210 gm. weight and 120 mm length. Then the paste was filled into consistency mould placed on a non- porous plate (as per IS 10086:1982). The surface of the paste was smoothened after completely filling the mould to make its level with top of mould and also the mould was slightly shaken to expel the air. Then the mould was kept under vicat apparatus. The vicat apparatus was of IS: 5513:1996 certified and the weight of the vicat apparatus including plunger was 300 gm. and weight of the plunger was 9 gm. After that, the plunger was lowered slowly to the surface of the paste and then the plunger was released quickly and allowed to penetrate the paste. The test was repeated with varying quantity of water till the achieved condition i.e. 5-7 mm from the bottom of mould. The normal consistency of cement was determined by the following formula:

Normal consistency of cement = P = water required/4

Normal consistency of the cement: the normal consistency for the $(PC)_{\text{without slag}}$ and $(PS)_{\text{with slag}}$ was reported in the Table 3.16

Table 3.16: The normal consistency for the $(PC)_{\text{without slag}}$ and $(PS)_{\text{with slag}}$

cement	Normal consistency (%)
$(PC)_{\text{without slag}}$	27
$(PS)_{\text{with slag}}$	28

The Table 3.16 shows the normal consistency for the $(PC)_{\text{without slag}}$ and $(PS)_{\text{with slag}}$. The $(PC)_{\text{without slag}}$ contains less normal consistency than the $(PS)_{\text{with slag}}$.

3.4.2.3: Setting time of cement

The setting time (as per IS 4031: Part 5: 1988) was determined by the following procedure:

400 gm. of cement sample was taken in a tray and then 0.85 times of normal consistency amount of water was mixed with it and the mixing was done by the gauging trowel (specification stated above) for 3-5 min to make a paste. The time was noted down. Then the paste was filled in the mould, making its level with the top of the mould and the mould was rest on a non-porous plate and the block was placed in a moist room (27°C and 90% humidity). Now the mould was kept under the vicat apparatus. As per IS: 5513 : 1976, the weight of the vicat apparatus including the initial or final needle was 300 gm. and the weight of initial or final needle was 9 gm. Then after every five minutes, the initial setting time needle was slowly lowered to the surface of the paste and then released quickly and allowed to penetrate the paste. Now when the needle stopped above 5mm from the non-porous plate, the time was noted down and the initial setting time was determined by the following formula:

Initial setting time = difference the noted time

Then the initial setting time needle of vicat apparatus was replaced by the final setting time needle and then the needle was applied gently to the surface of the test block, the needles made a circular impression 'O' along with dot'.' at mid-point. Now after every five minutes, the test was carried out and when the needle failed to make circular impression upon the paste, the time was noted down and the final setting time was calculated by the following formula:

Final setting time = difference in noted time.

3.4.2.4: Hydration behavior of cement

10 gm. of both cement sample was taken in plastic mould and then 3 ml of water (w/c=0.3) was added to it and mixing was done. After well mixing, the mixture was kept in a humidity chamber. Now after the specific time period(1 hour, 1 day, 3 days, 7 days, 14 days and 28 days), the sample was taken out and then quenched under acetone solution to stop the hydration reaction of cement. After that, it was filtered through normal filter paper and also washing was done by the acetone. Then the sample was dried and stored under vacuum. Then the phases were determined by X-ray diffraction by using the previously stated procedure.

3.4.2.5: Determination of the non-evaporable water content (W_n)

10 gm. of both cement sample was taken in plastic mould and then 3 ml of water (w/c=0.3) was added to it and mixing was done. After well mixing, the mixture was kept in a humidity chamber. Now after the specific time period(1 hour, 3hours, 5 hours, 7 hours, 9 hours, 11 hours, 13 hours, 15 hours, 17 hours, 19 hours, 21 hours, 1 day, 3 days, 7 days, 14 days and 28 days), the sample was taken out and then quenched under acetone solution to stop the hydration reaction of cement. After that, it was filtered through normal filter paper and also washing was done by the acetone. Then the sample was dried and stored under vacuum. The L.O.I of the cement was determined by the previously stated procedure. Now, for the determination of the non-evaporable water content (W_n), the hydrated sample was ignited at 950°C for 1 hour in an electrical muffle furnace and the calculation was as follows:

W_n (%) = [100 x (dried weight of paste - ignited weight of paste)/ignited weight of paste] – L.O.I. of cement

3.4.2.6: La- chateleir expansion of the cement

The expansion was measured by the le- chateleir method (as per IS: 4031: Part 3 - 1988) by the following procedure:

100 gm. of cement sample was taken in a tray and then 0.78 times of normal consistency amount of water was mixed with it and mixed it well for 3-5 min. with trowels(as specified earlier) to make a paste. Then the light oiled mould (as per IS: 5514:1996) was placed on a lightly oiled glass sheet and filled with cement paste. Then the mould was covered with another piece of highly oiled glass sheet and also placed a small weight on this covering glass sheet and immediately submerged the whole assembly in water (27±2°C) for 24 hours. After that, the glass sheet was opened and the distance separating the indicator point was measured (L1). Further the mould was submerged into the water bath and then switched on the water bath. It was kept for 3 hrs. after water temperature attained the boiling point. Then the mould was removed from the water and allowed to cool and then the distance separating the indicator point was measured (L2). Now the expansion of cement was measured by the following formula:

Expansion of cement = L2-L1.

3.4.2.7: Compressive strength of the cement

The compressive strength (as per IS: 4031: Part 6-1988) was determined by the following procedure:

200 gm. of cement sample was taken in a tray and 600 gm. of standard sand (200 gm. of grade 1(size 1mm. – 2mm.), 200 gm. of grade 2(size 0.5 mm. – 1mm.) and 200 gm. of grade 3(size 90µ - 500 µ)) was mixed with the cement sample. Mixing was done properly by gauging trowel and then (P/4+3) x 8 ml (where P= normal consistency of cement) of water was added to it and mixed it for 3-5 min by the gauging trowel, as specified before. Then the mixture was taken into the frame mounted on coil spring carrying cube mould (as per IS: 10086: 1982) and after poking the sample into the mould, the vibrating machine was started. The vibrating machine was as per IS: 10080:1982 certified and it had mechanical compaction in 2 min (with 12000±400 vibration per minutes). The vibrating machine was run exactly for 2 minutes and it was automatically tripped. Then the cube mould was taken out from the machine and kept it in humidity chamber for 24 hours. After 24 hours, the cube was taken out from the mould and kept it in water. After the 1 day, one sample was taken out and the compressive strength was measured. Like that, the others sample was measured after 3 days, 7 days and 28 days. The compressive strength was determined by the following formula:

Compressive strength = load / area.

Chapter 4

Results & Discussions

CHAPTER 4

RESULTS & DISCUSSIONS

4.1: Characterization of raw mix

4.1.1: Decomposition Behavior

The decomposition behaviors for two types of raw mix were studied using thermo gravimetric and differential scanning calorimetric analysis.

Fig 4.1 and 4.2 shows the TG-DSC plot for two types of raw mix. TG curves show that there was a major weight loss in the temperature range 700 - 900°C. Weight losses of the raw mix were about 34.77 and 32.12 % for normal and slag composition respectively. The weight loss of slag composition was lower than other. This is due to the presence of lower amount of clay and limestone in the raw mix. In the DSC curve, the major endothermic peak at ~850°C was due to the decomposition of $CaCO_3$ [8].

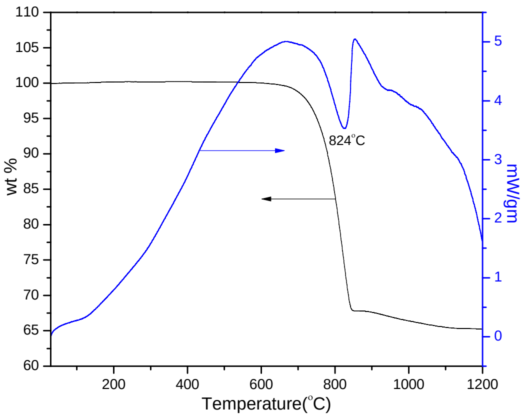


Fig 4.1: TG- DSC of the normal raw mix

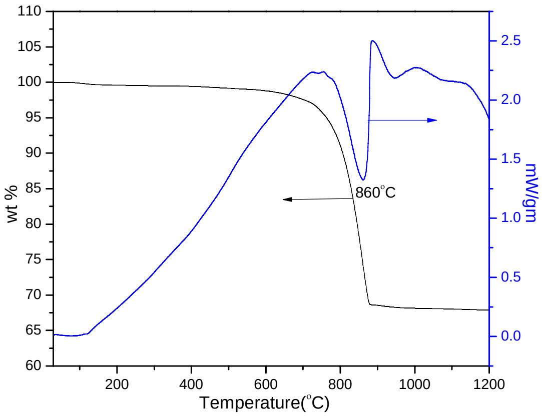


Fig 4.2: TG- DSC of the slag-raw mix

4.2: Characterization of Clinker

4.2.1: Phase evaluation during clinkerisation

To study the phase formation behavior, the raw mixes were fired at different temperatures ranging from 500-1500°C in a laboratory muffle furnace. After firing the material was quenched to room temperature.

The Fig 4.3 and 4.4 shows the XRD pattern of the two different raw mix, and those after heating at 600 and 700°C respectively. The major phase of the raw mix is calcite ($CaCO_3$). The Figure also shows that the presence of dolomite ($CaMg(CO_3)_2$) phase as the limestone contain dolomite impurities. Quartz phase was found in the raw mix. A little amount of aluminum silicate hydroxide ($Al_2O_3.2SiO_2.2H_2O$) phase was found which came from the laterite (Fig 3.6 and 3.7).

After calcination of the raw mix at 600°C, the material shows a new phase, aluminum silicate ($Al_2O_3.2SiO_2$) along with calcite, dolomite and quartz. Aluminum silicate was formed due to the decomposition of kaolinite clay[8]:

$$Al_2O_3.2SiO_2.2H_2O \longrightarrow Al_2O_3.2SiO_2 + 2H_2O$$

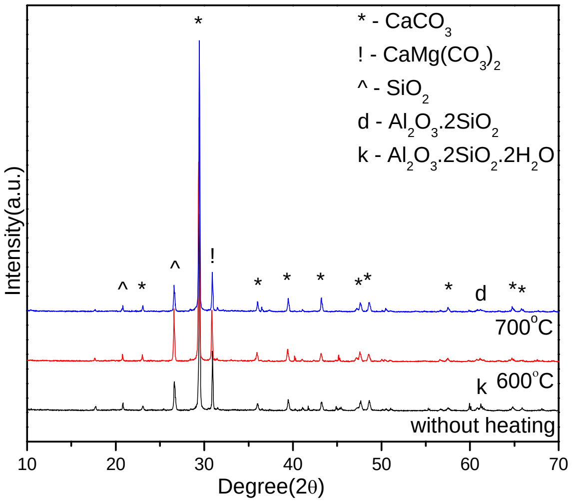


Fig 4.3: XRD pattern of the normal raw mix and that after heating at 600 and 700°C.

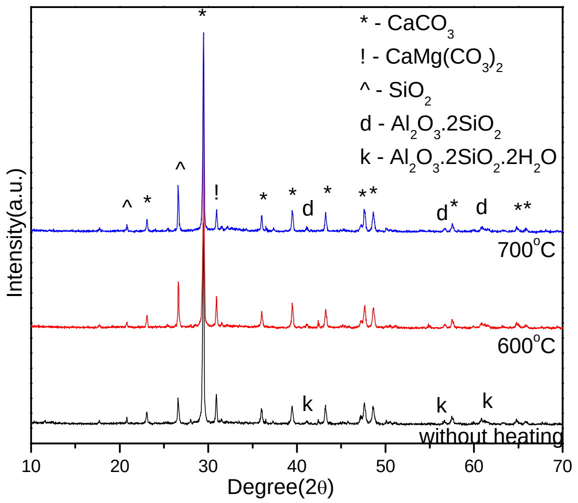


Fig 4.4: XRD pattern of the slag-raw mix and those after heating at 600 and 700°C.

The Fig 4.5 and 4.6 shows the XRD pattern of two raw mix after heating at 800, 900, 1000 and 1100°C respectively. The Fig 4.5 at 800°C heated raw mix indicates that the presence of calcite, quartz, calcia and spurrite ($2C_2S.CaCO_3$) and the disappearance of aluminum silicate phase and dolomite phase. So, the respective reactions [8] at this temperature are:

$$CaMg(CO_3)_2 \longrightarrow CaCO_3 + MgO + CO_2$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$5CaO + Al_2O_3.2SiO_2 \longrightarrow 2(2CaO.SiO_2) + CaO.Al_2O_3$$

$$2(2CaO.SiO_2) + CaCO_3 \longrightarrow 2(2CaO.SiO_2).CaCO_3$$

The Fig 4.6 shows the presence of similar phase found in the without slag raw mix fired at 800°C with increased amount of calcia and spurrite phase.

The Fig 4.5 contains calcia, calcite, spurrite and a new phase C_2F phase at 900°C. So, the respective reactions are:

$$2CaO + Fe_2O_3 \longrightarrow 2CaO.Fe_2O_3$$

The Fig 4.6 shows the presence of similar phases as present in raw mix without slag at 900°C.

In the Fig 4.5, calcia, calcite, quartz, C_2F and one new phase CF was formed at 1000°C. The reaction is as follows:

$$CaO + Fe_2O_3 \longrightarrow CaO.Fe_2O_3.$$

In the Fig 4.6 the XRD pattern shows that the presence of similar phases found in raw mix without slag fired at 1000°C with increased amount of spurrite phase and decreased amount of calcia and quartz phase.

The Fig 4.5 indicates that the presence of calcia, C_2F, CF, spurrite, calcite, quartz and a new phase $C_{12}A_7$ with increased amount of spurrite, C_2F, CF and decreased amount of calcia, quartz and calcite phase at 1100°C. The probable reaction is:

$$40CaCO_3+7(Al_2O_3.2SiO_2) \longrightarrow 12CaO.7Al_2O_3+14(2CaO.SiO_2) +40CO_2$$

The Fig 4.6 shows the presence of similar phases found in normal raw mix fired at 1100°C with decreased amount of quartz and calcia phase and increased amount of spurrite phase.

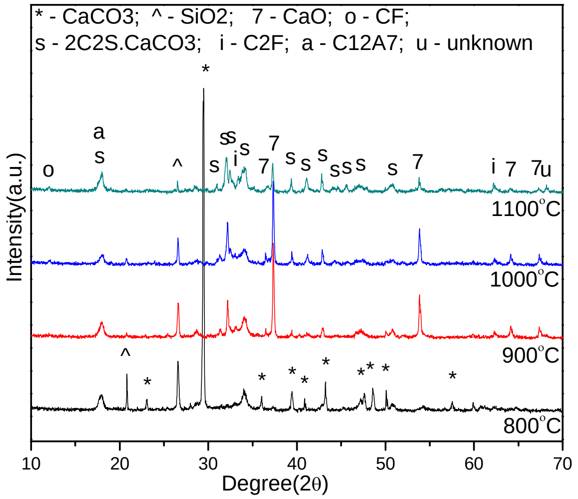


Fig 4.5: XRD pattern of the normal raw mix after heating at 800, 900, 1000 and 1100°C

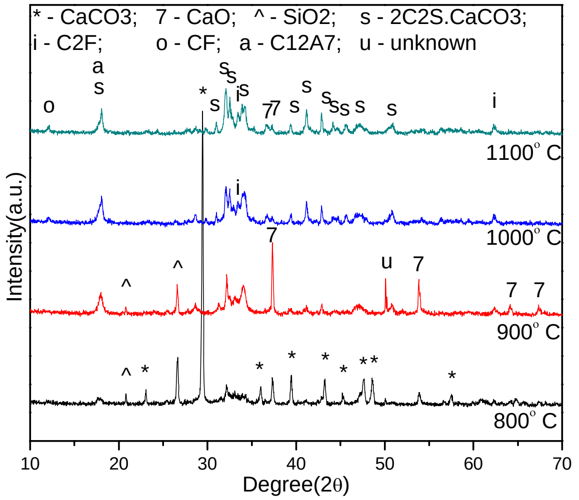


Fig 4.6: XRD pattern of the slag-raw mix after heating at 800, 900, 1000 and 1100°C.

The Fig 4.7 and 4.8 shows the XRD pattern for two types of raw mix after firing at 1200, 1300, 1350 and 1400 respectively. The Fig 4.7 shows the presence of C_2S, calcia, C_2F, CF, $C_{12}A_7$ phase and also the complete disappearance of the calcite and quartz phase and increased amount of C_2S phase and decreased amount of spurrite phase at 1200°C. So the probable reaction is:

$$2(2CaO.SiO_2).CaCO_3 \longrightarrow 2(2CaO.SiO_2) + CaO + CO_2$$

The Fig 4.8 indicates the presence of similar phases present in normal raw mix fired at 1200°C with increased amount of C_2S and calcia phase due to the above reaction.

The Fig 4.7 shows the presence of C_2S, C_2F, calcia, CF and three new phases γ-C_2S, C_3A and little amount of C_3S with disappearance of $C_{12}A_7$ phase which is converted to C_3A phase[8] and due to formation of γ-C_2S, dusting phenomena occurred at 1300°C. So the probable reaction [8] is:

$$12CaO.7Al_2O_3 + 9CaO \longrightarrow 7(3\ CaO.Al_2O_3)$$

$$2CaO.SiO_2 + CaO \longrightarrow 3CaO.SiO_2$$

$$7CaCO_3 + Al_2O_3.2SiO_2 \longrightarrow 2(3CaO.SiO_2) + CaO.Al_2O_3 + 7CO_2$$

$$\alpha`\text{-}2CaO.SiO_2 \longrightarrow \gamma\text{-}2CaO.SiO_2$$

The Fig 4.8 shows the presence of similar phase except the γ-C_2S phase present in normal raw mix fired at 1300°C with increased amount of C_3S phase and C_3A phase.

The Fig 4.7 indicates the presence of C_3S, C_2S, C_3A, calcia and a new phase C_4AF with increased amount C_3S and disappearance of C_2F and CF phase at 1350°C. So, the probable reaction is as follows:

$$C_2F + CF + CaO.Al_2O_3 \longrightarrow C_4AF$$

The Fig 4.8 indicates the presence of similar phases present in normal raw mix at 1350°C with increased amount of C_3S and C_3A phase.

The Fig 4.7 shows the presence of C_3S, C_2S, C_3A, C_4AF and phase at 1400°C.

The Fig 4.8 shows the similar phases found in normal raw mix fired at 1400°C with increased amount of C_3S and C_3A phase and decreased amount of C_2S phase.

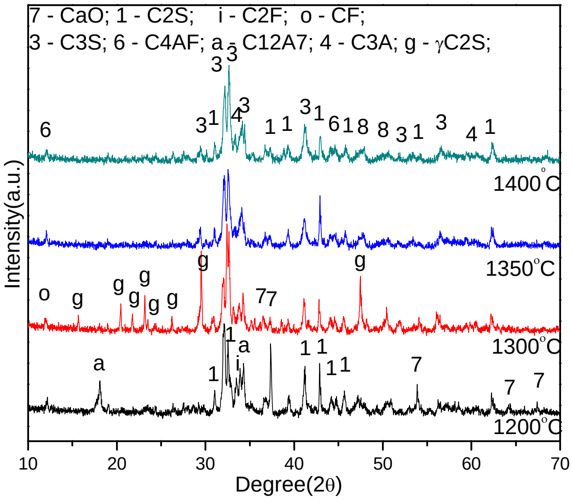


Fig 4.7: XRD pattern of the normal raw mix after heating at 1200, 1300, 1350 and 1400°C

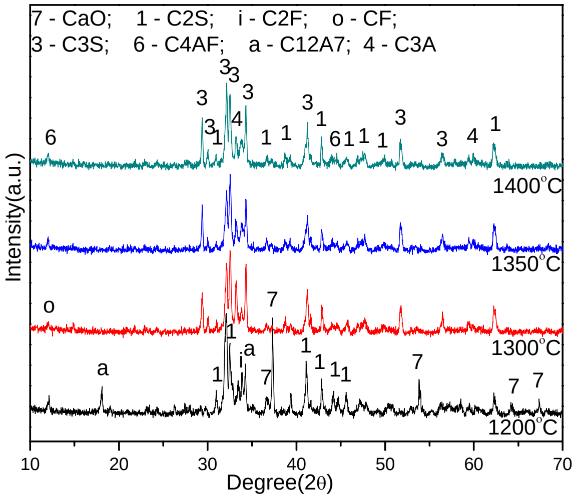


Fig 4.8: XRD pattern of the slag-raw mix after heating at 1200, 1300, 1350 and 1400°C.

The Fig 4.9 and 4.10 shows the XRD pattern of the two types of raw mix heating at 1450, 1500 respectively. The Fig 4.9 shows the presence of C_3S, C_2S, C_3A and C_4AF phase at 1450°C.

The Fig 4.10 indicates the presence of similar phases as present in the normal raw mix fired at 1450°C with increased amount of C_3S and C_3A phase and decreased amount of C_2S phase.

The Fig 4.9 shows the presence of C_3S, C_2S, C_3A and C_4AF phase at 1500°C.

The Fig 4.10 indicates the presence of similar phases at 1500°C as present in the normal raw mix fired at 1450°C with increased amount of C_3S and C_3A phase and decreased amount of C_2S phase.

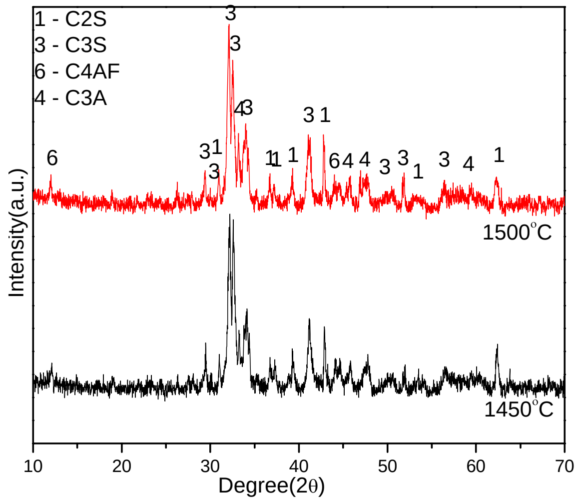


Fig 4.9: XRD pattern of the normal raw mix after heating at 1450 and 1500°C

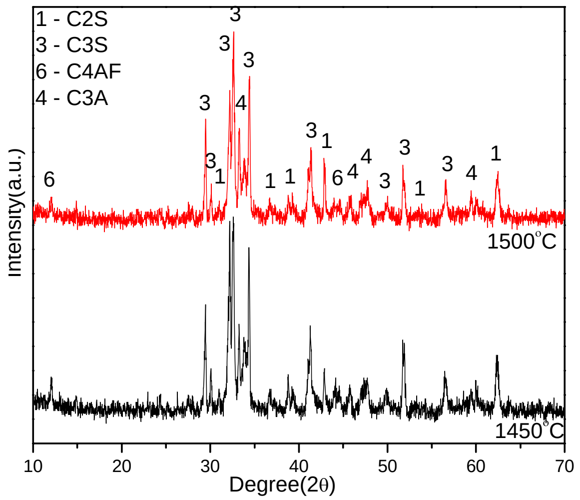


Fig 4.10: XRD pattern of the slag-raw mix after heating at 1450 and 1500°C.

4.2.2: Free lime content in clinker:

Fig 4.11 indicates the free lime content (wt. %) for both clinker firing at 1300, 1350, 1400, 1450 and 1500 °C. The free lime (unreacted lime) indicates the burnability parameter of the raw mix. For the normal clinker, the free lime content decreased with increase in temperature. According to the Taylor et al [24], aluminates and ferrites begin to melt and free lime combined with the free silica and belite (C_2S) to form alite (C_3S) above 1300°C during clinkerisation process. The free lime content is lowered in case of the slag clinker than the normal clinker which is due to the increase in C_3S content in slag clinker. So, the slag helps in clinkerisation by lowering the liquid formation temperature.

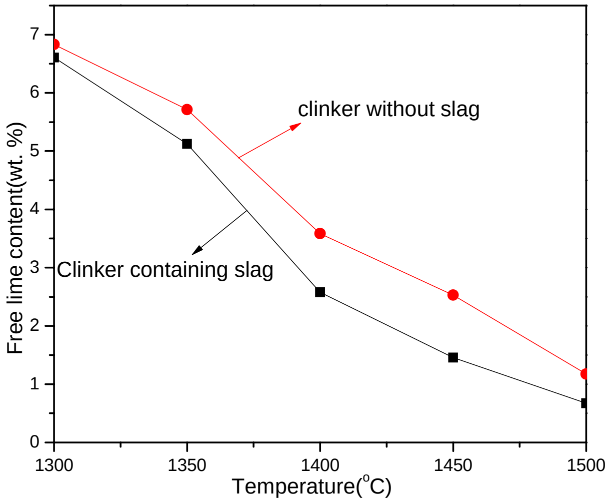


Fig 4.11: Free lime content of the normal clinker and slag clinker at 1300 - 1500°C

4.2.3: Characterization of rotary kiln produced clinker

4.2.3.1: Chemical constituents of the rotary kiln produced clinker

The chemical analysis of the rotary kiln produced clinker is shown in the Table 4.1.

Table 4.1: Percentage amount of chemical constituents for normal clinker and slag clinker

Constituents(as per design)	Normal clinker	Slag clinker
L.O.I.	0.14	0.44
SiO_2 (21.79%)	21.22	21.2
Al_2O_3 (5.36%)	5.45	6.05
Fe_2O_3 (4.12%)	4.20	3.6
CaO (63.11%) (Free-CaO)	63.09 (1.84)	63.56 (1.8)
MgO (4%)	3.83	3.44
L.S.F.(0.9)	0.92	0.922
S.M.(2.3)	2.2	2.2
A.M.(1.3)	1.3	1.68

The chemical composition differs slightly from the designed one. In the design, the CaO is maintained at 63.11%, but in the case of normal clinker and slag clinker, it is 63.09% and 63.56% respectively. In the case of SiO_2 also, the designed parameter is 21.79%. But in practical, the normal clinker and slag clinker contains 21.22% and 21.2% respectively. In the design, the Al_2O_3 is maintained at 5.36%, but in the normal clinker and slag clinker, the percentage of Al_2O_3 is 5.45% and 6.05% respectively. In case of Fe_2O_3, the designed parameter is 4.12%, but in practically, the normal clinker and slag clinker contains 4.2% and 3.6% Fe_2O_3 respectively. For the MgO, the designed parameter is 4%, but in the normal clinker and slag clinker, the percentage of MgO is 3.83% and 3.44%. Also, the normal clinker contains 1.84% of free CaO and slag clinker contains 1.8% of free CaO. L.S.F. value for the slag clinker is 0.922 which is slightly high from the designed value. But this value is within the preferable range (see Table 2.1) and for the normal clinker is 0.92. For S.M. and A.M values are also slightly varied from the designed value. But all are within the preferable range.

4.2.3.2: Phase evaluation of the rotary kiln produced clinker

The phase analysis of the rotary kiln produced normal clinker and slag clinker are shown in Fig: 4.12 and Fig: 4.13 respectively.

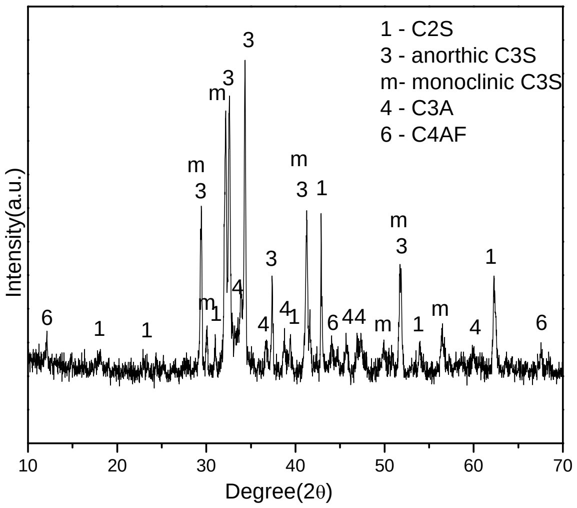


Fig 4.12: XRD pattern for the rotary kiln produced normal clinker

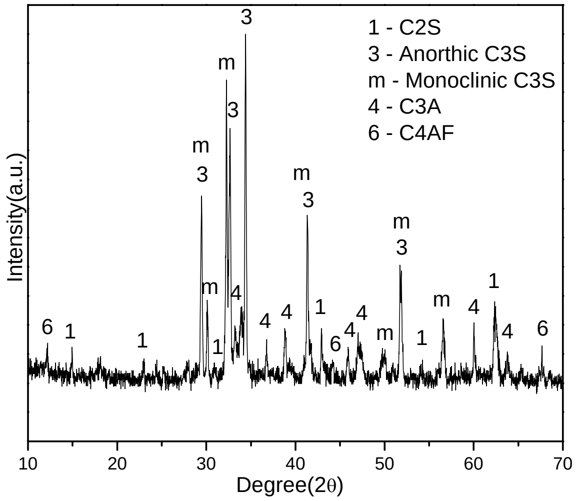


Fig 4.13: XRD pattern for the rotary kiln produced slag clinker

Phases are identified to be Anorthic C_3S, Monoclinic C_3S, C_2S, C_3A and C_4AF present in the normal clinker. The stabilization of monoclinic and anorthic C_3S phases are due to the impurity present in the system [1]. Figure 4.13 shows the presence of similar phases found in normal clinker with increased amount of C_3S and C_3A phase and decreased amount of C_2S phase.

4.2.3.3: Phases present in the rotary kiln produced clinker

The cementing phases which are expected to be formed after complete reaction can be calculated through Bogue calculation. Table 4.2 shows the quantitative phases obtained by bogue calculation. The Table shows around 50% C_3S and 15 % C_2S. However, the phase formation does not obey the equilibrium condition in actual rotary kiln production. The rotary kiln produced clinkers were analyzed for their semi quantitative phase content using X'Pert highscore software on their XRD pattern. Table 4.3 shows semi quantitative analysis of the two clinkers. It is very much difficult to quantify cement phases through XRD analysis without using internal standard. No internal standard was used in this analysis as it is very difficult to prepare to same. However, an idea about the major phases can be get from semi quantitative XRD analysis, the analysis shows that there was higher amount of C_3S formation in slag containing clinker. This may be due to the lowering of clinkerising temperature by the slag which promotes more liquid phase formation and associated higher C_3S formation.

Table 4.2: Phases present in the clinker as per Bogue calculation:

Phases present	Normal clinker	Slag clinker
C_3S	51.5	53
C_2S	28.4	26.1
C_3A	7.3	9.9
C_4AF	12.8	11.0

Table 4.3: Phases present in the clinker as per semi quantitative XRD phase analysis :

Phases present	Normal clinker	Slag clinker
C_3S	35	45
C_2S	54	45
C_3A	7	5
C_4AF	4	5

4.3: Characterization of the Portland cement

4.3.1: Setting time of the cement

The setting time of the cement is shown in Table 4.4. The initial and final setting time of both the cement were similar.

Table 4.4: The initial setting time (IST) and final setting time (FST) of the OPC cement containing $(PC)_{\text{without slag}}$ and $(PS)_{\text{slag}}$

Cement	IST(min)	FST(min)
Cement containing $(PC)_{\text{without slag}}$	100	250
Cement containing $(PS)_{\text{slag}}$	90	230

4.3.2: Phase formation behavior of the cement hydration product

The XRD pattern of the cement hydration product is shown in Fig 4.14 and Fig 4.15 for normal and slag clinker cement:

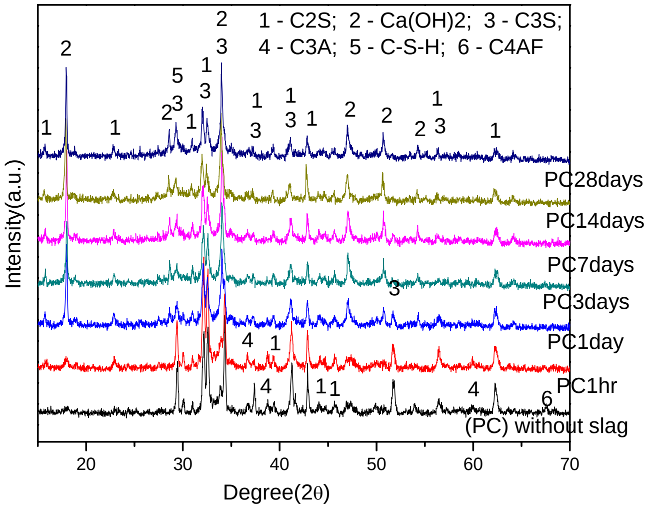


Fig 4.14: The XRD pattern of the cement (using normal clinker) hydration product for $(PC)_{\text{without slag}}$ and for different time of hydration

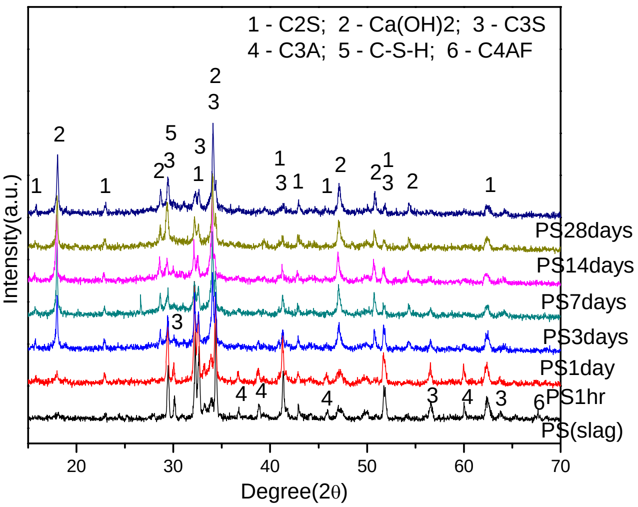


Fig 4.15: XRD pattern of the cement (slag clinker) hydration product for $PS_{(slag),}$ and for different time of hydration.

Both the figure show the presence of C_3S, C_2S, C_3A, C_4AF phases in normal and slag clinker cement.

After 1 hr. hydration, the major change was the formation of $Ca(OH)_2$ phase and decrease in C_3A and C_4AF content for both the cement. The $Ca(OH)_2$ formation may be due to the following reaction:

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH$$

The C-S-H phase is not found in the Figure due to the amorphous nature of the C-S-H . [5]

After 1 day hydration, the major change was the increase in $Ca(OH)_2$ content and simultaneous decrease in C_3S, C_3A content for both the cement.

After 3 days hydration, there was no C_3A phase present and as expected $Ca(OH)_2$ increased and C3S decreased for both the cases.

After 7 days hydration, the major finding was formation of crystalline tobermorite (C-S-H) new phase due to the nucleation and grain growth of C-S-H phase.

After 14 days hydration, similar results were obtained that is, C_3S decreased. It has been found that the hydration of C_2S was started [1] is per reaction:

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH$$

After 28 days hydration the major finding was the disappearance of the C_3S phase. There was a substantial amount of C_2S phase in both the cement even after 28 days hydration. So, both the cement follows typical cement hydration behavior.

4.3.3: The non–evaporable water content in the cement hydration product

The non-evaporable water content in the cement hydration product is shown in the Fig 4.16.

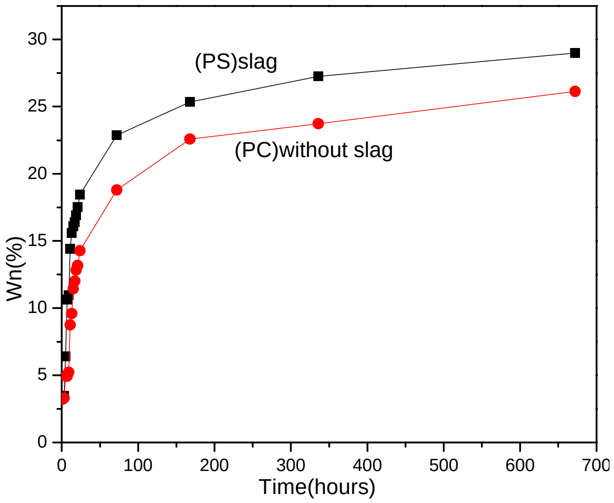


Fig 4.16: The non-evaporable water content in the hydrated sample of the $(PC)_{\text{without slag}}$ and $(PS)_{\text{slag}}$

The Fig shows that the amount of non-evaporable water is higher in case of slag-clinker cement which indicates that the hydration reaction rate or degree of hydration is more in case of slag-clinker cement due to the presence of higher amount of C_3S phase in the cement.

4.3.4: La chateleir expansion of the cement

The La chateleir expansion results of two cements are shown in the Table 4.5.

Table 4.5: The La Chateleir expansion for the $(PC)_{\text{without slag}}$ and $(PS)_{\text{slag}}$

Cement	Expansion(mm)
$(PC)_{\text{without slag}}$	2
$(PS)_{\text{slag}}$	3.5

Both the cement shows a similar very nominal expansion and they should be considered very sound cement

4.3.5: Compressive strength of the cement

The variations of compressive strength with different aging time for two types of cement mortar are shown in Fig 4.17:

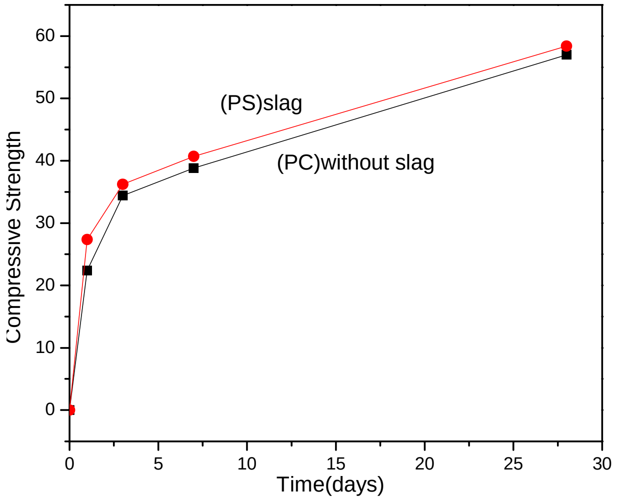


Fig 4.17: The compressive strength for the $(PC)_{\text{without slag}}$ and $(PS)_{\text{slag}}$

The figure shows a similar increase in strength with time for both the cases. A small higher strength was found in slag clinker cement compared to normal cement which may be due to the presence of higher amount of C_3S in slag clinker cement.

Chapter 5

Summary

CHAPTER 5

SUMMARY

5.1 Summary

In the present study, blast furnace slag has been used successfully as a raw material for the manufacturing of Portland cement clinker. From the detailed investigation and the results obtained, the following points may be summarized:

1. Major weight loss in cement raw-mix has been occurred at the temperature range of 700 - 900°C
2. The clinkerisation reaction was quicker when slag was used in the raw mix. This was due to the high reactivity of the slag.
3. The free lime content in the clinker can be decreased by using slag in the raw-mix which is another beneficial point.
4. The C_3S phase formation was higher in amount in case of slag-clinker due the early formation of liquid phase in presence of slag.
5. The hydration rate of slag-clinker was slightly higher than other due to the presence of higher amount of C_3S.
6. The compressive strength was slightly high in case of slag containing cement due to the presence of higher amount of C_3S phase.

5.2: Scope of future work

In the present investigation, the amount utilization of slag as a raw material was very low about 3 percent.

So, there is a enough future scope to increase the amount utilization of slag by changing raw material (For example, in this case study the clay and laterite source must be changed to accommodate more slag in the raw mix).

Chapter 6

References

CHAPTER 6

REFERENCES

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