CHAPTER I

INTRODUCTION
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1.1 History of Cement

The word 'cement' is used to define adhesive substances and is presumed to have been derived from Latin 'caementum'. Cements are used primarily to bind together bricks, stones and other materials employed in construction. The history of development of cement from the prehistoric days is shown in Fig.1.1 (1).

It appears from the figure that there was no human activity of construction prior to and during the palaeolithic age and the first concept of construction was introduced by man in the neolithic age which began about eight thousand years ago when he started enclosing space with juxtaposition of stone blocks, animal skin, natural wood etc. These structures were devoid of any binder. About five thousand and five hundred years ago, at the advent of the bronze age, there was a chance discovery that the baking of wet clay would make it hard and could give rise to moulded shapes of some use like bricks. Contemporaneous with this, man came to learn the use of clay as binder. Thereafter, gradually with the progress of time, the binding properties of many other materials like lime, air polymerizing vegetable oil, lime pozzolona mixes were made use of in the construction activities till the eve of the age of revolutionary industrial progress which commenced in the middle of the nineteenth century (1). The discovery of lime-based binder in the annals was much
Fig. 1.1 History of cement: Change of cement characteristics with time.
belated and followed the discovery of the art of brick making. The gradual development of binders or cements, since the days of clay-binder, culminated in the introduction of the first generation of Portland cement by Joseph Aspdin in 1824. After this event, over the past one hundred and seventy five years, the developmental trends in cement applications branched off in the directions of obtaining high ultimate strength, higher early strength, greater durability and more effective conservation of materials used in constructional concrete (2-5).

1.2. Portland Cement

Portland cement is a hydraulic material which sets and hardens as a result of chemical reaction with water to form a hard rock like mass when mixed with appropriate amount of water and continues to harden if stored under water after setting. Portland cement is obtained by grinding Portland cement clinkers together with adequate quantity of gypsum to a very fine powdery state. Clinkers are produced by burning a mixture of an argillaceous material, such as clay, and a calcareous material, generally lime stone, at a temperature of 1400 to 1500° C (3,5). During burning, lime is generated from lime stone which subsequently combines with silica, alumina, iron oxide etc. derived from the argillaceous material to produce a number of phases. These phases together impart the characteristic properties of Portland cement.
1.2.1. Composition of Portland Cement

The general composition of Portland cement is 67% CaO, 22% SiO₂, 5% Al₂O₃, 3% Fe₂O₃ and 3% other components like MgO, SO₃, free lime etc. (5). The MgO content is usually limited to 3-5% (3). It occurs as periclase and its content beyond this amount may impart unsoundness to the cement causing expansion in hardened concrete and decrease its durability. SO₃ beyond 2.5-4% can also lead to delayed expansion. Alkali (Na₂O+K₂O) may react with aggregate and its content is limited to 0.6% equivalent of Na₂O (3,5).

1.2.2. Phases in Clinkers and Their Formation

Clinkers are composed of phases like tricalcium silicate, also called alite (3CaO. SiO₂ or C₃S), dicalcium silicate, also called belite (2CaO. SiO₂ or C₂S), tricalcium aluminate, also called the aluminate phase (3CaO. Al₂O₃ or C₃A), tetracalcium alumino-ferrite, also called the ferrite phase (4CaO. Al₂O₃. Fe₂O₃ or C₄AF) together with many other minor phases like alkali metal oxides, magnesium oxide, uncombined free lime etc. (3,5).

The formation of these phases during burning is a complex chemical process and is influenced by numerous factors like temperature, chemico-mineralogical characteristics of the raw materials, their proportions, particle sizes etc.(3,5-10). As a result, the proportion of various phases in the clinkers and hence
The properties of cements vary from plant to plant depending upon the raw materials used and the process parameters adopted.

The reactions leading to the formation of different phases in Portland cement clinker may be depicted as follows (6,8,11).

Clay \((x \text{Al}_2\text{O}_3 \ y \text{Si}_2 \ z \text{H}_2\text{O})\) \(\xrightarrow{660-900^\circ\text{C}}\) \(x \text{Al}_2\text{O}_3 + y \text{Si}_2 + z \text{H}_2\text{O}\)

Limestone \((\text{CaCO}_3)\) \(\xrightarrow{950^\circ\text{C}}\) \(\text{CaO} + \text{CO}_2\)

\(2\text{CaO} + \text{Si}_2 \xrightarrow{1100^\circ\text{C}}\) \(2\text{CaO}\cdot\text{Si}_2\) \((\text{C}_2\text{S})\)

Spurrite \(5\text{CaCO}_3 + 2\text{Si}_2 \xrightarrow{1100^\circ\text{C}}\) \((2\text{CaO} \cdot \text{Si}_2)_2 \text{CaC}_0 + \text{CO}_2\)

\(2(2\text{CaO} \cdot \text{Si}_2)_2 + \text{CaC}_0 \xrightarrow{1400^\circ\text{C}}\) \(3\text{CaO} \cdot \text{Si}_2 + 2\text{CaO}\cdot\text{Si}_2 + \text{CO}_2\)

Gehlenite \(2\text{CaO} \cdot \text{Si}_2 + \text{CaO} \xrightarrow{1400^\circ\text{C}}\) \(3\text{CaO} \cdot \text{Si}_2\) \((\text{C}_3\text{S})\)

\(\text{CaO} + \text{Al}_2\text{O}_3 \xrightarrow{<1000^\circ\text{C}}\) \(\text{CaO} \cdot \text{Al}_2\text{O}_3\) \((\text{CA})\)

\(\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{CaO} \xrightarrow{}\) \(2\text{CaO} \cdot \text{Al}_2\text{O}_3\) \((\text{C}_{2\text{A}})\)

\(2\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Si}_2 \xrightarrow{}\) \(2\text{CaO} \cdot \text{Al}_2\text{O}_3\cdot\text{Si}_2\) \((\text{C}_{2\text{AS}})\)

Oehlenite \(12\text{CaO} + 7\text{Al}_2\text{O}_3 \xrightarrow{}\) \(12\text{CaO} \cdot 7\text{Al}_2\text{O}_3\) \((\text{C}_{12\text{A}_7})\)

\(5\text{CaO} + 3\text{Al}_2\text{O}_3 \xrightarrow{}\) \(5\text{CaO} \cdot 3\text{Al}_2\text{O}_3\) \((\text{C}_{3\text{A}_3})\)

\(3\text{CaO} + \text{Al}_2\text{O}_3 \xrightarrow{}\) \(3\text{CaO} \cdot \text{Al}_2\text{O}_3\) \((\text{C}_3\text{A})\)
CaO + Fe₂O₃ \rightarrow \text{CaO, Fe₂O₃ (CF)}

2CaO + Fe₂O₃ \rightarrow 2\text{CaO, Fe₂O₃ (C₂F)}

3CaO \cdot \text{Al₂O₃} + \text{CaO, Fe₂O₃} \rightarrow \text{CaO Al₂O₃, Fe₂O₃ (C₄AF)}

C₅A₃ + 3\text{C₂F} + C \rightarrow 3\text{C₄AF}

2\text{C₂F} + \text{Al₂O₃} + 2\text{CaO} \rightarrow \text{C₆AF₂}

\text{C₆AF₂} + \text{Al₂O₃} + 2\text{CaO} \rightarrow 2\text{C₄AF}

\text{C₄AF + Al₂O₃ + 2CaO} \rightarrow \text{C₆A₂F}

Some other intermediate compounds and side reactions have also been reported (2,3,5). All these compounds crystallize usually with some impurities entrapped in them.

1.2.3. Characteristics of the Phases

In cement clinkers, the four major phases are present in various proportions. Each of them impart special property to the resultant Portland cement (3,5).

The alite phase constituting 50-70% of the clinker, reacts readily with water and is the most important constituent for strength development at ages up to 28 days. It is tricalcium silicate, C₃S, modified in composition and crystal structure by incorporation of foreign ions like Mg²⁺, Al³⁺, Fe³⁺. The belite phase (15-30%) reacts slowly with water and contributes substantially to the strength at later age, after 28 days. It is dicalcium silicate, C₂S, modified by incorporation of foreign...
ions. The aluminate phase constituting 10-15 % of the clinker reacts rapidly with water and causes undesirable rapid setting unless a set-controlling agent, such as gypsum, is added. It is tricalcium aluminate, C₃A, substantially modified in composition and sometimes in structure by incorporation of foreign ions like Si⁺⁴, Fe⁺³, Na⁺, K⁺ etc. The ferrite phase, constituting 5-15% of the clinker, has variable rate of reaction with water. It is tetracalcium alumino ferrite C₄AF, substantially modified by variation of Al/Fe ratio and incorporation of foreign ions (2,3).

The most important physical properties of Portland cements are their setting times, the values of heat of hydration and the strength characteristics. Each of these properties may be varied by varying the compositions and quantities of different phases in the cement. Cement for a particular purpose must possess certain specific properties (5).

1.2.4. Types of Portland Cement

Several types of Portland cement are manufactured to meet specific requirements of different constructions. As per U.S. classification, Type-I, or Ordinary Portland Cement (O.P.C.) in U.K. and India, is the common Portland cement used in general purpose constructions which hardens to almost full strength in about four weeks time. Type-II is a modified form of O.P.C., which has a moderate heat of hydration and is characterized by higher C₂S/C₃S ratio. Type-III is rapid hardening Portland cement containing a higher percentages of C₃S and C₃A phases and ground to a much finer state. Type IV is a very low heat cement...
containing low percentages of C\textsubscript{3}S and C\textsubscript{3}A. Type V is a sulfate-resisting Portland cement containing a low percentage of C\textsubscript{3}A but higher amount of C\textsubscript{4}AF (5).

1.2.5. Setting and Hardening of Cement

When cement is mixed with water and allowed to stand, it absorbs water and sets to become hard and very resistant to pressure. Setting and hardening of cement occur through a series of very complex chemical reactions involving almost every component present in it. The setting times of different cements vary from a few minutes to several hours. The process of setting is over within about twenty four hours from mixing cement with water. The subsequent process of hardening continues and requires a period of two to three weeks or even more (3,5).

During setting and hardening, the various silicate and aluminate phases present in cement form hydrates (3). This occurs initially on the surface of the fine cement grains.

\[
\begin{align*}
C_3S + xH_2O & \rightarrow 3CaO.SiO_2.xH_2O \\
C_2S + xH_2O & \rightarrow 2CaO.SiO_2.xH_2O \\
C_3A + 6H_2O & \rightarrow 3CaO.Al_2O_3.6H_2O \\
C_4AF + 6H_2O & \rightarrow 3CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3
\end{align*}
\]

The hydrated compounds form gels with excess of water. Certain anhydrous silicates and aluminates present in cement also undergo hydrolysis releasing
Ca(OH)$_2$, Al(OH)$_3$ and silica gel. The hydrolysis reaction may progress further under suitable conditions to eventually leave a solid composed only of hydrated silica, all the lime having been removed:

\[
\begin{align*}
3\text{CaO} \cdot \text{SiO}_2 + \text{H}_2\text{O} &\rightarrow 2\text{CaO} \cdot \text{SiO}_2 + \text{Ca(OH)}_2 \\
2\text{CaO} \cdot \text{SiO}_2 + \text{H}_2\text{O} &\rightarrow \text{CaO} \cdot \text{SiO}_2 + \text{Ca(OH)}_2 \\
\text{CaO} \cdot \text{SiO}_2 + \text{H}_2\text{O} &\rightarrow \text{Ca(OH)}_2 + \text{Si(OH)}_4 \\
3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} &\rightarrow 3\text{Ca(OH)}_2 + 2\text{Al(OH)}_3
\end{align*}
\]

The gels gradually lose water, partly by evaporation and partly by forming hydrates of the anhydrous core of the cement grain. Due to drying of the gels, the surface hardens and the core becomes progressively hydrated. This is followed by crystallization of hydrated salts and Ca(OH)$_2$ in silica gel. The crystals interlace with silica grains and impart strength to the hardening mass. Al(OH)$_3$ formed also fill the interstices and helps in the process of hardening (5).

1.2.6. Disadvantages of Portland Cement

Ordinary Portland cement is used as a general purpose construction material. But it has several ill-effects on long term durability of the mortar or concrete as indicated below (12,13).

1. Water solubilizes and removes calcium hydroxide, a product of cement hydration, present in cement paste. Calcium hydroxide constitute 20-25% of the Portland cement paste and its removal increases the permeability of the concrete and causes its destabilization. The cement composition plays an important role in
determining the permeability. The lower the amount of CaO in the cement, the lower is the amount of leachable lime and hence lesser is the permeability of the concrete.

(2) Water containing CO$_2$ can also solubilize Ca(OH)$_2$ forming bicarbonate.

$$2\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{Ca(HCO}_3\text{)}_2$$

Carbonic acid can also attack silicates, aluminates and ferrites. The attack depends on the permeability of the concrete mass.

(3) Water containing calcium sulphate deteriorates concrete. It reacts with calcium aluminate hydrate forming ettringite.

$$3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O} + 3\text{CaSO}_4 + 26\text{H}_2\text{O} \rightarrow 3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O}.3\text{CaSO}_4.32\text{H}_2\text{O}$$

The reaction forming ettringite is accompanied by considerable volume change. Ettringite crystallizes in the form of bushes made of sticks or needles which exert an expansive stress in the preferential growth direction. The sulphate attack is deeper and quicker as the permeability and porosity of the concrete have increased.

MgSO$_4$ and Na$_2$SO$_4$ present in water attack not only aluminates but also free lime and calcium silicate as shown below:

$$\text{Ca(OH)}_2 + \text{MgSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} + \text{Mg(OH)}_2$$

$$3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O} + 3\text{MgSO}_4 + 6\text{H}_2\text{O} \rightarrow 3(\text{CaSO}_4.2\text{H}_2\text{O}) + 2\text{Al(OH)}_3 + 3\text{Mg(OH)}_2$$
\[
5\text{Ca(OH)}_2 + 3\text{CaO}.2\text{SiO}_2.3\text{H}_2\text{O} + 8\text{MgSO}_4 + 24\text{H}_2\text{O} \rightarrow 8(\text{CaSO}_4.2\text{H}_2\text{O}) + 2(4\text{MgO}.\text{SiO}_2.8\text{H}_2\text{O})
\]

\[
3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O} + 3(\text{CaSO}_4.2\text{H}_2\text{O}) + 20\text{H}_2\text{O} \rightarrow 3\text{CaO}.\text{Al}_2\text{O}_3.\text{CaSO}_4.32\text{H}_2\text{O}
\]

(4) Chloride ion, if comes in contact with concrete, can cause serious damage to reinforcing agent. It reduces passivation of steel caused by alkaline environment. Steel corrosion results in formation of voluminous iron oxide hydrates which cause stresses capable of breaking the concrete. Chloride attack on concrete may be minimized by reducing the porosity and permeability.

(5) Reaction between reactive aggregates (some forms of silica, such as opal, chalcedony and tridymite) and the alkali of cement may occur. The reaction results in formation of an alkaline silica gel which tend to absorb water and cause expansion. The expansion causes internal stress that cracks the concrete when it exceeds the mechanical strength. This can be avoided if the cement contain less than 0.6% \(\text{Na}_2\text{O}\) equivalent alkali.

1.3. **Blended Cements**

Many of the disadvantages of ordinary Portland cement may be overcome by using blended cements. Porosity and permeability of concrete are the roots of many such disadvantages and are results of solubilizing \(\text{CaO}\) by water. These may be lessened by decreasing the \(\text{CaO}\) content of the cement. \(\text{CaO}\) content of ordinary Portland cement is about 67% and it can be decreased by blending the cement with other suitable materials. Modern trend in selecting cement for various purposes
is towards composite or blended cements. Many such cements have emerged and have been accepted for their specific characteristics and applications (13-15). These cements contain less than 95% Portland cement clinker and the rest comprises of various quantities of additives together with gypsum.

1.3.1. Mineral Admixtures

The additives used in blended cements are also called mineral admixtures or secondary additions or mineral additions. A variety of naturally occurring substances, either in raw or in calcined state, and many industrial by-products are used as mineral admixtures for making composite or blended cements (13-16).

Blending materials or mineral admixtures used in blended cements may be broadly categorized as latent hydraulic cements and pozzolanic materials (5). Besides these, finely divided materials like limestone, CaCO₃, which are neither hydraulic nor pozzolanic, are also used for blending in various proportions with Portland cement. Such additions are classed as fillers (16).

1.3.1.a. Latent Hydraulic Cements

These are substances comprising mostly of CaO, SiO₂ and Al₂O₃. Normally these are non-hydraulic in nature but in presence of activators (alkaline) they behave as a hydraulic cements. Blast furnace slag is an example of latent hydraulic cementitious admixtures. During production of cast iron, it is formed as a liquid at 1350-1500°C. On cooling rapidly to below 800°C, it forms a glass which is a latent hydraulic material. Blast furnace slag essentially comprises of CaO, SiO₂ and
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AI\textsubscript{2}O\textsubscript{3} with trace to small amounts of other oxides like MgO, Na\textsubscript{2}O, K\textsubscript{2}O, P\textsubscript{2}O\textsubscript{5}, etc. This non-hydraulic material turns hydraulic when crushed and mixed with water and small amounts of other substances like Ca(OH)\textsubscript{2}, CaSO\textsubscript{4}, 2H\textsubscript{2}O, alkali etc. When mixed with Portland cement, it is activated by the lime liberated during hydration of the cement.

1.3.1.b. Pozzolana

Pozzolana is defined as a silicious or silicious and aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. The name has been derived from Pozzoli or Pozzuoli, a locality in Italy, in the neighbourhood of which the Romans discovered deposits of volcanic origin that possessed such properties (3).

Natural pozzolana is defined as either raw or calcined natural material that has pozzolanic properties. Examples of natural pozzolana are volcanic ash or pumice, opaline chert and shale, tuffs and some diatomaceous earths etc.

Pozzolanas or pozzolanic materials are rich in SiO\textsubscript{2} and often in Al\textsubscript{2}O\textsubscript{3}, but low in CaO. They are sufficiently reactive and when mixed with water and CaO they produce C-S-H at ordinary temperature and, thereby, act as hydraulic cements. If these materials contain Al\textsubscript{2}O\textsubscript{3}, they also form CA and C-A-H. As these materials
are low in CaO, this compound must be supplied with stoichiometric quantity for proper progress of the reaction. In a blended or composite cement it is provided by the Portland cement in the form of calcium hydroxide produced during hydration. As a result, the C/S ratio of the C-S-H formed becomes low (3,5).

1.3.2. Factors Effecting Pozzolanic Activity

The pozzolanic activity depends on the molecular structure and the amount of the silica present in the pozzolana (5). Generally, amorphous silica reacts with calcium hydroxide and alkalies more rapidly than does silica in the crystalline form. Further, the larger the size of the particles or the lower the surface area, the less rapid is the rate of reaction. Thus, the chemical composition of a pozzolana does not clearly determine its ability to combine with calcium hydroxide and alkalies. Volcanic glasses and zeolitic tuffs were proved to be good pozzolanas long ago. Clays and shales are not pozzolanic or only weakly so, since clay minerals do not readily react with lime unless their crystalline structure is destroyed by heat (3,5).

1.3.3. Classification of Mineral Admixtures

Mehta (17) classified the mineral admixtures on the basis of mineralogical compositions and particle characteristics as shown in Table 1.1.
Table 1.1: Classification, composition and particle characteristics of mineral admixture for blended cements and concrete (17).

<table>
<thead>
<tr>
<th>Classification</th>
<th>Chemical and Mineralogiological</th>
<th>Particle Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cementitious</td>
<td>Mostly silicate glass containing mainly calcium, magnesium, aluminium and silica. Crystalline compounds of melilithe group may be present in small quantites.</td>
<td>Unprocessed material is granular or pelletized and contains 5 to 15% moisture. Before use it is dried and ground to particles less than 45 micron</td>
</tr>
<tr>
<td>Rapidly cooled blast furnace slag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Cementitious and pozzolanic</td>
<td>Mostly silicate glass containing mainly calcium, magnesium, aluminium and alkalies. The small quantity of crystalline matter present generally consists of quartz and C₃A; free lime and periclase may be present; CS and C₄A₃S may be present. and C₃A; free lime and periclase may be present; CS and C₄A₃S may be present in the case of high-sulfur coals. Unburnt carbon is usually less than 2%.</td>
<td>Powder corresponding to 10-15% particle larger than 45 mic.. Most particles are solid and spheroidal with less than 20 Micr. diameter. Particle surface is generally smooth but not as clean as in low-alumina fly ash.</td>
</tr>
<tr>
<td>High calcium fly ash (&gt;10% CaO)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Contd. Table 1.1

<table>
<thead>
<tr>
<th>Classification</th>
<th>Chemical and Mineralogical</th>
<th>Particle Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. Normal Pozzol (Low-calcium flash (&lt;19% CaO))</td>
<td>Mostly silicate glass containing aluminium and iron. The small quantity of crystalline matter present consists generally of quartz, mullite, hematite and magnetite. Unburnt carbon is usually less than 5%, but at times may be up to 10%.</td>
<td>Powder corresponding to 15-30% particles larger than 45 μm (usually 250-350 m²/kg Blaine). Most particles are solid and spheroidal with average 20 μm diameter. Cenospheres and plerospheres may be present.</td>
</tr>
<tr>
<td>5. Others</td>
<td>Consist essentially of crystalline silicate minerals, and relatively small amount of non-crystalline matter</td>
<td>The materials must be pulverized to very fine particle size in order to develop satisfactory cementitious of pozzolanic activity. Ground particles are rough in texture.</td>
</tr>
<tr>
<td>a) Slowly-cooled blast furnace slag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) Bottom ash, boiler slag, field-burnt rice husk ash</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.3.4. Composition of Mineral Admixtures

The compositions of these mineral admixtures with respect to Portland cement are shown in Fig. 1.2. It shows the position of Portland cement and different blending components in ternary CaO-Al₂O₃-SiO₂ system. Silica fume and rice husk ash are the richest in silica followed by natural pozzolana (18).

1.3.5. Natural Pozzolana

Many naturally occurring minerals and several industrial and agricultural by-products fall in the class of pozzolanic materials. Natural substances of volcanic origin, such as santorin earth, pozzolanic deposits, rheinish trass, rhyolite and pumicite are used without calcining. Many clays and shales are activated by calcination. Mehta (19) classified natural pozzolana into four categories on the basis of their principal lime reactive constituents:

i) Unaltered volcanic glass,
ii) Volcanic tuff,
iii) Calcined clay or shale, and
iv) Raw or calcined opaline silica.

1.3.6. Industrial Waste Materials

Fly ash, micro-silica or silica fume and rice husk ash are some industrial by-products suitable as pozzolanic additions in blended cements. Fly ash is a waste obtained from pulverized fuel burners in coal burnt thermal power stations. During
Fig. 1.2 Composition of different mineral admixtures with respect to Portland Cement: position of the blending components in the ternary CaO-Al₂O₃-SiO₂ system.
combustion of coal, the products formed are fly ash, bottom ash and gas or vapours. Fly ash is the finer part of the ash which is entrained in the flue gases, whereas the bottom ash, is the residue consisting of coarser, discrete or fused particles, heavy enough to drop out of the combustion zone onto the bottom of the furnace. Fly ash makes up 75-85 % of the total ash and the remaining is bottom ash or boiler ash (20). In 1989, the total coal ash production in the world was in the order of 400 million tonnes annually and India produced 36 million tonnes (21). The properties of fly ash varies with the type and origin of the coal and other factors. The vast majority of the available fly ashes for use in cement are low calcium fly ash (ASTM, Class F) and are basically the by-products of burning anthracite or bituminous coal. These fly ashes themselves possess little or no cementitious value, but in finally divided form and in the presence of moisture, will chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. High calcium fly ashes (ASTM, Class C) are the by-products of burning lignite or sub-bituminous coal. These have cementitious properties in addition to being pozzolanic and have come to the market recently. Fly ash contains about 15 % crystalline matter, comprising mostly of quartz, mullite, heamatite and magnetite. The rest is amorphous, consisting of siliceous, aluminous and ferruginous glasses and carbon particles. Silica, SiO$_2$, is the principal component of fly ash, others being Al$_2$O$_3$, Fe$_2$O$_3$, CaO, MgO, SO$_3$ etc. The composition vary widely depending upon the coal used (22-24). Indian fly ashes are relatively rich in SiO$_2$, Al$_2$O$_3$ and unburnt carbon (25).
In the process of producing metallic silica or ferrosilicon from quartz, SiO₂, by reduction with carbon in electric furnace, microsilica or silica fume is a by-product. A very fine particulate solid, microsilica, is formed from SiO vapour on being oxidised by air to SiO₂. Its purity depends upon the raw material used and it contains 89-90% SiO₂ and minor constituents like Fe₂O₃, P₂O₅, CaO, TiO₂, alkali, carbon, sulphur etc. (26,27). The chemical composition of silica fume depends upon the composition of the raw materials such as silica sand, quartzite etc. as well as on the electrodes and the coal used. Silica fume is X-ray amorphous, with a wide scattering peak centered at about 4.04 Å, characteristic of cristobalite (28). The surface area of silica fume is very high and its particle size distribution lies below 0.1 µm which is one hundredth finer than slag and fly ash (17,28-32). It dissolves within 30 minutes in saturated calcium hydroxide solution (18). Addition of fly ash to cement increases the rate of cement hydration (33,34).

Rice husk is an agro-industrial by-product. By burning the husk under controlled conditions and temperature carbon-free, highly reactive rice husk ash can be produced. Such ash is a super pozzolana. It resembles silica fume in physical and chemical properties as well as in lime reactivity (35). Depending upon the source, rice husk ash may contain 85-95% SiO₂, 0.25-2.50 % CaO, 0.23-1.3% MgO and trace to small quantities of oxides of Al, Fe, Mn, alkali, P, S etc. (36).
In addition to the materials discussed above, many other material like kiln dust, wheat straw ash, geothermal silica, etc. have been found suitable as mineral admixtures (37-42).

1.3.7. Application of Blended Cement

Substances like natural pozzolana and calcined clay have been in use as blends in portland cement in Italy since 1929. In the U.S.A., natural pozzolana was used in concrete for the construction of dams, bridges and highways as early as in the 1920s and 1930s. In the erstwhile Soviet Union and Japan, pozzolanic cements have been in use since 1930s (43). In other parts of the world also, blended cements are gradually replacing ordinary Portland cement. There has been a significant increase in production of blended cement in the last few decades (16).

1.3.8. Advantages of Blended Cement

Production and utilization of blended cement offer many advantages as summarized below (15,44-50):

a) Economy in cement production,

b) Elimination of problem of disposal of waste,

c) Reduction of environmental problem and green house effect,

d) Conservation of natural resources, and

e) Enhancement of chemical durability and mechanical strength of concrete.
1.3.8. a. Economy in Cement Production

Manufacturing of Portland cement is a highly energy consuming process, especially in clinkerization and grinding stages. Since blending materials replace a good amount of clinker in cement production, there is a considerable saving in energy consumption. Blending of Portland cement was initially proposed to reduce cost. It has been calculated that blended cements allow an economy of 40% fuel and an increase in cement production by 1.5 to 2.0 times without altering the quality and the performance of the cement (44). Saad et. al. (45) reported that the cost of the manufactured calcined clay pozzolana used for the construction of several major Brazilian dams was one third of that of Portland cement.

1.3.8. b. Elimination of Problem of Disposal of Waste

Production and accumulation of various by-products and wastes from the widespread industrial and agricultural activities have been causing serious problems in their handling and disposal. Formulation and use of blended cements have been providing easy and profitable means to overcome many such problems.

1.3.8. c. Reduction of Environmental Problem and Green House Effect

Burning of coal and clinkerization of limestone are parts of the manufacturing process of Portland cement. These processes discharge huge quantities of CO₂, SO₂, NOₓ and many other gases to the atmosphere. Production of every tonne of cement contributes about 1 tonne of carbon dioxide, the major green house gas, into
the atmosphere. Globally, the production of cement was about 1.4 billion tonnes in
1995 which accounted for emission of about 1.4 billion tonnes of carbon dioxide
into the atmosphere, which was about 7% of the total 21.6 billion tonnes of
carbon dioxide produced from all sources (46). Most of the gases produced by the
cement plants contribute towards global warming through greenhouse effect,
several of them cause acid rain and all are responsible for massive atmospheric
pollution. General acceptance of blended cements for wide range of applications in
place of ordinary Portland cement has helped in cutting the emission of the
pollutant gases considerably and thereby, in reducing atmospheric pollution.

1.3.8.d. Conservation of Natural Resources

With the growth of industries and construction activities and with the ever
increasing demand for cement, the natural deposits of raw materials are depleting,
giving rise to an acute mineral imbalance in the nature. Large scale mining of coal
for energy has been emptying the deposits and degrading the environment. Use of
blended cement has been putting a check upon the wanton consumption of these
natural resources.

1.3.8.e. Enhancement of Chemical Durability and
Mechanical Strength of Concrete.

Mineral admixtures having pozzolanic properties contain components like
SiO₂, Al₂O₃ and Fe₂O₃ which react with lime and alkali of the Portland cement
undergoing hydration. This reduces the amount of free calcium hydroxide with
time and produces C-S-H and C-A-S-H which are similar to the products of
hydration of Portland cement. Removal of free calcium hydroxide formed during hydration of Portland cement increases the resistance of concrete towards sulphate and sea water attack. Blending of cement with pozzolanic admixtures remarkably enhances chemical durability and mechanical strength of the concrete by segmentation of large pores and increasing the nucleation sites for the hydration product precipitation (47). These, together with the filler effect (16,48,49) of the admixture materials, improve the performance of the cement.

Hydration of Portland cement is an exothermic process. Although the heat generated during hydration, accelerates the hardening process, a higher rate of heat evolution is undesirable on occasions like construction of dams. Use of blended cement helps in reducing the amount and the rate of heat evolution (50). Blended cements also impart water tightness to the dams by reducing porosity of the concrete. Furthermore, the alkali level in the concrete can be reduced and the general characteristics of fresh concrete can be improved by using blended cements (15).

Therefore, blended cement imparts the following characteristics to the concrete and mortar:

- Low permeability to water,
- Low permeability of Cl⁻, SO₄²⁻ and oxygen,
- Low expansion in sea water,
- Improved resistance to lime leaching, and
- Low heat of hydration.
1.4. Present Investigation

Many of the materials listed in Table 1.1 are region-specific. In Indian context, the steel plants and ferrosilicon plants are located at a few places only. No industry producing blast furnace slag or silica fume exists in the North East region of India. The major power plants in the region are based on natural gas and hydro-power only. There is no naturally occurring pozzolana in this part of the country. On the other hand, economics in blended cement production necessitate availability of the blending materials near the cement production units. The most commonly available materials for blending cement in this part of the country are RHA and clay-rich soil.

1.4.1. Rice Husk Ash (RHA)

Rice is one of the largest produced cereal crop around the world. It is grown in more than seventy five countries world-wide, using more than 11% of the world’s cultivable land. Eighty million tonnes of paddy were produced in India during 1994-95 (51). The proportion of the husk in paddy varies from place to place in a range from 16 to 25% by weight of the grain. Utilization of the enormous quantity of the husk has been attempted in numerous ways. Reviews in its application potentials has been detailed by several authors (52,53).

Rice husk yields ash on burning which constitutes 20-25 % by weight of the husk. The elemental and mineralogical composition of the husk vary from location
to location. The ash possesses around 90% silica. Besides that, ash contains traces to small amounts of oxides of Ca, Mg, Al, Fe, K, Na, S, P etc. (54).

Burning rice husk to produce the ash and application of the ash as a binding material is found on record since 1924 (55). The reactivity of RHA produced by burning the husk at different temperatures was investigated by many (36, 56-69). The ash produced by burning husk at low temperature has higher surface area, porosity and reactivity towards lime and alkali in comparison to high temperature ash (67). The ash obtained by burning husk under controlled conditions (350-600°C) and controlled supply of air is a super pozzolana in terms of its lime reactivity (35). It is comparable to highly pozzolanic silica fume in amorphous nature and surface area (17, 70). The reactivity of RHA is due to the amorphous nature of silica present in it. Besides containing amorphous silica, RHA has high specific surface area and retains the cellular microstructure of the original husk. It can be ground with ease to high fineness (35, 71). For these reasons, RHA is a superior pozzolana in comparison to burnt clay or fly ash.

Mehta pioneered exploitation of the high pozzolanic activity of RHA and developed rice husk ash cement (72, 73). These cements were prepared by intermixing RHA with quick lime, hydrated lime or Portland cement (63, 68, 69).

Since then many cements and cement like products based on RHA have been developed (56-62, 64, 74). These were essentially composed of hydrated lime and RHA and based on the pozzolanic property of the ash. I.I.T. Kanpur, has developed
a process based on heap burnt or boiler burnt RHA, the final product of which is suitable for mortars ((65,66). Shresta (59) obtained a lime-RHA cement by burning lime sludge or press mud from sugar industries and rice husk followed by grinding. Cook and Suwanvitaya (64) investigated carbonaceous RHA and hydrated lime. Dass and Rai (75) suggested a method of producing lime pozzolana based on RHA using a method similar to that of Shresta. In this method rice husk and lime were mixed, shaped in the form of balls and burnt. Sooriyakumaran and Ismail (60) investigated the cementitious properties of 650°C burnt RHA, containing different carbon contents and hydrated lime. Cook (61) investigated the properties of the cements based on hydrated lime and RHA from different sources.

The properties of blended cement containing different proportions of RHA were also investigated by many workers (35,62,76-79). The results of different workers differed. The ash when blended with cement and concrete in general, however, imparted high strength, better chemical resistance, increased impermeability, improved setting times, creep resistance and drying shrinkage to the material (35). In Portland cement, RHA can replace higher quantity of cement than any other pozzolana, like burnt clay or fly ash, and can impart good strength (77). The C-S-H produced during hydration of the cements has lower C/S ratio and the value decreases markedly as the content of the silica increases (33).

Cook et al. (76) also investigated the properties of Portland pozzolana cement in which 20% of the cement was replaced by controlled-burnt RHA. The physical properties of the blended cement were found to be equivalent to and even better
than those of the parent OPC. They also reported that compared to mill burnt ash, controlled burnt ashes give better strength characteristics.

The strength characteristics of mortars made from RHA burnt at different temperatures as well as white mill burnt RHA and lime were investigated by Seng (62). Mortars made from ash burnt at high temperature and from white mill burnt ash exhibited higher strength in comparison to those made from ash burnt at lower temperatures.

Singh et al. (78) investigated the effects of RHA and mixture of RHA and fly ash on the hydration of white Portland cement and found that the reaction between RHA and Ca(OH)$_2$ was increased by increase in reaction temperature. Activity of RHA was also enhanced by the presence of fly ash.

Sugita et al. (79) investigated the influence of the active RHA produced in the semi-industrial furnace developed by them, on properties of the cement blended with it, and found that not only the strength of cement was increased but also the resistance of concrete to 2% HCl solution attack, Cl$^-$ penetration and carbonation was improved greatly.

The high reactivity of controlled burnt RHA has led to the development of various techniques for burning husk (65,66,78-80). In most of the techniques, the calorific value of the husk is lost (65).
Results of the investigations on the reactivity of RHA carried out by different workers agreed on the mineralogical aspects and proved unequivocally the superior pozzolanic activity of the material, particularly, of the ash produced under controlled temperature condition. However, there were disagreements on the temperature-dependence of the pozzolanic properties and the mineralogical changes of the silica in ash with burning temperature. Furthermore, in determination of pozzolanic property of the ash most of the investigators allowed limited time for reaction. The composition of the ash also varied from place to place (36).

Although, the potential of RHA is about 1 million tonnes world-wide (81), the material is not yet available commercially. It has been predicted that when it becomes commercially available it will be one of the most significant supplementary cementitious materials for partial replacement of Portland cement in concrete (82).

In India alone, more than fifteen million tonnes of rice husk is produced annually. Till a few years back, rice husk was a total waste. Of late, however, a small fraction of this huge agricultural waste is finding use, mainly as fuel, and a little, in other ways, but the rest is lying unutilized. The density of the rice husk is low. While its specific gravity is 750 kg/m$^3$, the bulk density lies between 100 and 150 kg/m$^3$ (83). Bacterial decomposition of rice husk occurs unusually slowly. The husk also resists rapid burning even in the open air. Consequently, disposal of the light weight, fibrous material with high silica content creates many problems, economically and environmentally.
As an easier means for disposal of the husk most of the rice mills in the North Eastern region of India burn the material in large heaps in open air. The slow burning material continues to burn while fresh batches of raw husk are dumped over it one after the others. As a result of prolonged burning of the husk, a whitish ash is formed and accumulates. Such white ash in stacks or heaps is a common sight in many places, particularly in the North East region of India. Utilization of the stack burnt ash as a pozzolanic material for blended cement is a proposition with immense potential, but it requires thorough characterization of the materials.

Published work on the use of stack burnt RHA as pozzolanic addition is scarce. This kind of ash reportedly loses the original reactivity of silica (36). Moreover, the compositions and physico-chemical characteristics of the ash varies from place to place (54). The ash, however, can be used well in making high alite cements (84). Carbonized RHA has also been established as a raw material and fuel for making Portland cement with good technological properties (85).

1.4.2. Clay

Historically, burnt or calcined clay is one of the earliest known pozzolanic material. The early Romans made use of powdered tiles or potteries with lime which produced effects similar to natural pozzolana of volcanic origin (3). Those earthen-wares contained clay minerals which on calcining changed into materials with pozzolanic properties. Calcined clay is still in use as an additive in production
of blended cement in many places, especially those where other additives like fly ash, blast furnace slag, natural pozzolana of volcanic origin etc. are not found. Meissner (86) reported that in 1930s and 1940s several major US construction projects were carried out using Portland pozzolana cement which contained as much as 25% calcined pozzolana.

A clay can be activated to a pozzolana by calcination. It is a less energy intensive process, in comparison to clinkerization. Activation of clay can be brought about at a relatively lower temperature. Calcined clay produced under the said conditions may contain quartz, cristobalite, gehlenite, orthoclase, calcite, dicalcium silicate, \( \text{C}_2\text{S} \), and muscovite, besides glass and lime reactive silica (35).

Different clay minerals have been investigated as pozzolanic materials by various workers (87-109). Kaolin is an important clay mineral. It is also used as an argillaceous raw material in cement production (92). Effect of heat on this material has been studied extensively (92,96,98,106,110-118). When calcined at 700-800\(^\circ\)C, it transforms through dehydroxylation to metakaolin (92,110,111). Metakaolin reacts readily with calcium hydroxide to give product similar to the gel-like C-S-H formed in hydration of Portland cement (98). Calcined kaolin is one of the major clay minerals generally used as mineral addition in blended cement (96,99,102).

All clays are not suitable as pozzolana. There is no quantitative relation between various physico-chemical and mineralogical parameters and pozzolanic
activity of natural pozzolana or calcined clay. Although it is found that addition of thermally or chemically activated clay significantly increases early hydration of Portland cement, the activity of pozzolana varies significantly within the type and with the source of the clay, the heating schedule and the fineness to which ground (32).

In places where there are no working mines of kaolin or other usable clay minerals, as well as no natural deposits of pozzolana and where industrial wastes like fly ash, blast furnace slag, silica fume etc. are not readily available, one of the alternative blending material for making blended cement is clay-rich soil or clayey soil. In North Eastern part of India, there are several cement factories, but there is a dearth of conventional pozzolanic materials and other mineral additions. In this region clayey soil is used as argillaceous component for making cement. Titabar clay, a clayey rich soil from Titabar region of Assam has been well-established as an argillaceous raw material for cement making (119-122). The mineralogical and pozzolanic characteristics of the clayey soil has not, however, been reported.

1.4.3. Mixed Pozzolana

The pozzolanic properties of calcined clay and RHA were separately investigated by many workers and utilized in designing Portland pozzolana cements. But limited published information regarding properties and application of mixed pozzolana containing calcined clay and RHA could be found (75,123). Singh (78) reported that when mixed with 2% fly ash, the
pozzolanic effect of RHA on the hydration of white Portland cement was enhanced. Isaia (124) investigated the effect of pozzolana mixture comprising of fly ash with silica fume and RHA. The results indicated that the fly ash presented synergic effect, that is, increase of the pozzolanic activity due to the combined use of fly ash with silica fume or RHA, in the ternary mixture.

Since each of RHA and calcined clay is an effective pozzolana and becomes reactive by thermal treatment of the materials at almost the same temperature region of 600-900°C, it is expected that both together will be effective mineral admixture for making blended cement.

The calorific value of rice husk is around 3200 kcal/kg (125) which may be utilized for calcination of clay. Dass and Rai (75) and Dutta and Dass (123) utilized the thermal energy of the husk for such purposes and manufacture of mixed pozzolana comprising of RHA and calcined clay (75,123). They burned a mixture of rice husk and clay in approximate proportion of 1:1 by weight and the product was subsequently ground. The material thus obtained was found to be a good pozzolana and could effectively replace 20% cement. The 28 days strength of the mortar prepared by using cement containing 20% of the prepared pozzolana was about 98% of the controlled cement. The mixed pozzolana prepared by the method contained the two components in one definite ratio only. The effect of variation in quantities of the components in the mixed pozzolana on the properties of the cement was not investigated.
1.5. Objectives

The objectives of the present investigation are therefore summarized below:

(i) To investigate the physico-chemical and pozzolanic characteristics of locally available stack burnt RHA compared to controlled burnt ash.

(ii) To investigate the physico-chemical and pozzolanic characteristics of a locally available clay-rich soil or clayey soil used as the argillaceous component in manufacture of Portland cement.

(iii) To investigate the physico-chemical property of the blended cements containing (a) RHA, (b) burnt clayey soil and (c) mixtures containing RHA and burnt clayey soil in various proportions.