CHAPTER 2

THEORIES

2.1 Portland Cement

Portland cement is an extremely common material that has adhesive and cohesive properties, which makes it capable of bonding mineral fragments into a compact whole. It is formed from burning a mixture of naturally occurring *argillaceous* (containing alumina) and *calcareous* (containing calcium carbonate or lime) materials to a partial fusion at a high temperature (about 1450 °C). The product obtained from burning, called *clinker*, is cooled and ground to a fine powder, with some gypsum added, and the resulting product is known as Portland cement [30].

2.1.1 Manufacture of Portland Cement

The processes used for the manufacture of cement can be classified as dry and wet, depending on the raw material condition.

2.1.1.1 The Wet Process

In the wet process, the raw materials are ground and mixed with water. The result is called slurry. The slurry is stored in tanks under constant agitation and fed into the kiln. The average moisture content of the slurry is about 35-50% and this moisture has to be dried off prior to calcining of the cement [31]. A diagram of the wet process kiln is shown in Figure 2.1.

The slurry, in its movement down the kiln, is subjected to progressively higher temperature. At first, the water is driven off and CO_2 is liberated. In addition, the dry material undergoes a series of chemical reactions until finally and in the hottest part of the kiln, the material is mixed with lime, silica and alumina again. The mass then fuses into balls of 3 to 25 mm in diameter, known as clinker. The clinker drops into coolers, which are of various types and often provide a means for an exchange of heat with the air subsequently used for the combustion of the pulverized coal [13].

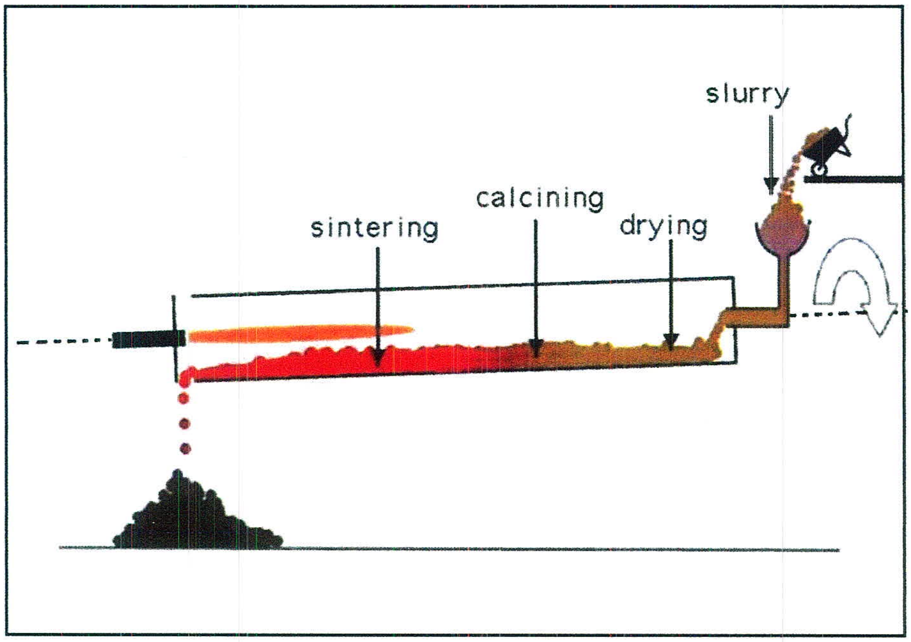

Figure 2.1 Wet process kiln [32].

2.1.1.2 The Semi-dry Process

In the semi-dry process, the moisture content of the feed material is about 10-15%. The feed material is pelletized into small nodules. These nodules are dried and ground to a fine powder. One advantage of the semi-dry process is the uniform size of the clinker that is produced in the kiln from the nodules. This can make grinding the clinker into cement powder easier [31].

2.1.1.3 The Dry Process

In the dry process, the raw materials are fed into the kiln in dry powder form. The dry powder, called raw meal, is collected in a blending silo, and then its proportions are adjusted for the manufacture of cement. Firstly, the raw meal is baked hard in a pre-heating grate by means of hot gases from the kiln, which then enter the kiln. The subsequent operations are the same as in the wet process of manufacturing [13]. A diagram of the dry process is shown in Figure 2.2.

Until recently, the trend of manufacturing Portland cement was a dry process because it had a lower cost for manufacturing cement than a wet process. Typically, the total consumption of coal in a dry process is 100 kg for producing a ton of cement, but in a wet process it is about 350 kg [30].

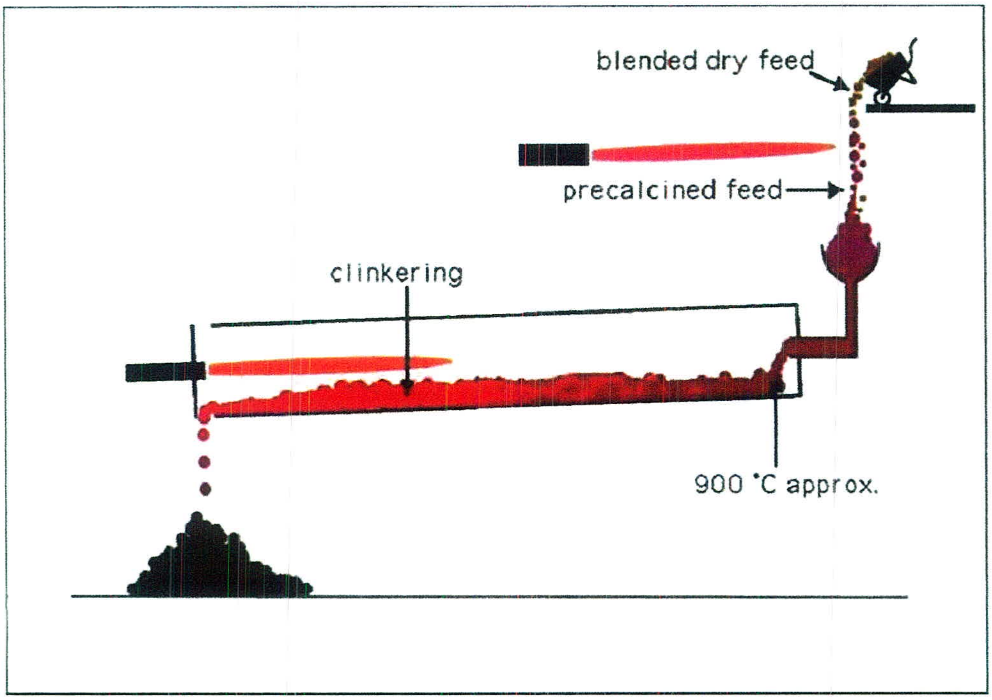

Figure 2.2 Dry process kiln [32].

2.1.2 Chemical Composition of Portland cement

Portland cement consists mainly of lime, silica, alumina and iron oxide, with a fraction of magnesia, sulphur trioxide and alkalis, which are formed into the compounds of Portland cement in the process [30]. The oxide compositions of Portland cement are given in Table 2.1.

Table 2.1 Oxide composition of ordinary Portland cement [30].

Oxide	Percent
Lime, CaO	60-65
Silica, SiO_2	17-25
Alumina, Al_2O_3	3-8
Magnesia, MgO	0.5-6
Sulphur trioxide, SO_3	1-2
Alkalis, i.e. soda and/or potash, Na_2O+K_2O	0.5-1.3

2.1.2.1 Lime

Lime has been known as a building material for many centuries. It is easy to imagine how lime mortar have been discovered: a camp fire was lit on a limestone then a sudden fall of rain extinguished the fire, and water soaked into the rock underneath, which suddenly disintegrated to a fine powder and formed a white slurry with the rainwater. Some days or weeks later in the same place, the slurry was found to have solidified and recovered progressively its initially stony appearance. Lime mortar was discovered about a thousand years before the process involved could be expressed in the form of the chemical reaction [33]:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2 \qquad (2.1)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat} \qquad (2.2)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (2.3)$$

Lime is usually made by heating limestone or calcium carbonate ($CaCO_3$). At a temperature of 1000°C, the limestone decomposes into quicklime (CaO) and carbon dioxide (CO_2), as shown in Eq. 2.1. When quicklime reacts with water, it generates calcium hydroxide ($Ca(OH)_2$) and heat, as shown in Eq. 2.2. After that, when lime is used as the cementing agent in mortar for masonry or plaster, it is used in the hydrated form. Lime mortar ultimately hardens by a reaction with carbon dioxide from the atmosphere, reverting to calcium carbonate, as shown Eq. 2.3. This process is very slow, however, and straight lime mortars are now seldom used for construction.

In Portland cement, the lime is largely combined in the form of calcium silicates and calcium aluminates. Some small amounts of un-combined lime (CaO) and the hydrate $Ca(OH)_2$ are generally present in finished cement, for one reason or another [20].

2.1.2.2 Silica

Silica (silicon dioxide, SiO_2) is found in most natural rock and stone, with forms of silica often encountered in a more or less pure form, such as quartz, quartz sand and sandstone. Silica of this type is highly stable. Silica can be changed into a series of crystalline structures when it is heated. In the Portland cement process, silica is an important oxide to combine in the form calcium silicates [33].

2.1.2.3 Alumina

In chemical terms, alumina is Al_2O_3. It can occur naturally as the mineral corundum, but it is not used in the manufacture of cement. Normally, the manufacture of cement uses clay for an alumina source, in which clay consists of silica, alumina and water. Alumina is important for cement chemistry because it can react with lime and water to generate a gel-like product [33].

2.1.2.4 Ferric Oxide

Ferric oxide or Fe_2O_3 can be one of the most important components in most iron ores. In the manufacture of Portland cement, raw materials contain some ferric oxide which react with lime and alumina to give calcium aluminoferrite [33].

2.1.3 The Main Compound of Portland Cement

Portland cement is not a simple mixture of lime, silica, alumina and ferric oxide, but is a mixture of different combinations of the basic oxides. Four compounds are usually considered to be the major compounds of Portland cement. These compounds, by chemical name and abbreviation, are listed in Table 2.2 and some of the characteristics of the main compounds are given in Table 2.3.

Table 2.2 Main compounds of Portland cement [34].

Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3CaO \cdot SiO_2$	C_3S
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF

Table 2.3 The behaviour of main compounds which occur in Portland cement [8].

Property	Relative behavior of each compound			
	C_3S	C_2S	C_3A	C_4AF
Rate of hydration	Fast	Slow	Immediately	Very fast
Heat hydration	Medium	Small	Large	Medium
Strength development	Fast	Slow	Very fast	Very fast
Ultimate Strength	High	High	Low	Low

2.1.3.1 Alite

Alite is the name of tricalcium silicate, $3CaO \cdot SiO_2$ (C_3S), and it is commonly used in the cement industry. Its content in Portland cement is about 50-70% and the appearance of Alite looks like a hexagon crystalline structure. When Alite mixes with water, it can set and harden in 2-3 hr., and the heat hydration of Alite is about 500 J/g. In addition, Alite gains strength over time mainly during the first 7-10 days and the ultimate strength of Alite is very high, as shown in Figure 2.3 [35].

2.1.3.2 Blite

Belite or dicalcium silicate, $2CaO \cdot SiO_2$ (C_2S), is a calcium silicate with less lime content than does Alite. Its content in Portland cement is about 15-30%. The appearance of Blite is round and twinning. Belite hydrates slowly and setting may take a few days. The strength development is also slow, but its ultimate strength is nearly the same as Alite, as shown in Figure 2.3. The heat hydration of Blite is about 200 J/g.

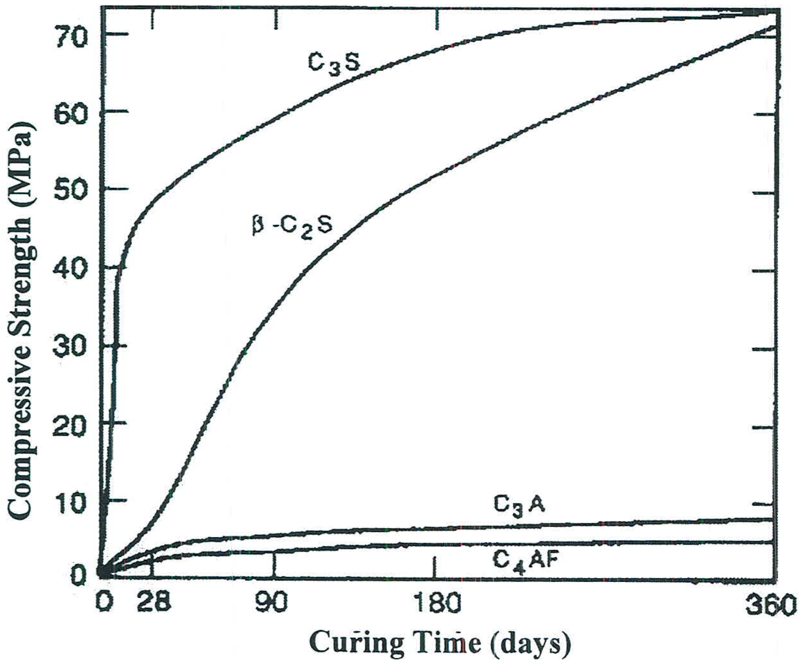

Figure 2.3 Compressive Strength of the main compounds of Portland cement [35].

2.1.3.3 Tricalcium aluminate

Portland cement contains tricalcium aluminate (C_3A) at approximately 7-15%. C_3A is angular in appearance and has a light gray color [8]. In the hydration of C_3A, it reacts with water almost immediately and is identified by a flash set, in which the heat hydration is about 850 J/g. The strength of C_3A is developed within one or two days, but the ultimate strength of C_3A is lower than Alite and Blite [35], as shown in Figure 2.3.

2.1.3.4 Celite

In chemical terms, Celite is tetracalcium aluminoferrite (C_4AF). Its content in OPC approximates 5-10% and its condition is a solid solution. The hydration of C_4AF is within minutes and the strength development is similar with C_3A. However, the ultimate strength of C_4AF is slightly lower than C_3A, as shown in Figure 2.3 [35].

2.1.4 Types of Portland Cement

Table 2.4 shows the typical compound composition for the five types of Portland cement covered by ASTM Specifications, and a brief explanation of each as follows.

Table 2.4 The compound composition of Portland cement [34].

Type of cement	Compound composition, %			
	C_3S	C_2S	C_3A	C_4AF
I. Normal	45	27	11	8
II. Modified	44	31	7	13
III. High early strength	53	19	10	7
IV. Low heat	20	52	6	14
V. Sulphate resistant	38	43	4	8

2.1.4.1 Type I

This is the normal type of cement where special properties are not required. It is commonly used for construction especially when making precast and precast-prestressed concrete that is not in contact with soils or ground water [20].

2.1.4.2 Type II

This type is the modified cement which can resist sulphate and low heat hydration slightly better than dose Type I. In addition, the strength of Type II is nearly the same as that of Type I. Therefore, this type is proper used for making moderate sulphate resistant and heat hydration concrete.

2.1.4.3 Type III

This type that it created for high early strength where the strength development of Type III is faster than Type I, about double, including the fact it hardens more rapidly than does Type I. Several factors can provide this high early strength. First, it can be improved by using a higher percentage of Alite and the other way it is improved is by grinding the cement finer [34]. However, the disadvantage of this type is the high temperature from the heat hydration reaction because Alite has a high amount of heat hydration [36], as shown in Figure 2.4. This leads to cracking of concrete. This type is usually used for repairing concrete and construction in cold weather [20].

2.1.4.4 Type IV

Type IV is used for low heat hydration and it is also a slow setting and hardening concrete [20]. It can be created by reducing the amounts of C_3S and C_3A, and increasing the amount of C_2S [36]. This type can reduce thermal cracking of concrete, therefore it is usually used for large-scale construction, such as dams [8].

2.1.4.5 Type V

Type V has a much greater sulfate resistance level than do all the other types [20]. Sulphate resistance can be improved by reducing the amount of C_3A because C_3A can lead to the cracking of concrete when exposed to water or soils containing sulfate, such as seawater [36].

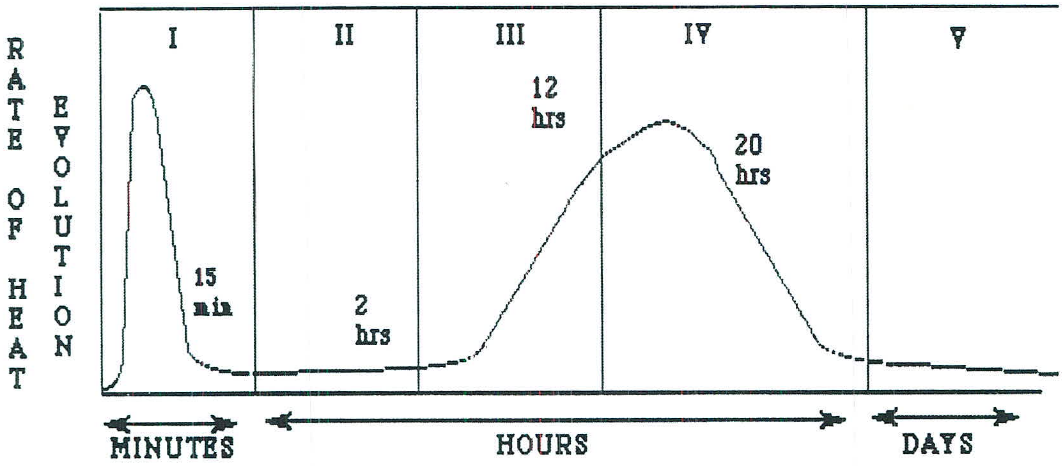

Figure 2.4 Rate of heat hydration of Portland cement [37].

2.1.5 Hydration of Portland Cement

Hydration is a reaction between cement and water, in which this process reacts with the main compounds of cement to form new compounds [20]. The products of hydration of cement have low solubility in water as shown by the stability of the hardened cement paste in contact with water [13]. The hydration reaction of cement can be explained by following the products of hydration that are calcium silicate hydrates and calcium aluminate hydrate.

2.1.5.1 Calcium Silicate Hydrate

Calcium silicate hydrate (CSH) is generated by the two calcium silicates, as shown in Eqs. 2.4 and 2.5. Their stoichiometry are very similar, differing only in the amount of calcium hydroxide formed.

$$2(3CaO.SiO_2) + 6H_2O \rightarrow 2CaO.2SiO_2.3H_2O + 3Ca(OH)_2 \quad \text{or}$$

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \quad (2.4)$$

$$2(2CaO.SiO_2) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 \quad \text{or}$$

$$2C_2S + 6H \rightarrow C_3S_2H_3 + CH \quad (2.5)$$

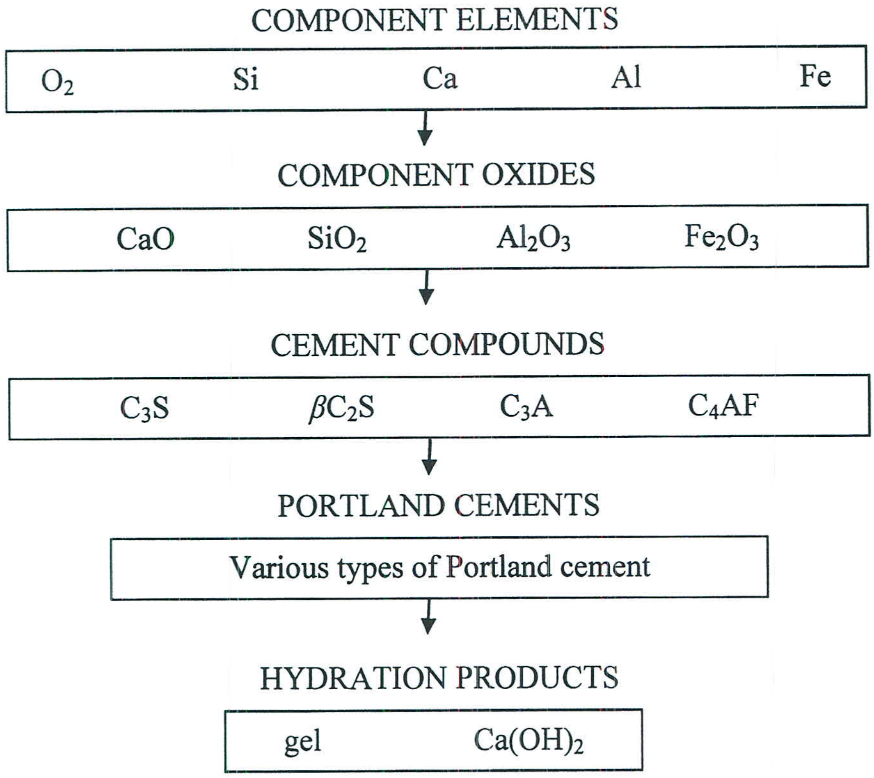

Figure 2.5 Schematic representation of the formation and hydration of Portland cement [13].

The main hydration product is a calcium silicate hydrate. The chemical formula is $CaO.2SiO_2.3H_2O$ (CSH). The reaction sequence is explained by reference to a calorimetric curve, as shown in Figure 2.6, which measures the rate of heat development over time. (This curve is measured in the case of C_3S because it can be measured easily. In stage 1, the heat hydration is immediately gained in about 15 min. This period is called a period of rapid evolution of heat. In stage 2, called the domain period, the reaction remains in the plastic stage for several hours. After about 2 to 4 h, the C_3S has begun the hydration reaction again. This period is called the acceleration period. The final set occurs in stage 4, after about 4 to 8 h, during this period the concrete has begun hardening and the reaction slows down again until it comes to the steady stage or stage 5 within 12 to 24 h.

When C_3S reacts with water, calcium ions and hydroxide ions are immediately formed and the pH of the solution increases to over 12 within a few minutes. This reaction is called hydrolysis, which is initially fast but slows down quickly and continues throughout the domain period. The decrease of the reaction depends on the increase of calcium and hydroxide ions, where the solution gains high concentration. When the calcium and hydroxide concentrations reach a critical value, the hydration products, CH and CSH, start to crystalline from the solution and the reaction of C_3S rapidly starts again. This reaction appears on the surface of C_3S that makes a covering of CSH around the surface. As hydration continues, the thickness of the hydration layer increases making it difficult to continue the hydration reaction, however, the hydration reaction still continues.

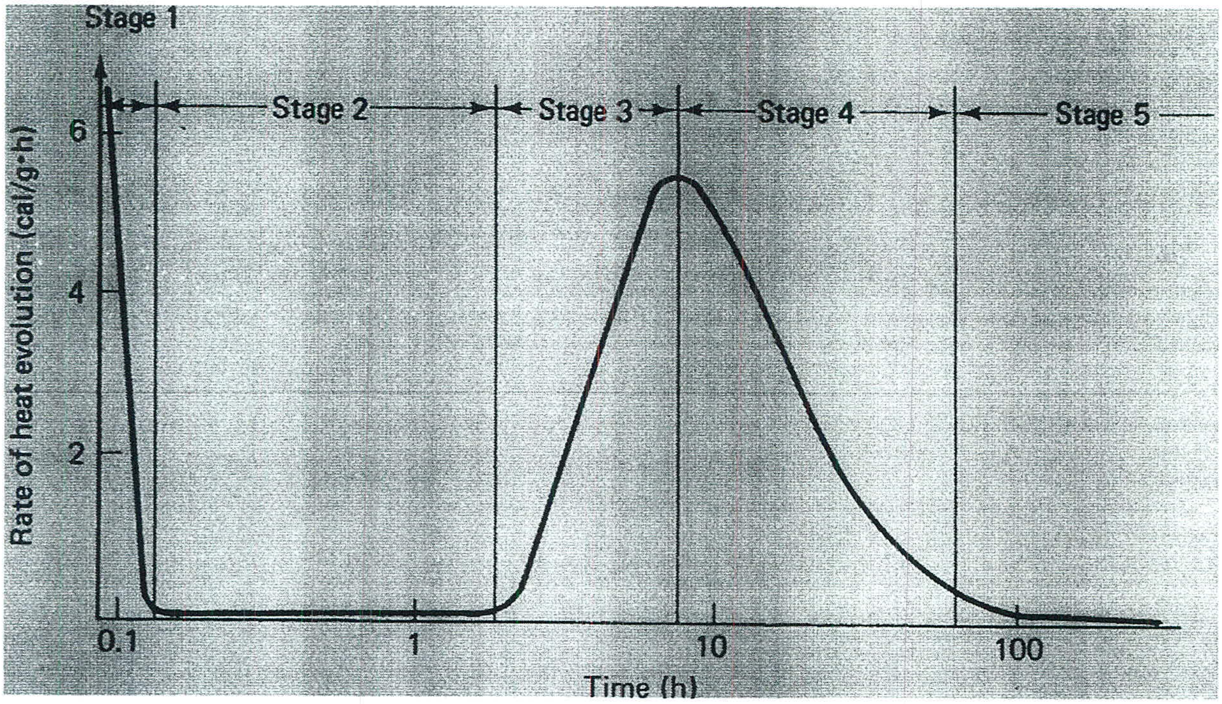

Figure 2.6 Rate of heat evolution during the hydration of C_3S [36].

C_2S hydrates in a similar manner, but it is much slower because it is a less reactive compound than is C_3S. In addition, the heat hydration of the C_2S is also lower than C_3S, as shown in Figure 2.4 [36].

2.1.5.2 Calcium Aluminate Hydrate

The rate of the hydration reaction of C_3A, as shown in Eq. 2.6, occurs rapidly, so gypsum must be added to the cement to retard the reaction. The reaction between C_3A and gypsum is shown in Eq. 2.7.

$3CaO.Al_2O_3 \quad + \quad 6H_2O \rightarrow \quad 3CaO.Al_2O_3.6H_2O$ or

$$C_3A \quad + \quad 6H \quad \rightarrow \quad C_3AH_6 \qquad (2.6)$$

$$3CaO.Al_2O_3 \; + \; 3(CaOSO_3.2H_2O) \; + \; 26H_2O \; \rightarrow \; 6CaO.Al_2O_3.3SO_3.32H_2O \qquad \text{or}$$

$$C_3A \; + \; C\bar{S}H_2 \; + \; 26H \quad \rightarrow \quad C_6A\bar{S}H_{32} \qquad (2.7)$$

The reaction between C_3A and water with gypsum can be separated into 3 stages, as shown in Figure 2.7. In Stage 1, the reaction has rapidly begun and occurs in calcium sulfoaluminate hydrate or ettringite ($C_6A\bar{S}H_2$), which has a needle crystalline appearance. The equation of the reaction is shown in Eq. 2.7. Ettringite occurs around C_3A which can make it difficult to continue the hydration reaction. After that, the reaction rapidly slows down to Stage 2. In this stage, the reaction slightly changes over several hours. When sulfate ions have reacted completely, ettringite reacts with C_3A to form calcium monosulfoalominate, $3CaO.Al_2O_3.CaSO_4.12H_2O$ ($C_4A\bar{S}H_{12}$), where this compound has lower sulphate than ettringite. This reaction is in stage 3. Calcium monosulfoalominate can be changed to ettringite again, which gains sulphate again because ettringite has a higher volume than calcium monosulfoalominate. This reaction can lead to the sulphate attacking the concrete which can result in cracking in the concrete.

C_4AF hydrates in a similar way to C_3A hydration, but it occurs slower and with a lower amount of heat hydration. Iron oxide obviously plays the same role as alumina during hydration. The hydration product is $C_6(A,F)\bar{S}_3H_{32}$, which is similar to the ettringite and has the same role, it can also change to calcium monosulfoalominate. However, C_4AF can resist sulphate attack; it means that the formation of ettringite from monosulfoalominate does not occur. It has not been established why this is so. It may be that an iron-substituted monosulfoalominate cannot react to form ettringite.

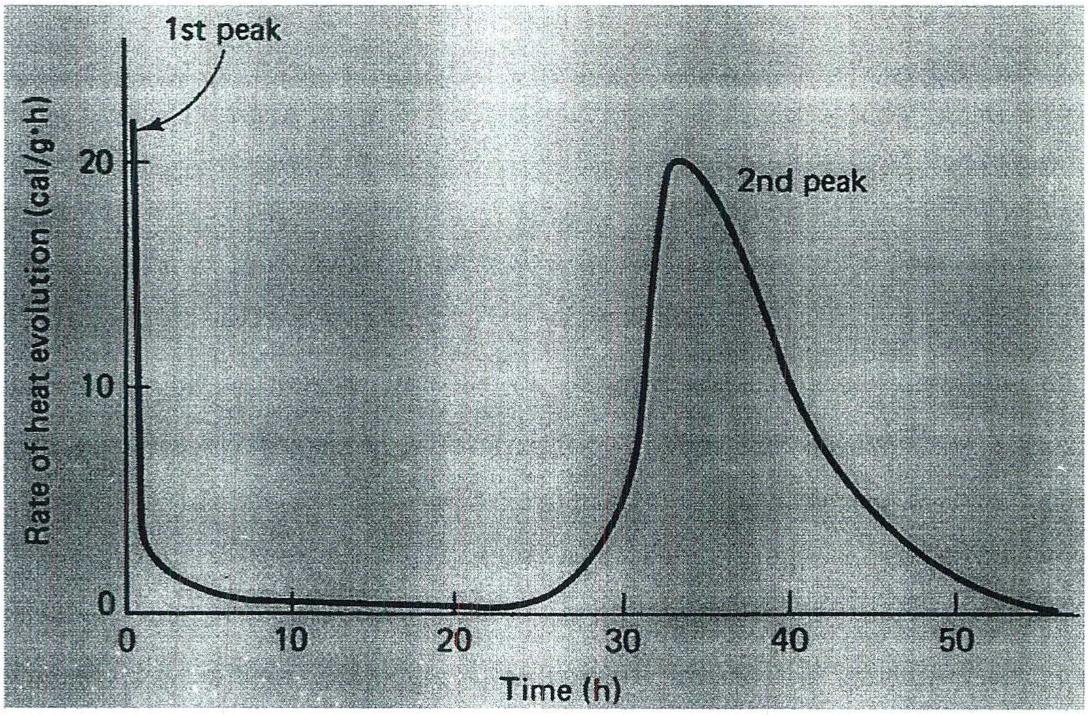

Figure 2.7 Rate of heat evolution during the hydration of C_3A [36].

2.2 Lightweight Concrete

Lightweight concrete is lighter than usual concrete in that is its density (unit weight) is lower and in the range of 2200 to 2500 kg/m^3 [14]. Normally, lightweight concrete can be produced with an over-dry density range of 300 to 2000 kg/m^3, with analogous cube strengths from 1 to over 60 MPa and thermal conductivities of 0.2 to 1.0 W/mK [14]. Normal concrete is in the the range of 2100-2500 kg/m^3, 15 to greater than 100 MPa and 1.6-1.9 W/mK [13]. The principle techniques used for producing lightweight concrete can be summarized as follows:

2.2.1 No-Fines Concrete (NFC)

No-fines concrete can be produced from cement, water and coarse aggregate with fines (sand) omitted. After mixing, the result is that each particle of coarse aggregate is coated with a layer (up to about 1.3 mm) of cement paste, which bonds it closely to the particles in point-to-point contact to leave interstitial voids.

These voids are interconnected to make a porous open-textured concrete that can reduce density, strength and shrinkage. Density depends mainly on the type and grading of the aggregate, in which the lowest densities are achieved with single-sized coarse aggregate. The maximum aggregate size is about 7-75 mm, but is usually from 10 to 20 mm. In addition, the aggregate should contain no more than 10 percent of undersized material, no particles less than 5 mm, (flaky or elongated) and should be clean to allow good cohesion with the cement paste [15]. The aggregate should be gravel or hard, and the aggregate should be crushed without any sharp edges that increase the likelihood of local crushing under load. The aggregate/cement ratio of lightweight aggregate of NFC is between 3 and 8 to create densities of 800 to 1400 kg/m^3, while the normal weight aggregate uses the aggregate/ cement ratio from 6 to 10 to produce densities of between 1200 and 1900 kg/m^3 [15].

Table 2.5 Typical properties of NFC made with normal weight and lightweight aggregates [15].

Item	Normal weight aggregate	Lightweight aggregate
Aggregate/cement ratio (by mass)	6-10	3-8
Water/cement ratio (by mass)	0.38-0.45	0.38-0.45
Air dry density (kg/m^3)	1200-1900	800-1400
Cube strength (MPa)	3-7	3-7

Table 2.5 shows the typical properties of NFC made with normal weight and lightweight aggregates. Density depends on the type and size of the aggregate with lower maximum aggregate sizes, creating higher strength, which is probably due to the larger number of contact points in a given volume. For a given type of aggregate, compressive strength depends on the density, which is controlled by the cement content. Moreover, strength increases with age in a similar manner to normal concrete.

The coefficient of the thermal conductivity of NFC is between 0.69 and 0.94 J/m^{2}s for normal weight aggregate and approximately 0.22 J/m^{2}s for lightweight aggregate. However, the coefficient increases with moisture content [15].

2.2.2 Lightweight Aggregate Concrete

The variety of lightweight aggregate can be classified into 3 types, as given in Table 2.6, which is recognized by RILEM/CEB.

Table 2.6 Classification of lightweight aggregate concrete [15].

Property	Class and type		
	I Structural	II Structural/ insulating	III Insulating
Compressive strength (MPa)	>15.0	>3.5	>0.5
Coefficient of thermal conductivity (W/mK)	-	<0.75	<0.30
Approximate density range (kg/m^3)	1600-2000	<1600	<<1450

Within class I, structural lightweight concrete is normally described as concrete with an oven-dry density of no higher than 2000 kg/m^3 [15]. However, each country has a slightly different density. For example, in Australia, structural lightweight concrete is made with lightweight coarse aggregate and normal weight fines, the result of which is a saturated surface-dry density of not less than 1800 kg/m^3 [15]. In Norway, using any combination of any type of aggregate for structural work provides the resulting concrete with (a) an oven-dry density of 1200-2200 kg/m^3 and (b) a strength grade of no greater than 85 MPa if the mix contains lightweight aggregate. In the USA, structural lightweight aggregate concrete is considered to be concrete with an air-dry density of less than 1810 kg/m^3 [15].

Lightweight aggregate can be classified into several categories:

(a) Natural aggregate
(b) By-product aggregate
(c) Processed aggregate

2.2.2.1 Natural Aggregate

Natural lightweight aggregates are pumice, scoria and diatomite. Normally, pumice is produced by excavation with a tractor-scraper, and then the pumice is crushed and thoroughly washed to remove anything adhering to it and anything that might pass a ⅛-in sieve. The final product will pass a ⅜-in. sieve and will be retained in a ⅛-in. sieve. The colour of pumice is white or grey to yellow, including having a froth like appearance. It is porous but yet has firmness. Pumice consists of acidic volcanic glass with fragments of ryholite, perlite, quartz, feldspar, and hornblende.

Scoria is produced from volcanic lava that is basically uncontaminated. The physical properties of scoria are angular and hard, and the colour of it is red to black. It has generally poor concrete-making properties and produces high strengths similar to pumice. Diatomite is a soft, porous aggregate that can be easily broken with the fingers. It is white in colour and angular [14].

2.2.2.2 By-Product Aggregate

By-product lightweight aggregates are comprised of cinders, expanded blast-furnace slag, and other industrial slags and sintered fly ash [14].

Cinders are a by-product of the high-temperature combustion of coal or coke. However, because the cost of trucking cinders is very high it is not widely used.

The use of blast-furnace slag for construction aggregates is over 25 million tons per year, but only 3 million tons are expanded slag. The chemical compositions of slag consist of silicates, aluminosilicates of lime and other bases developed simultaneously with the production of iron in a blast furnace. Expanded slag occurs by bringing the molten slag into contact with controlled quantities of water, and then is crushed, sieved and stockpiled. The colour of expanded slag is dark to light grey or cream with an occasional grey particle. However, it is limited in that it can only be produced at the site of a blast furnace.

Fly ash aggregate is made by spraying fly ash with water in a drum-type mixer that is called a pelletizer. The size of the pellets can be regulated by controlling the speed of the mixer. However, fly ash has much carbon, so it is burnt again. The combustion gets rid of carbon and drives off sulphur and other volatile compounds, giving a relatively inert product. Fly ash is smooth and less water resistant than other lightweight aggregates, and can be crushed to a fine or medium size, depending on the use to which it will be put.

2.2.2.3 Processed Aggregate

One method of manufacturing aggregates is the expansion or boating method. Stephen J. Hayde patented the rotary kiln under the name Haydite in 1917. In this method, raw clay, shale or state is fed into the upper end of a kiln. Then, it travels slowly to the lower or burning end, where during the process, gases are formed in the raw material expand at temperatures of 1800-2200°F [14]. After that, it is cooled at the end of the kiln and crushed screened and stockpiled. If the raw materials are pre-sized, the crushing operation may be bypassed.

The aggregates from this method have good to excellent concrete-making properties and can achieve high strength with a reasonable cement factor. These are the principal materials used as an aggregate in making structural lightweight concrete, and about 75 to 85% of all structure lightweight concrete uses these aggregates [14]. These lightweight aggregates range from grey or dull orange to light pink in colour.

2.2.3 Aerated Concrete

Aerated concrete means a lightweight concrete into which gas bubbles are introduced into the plastic cement mix in order to produce a material with a cellular structure. The processing to produce aerated concrete can be classified with two basic methods that are gas and foamed concrete.

Gas concrete is made by using a chemical reaction for generating a gas in fresh mortar. Aluminium powder is commonly used to produce the hydrogen gas and to form bubbles. Alternatively powdered zinc and hydrogen peroxide can also be used. The reaction for generating bubbles occurs with the hydroxide of calcium or alkali [38].

Foamed concrete is produced by adding a foaming agent (usually some form of hydrolyzed protein or resin soap) as this process is not a chemical reaction. The introduction of the pore is achieved by pre-foamed foaming or mix foaming [13].

The disadvantages of aerated concrete are a higher thermal movement and higher shrinkage and moisture movement compared to other lightweight concretes of the same strength, but it can be enhanced by high pressure stream curing, which improves the compressive strength. Therefore, aerated concrete is mostly used for partitions for heat insulation purposes because it has lower thermal conductivity and better fire resistance than does ordinary concrete.

2.2.3.1 Properties of Aerated Concrete

Table 2.7 gives the typical properties of autoclave aerated concrete, whose properties are explained below:

- Density

Normally, the density of aerated concrete is between 300 to 1800 kg/m^3 [18], which depends on the manufacturing processes. The pore structure, size and distribution affects the amount of density of aerated concrete, such as the development of larger macro pores in the matrix, which has been reported to reduce the density.

- Compressive Strength

The pore structure of the air pores and the mechanical condition of pore shells also affect the compressive strength of aerated concrete similar to the density. Moreover, the value of compressive strength varies with density. When the density is reduced by the formation of large macro pores, the compressive strength is also dropped [18].

Table 2.7 Typical properties of autoclave aerated concrete [15].

Dry density (kg/m^3)	Compressive strength (wet) (MPa)	Flexural strength (MPa)	E-value (GPa)	Thermal conductivity (3% moisture) (W/mK)
450	3.2	0.65	1.6	0.12
525	4.0	0.75	2.0	0.14
600	4.5	0.85	2.4	0.16
675	6.3	1.00	2.5	0.18
750	7.5	1.25	2.7	0.20

- Drying Shrinkage

Drying shrinkage means the loss of adsorbed water from the material, which is important in aerated concrete because it has a high total porosity of about 40-80% and specific surface pores (around 30 m^2/g) [18]. The drying shrinkage of aerated concrete depends on many factors. For example, shrinkage is increased by a small pore size, or when using only cement as a binder, or when the porosity is decreased.

- Water Absorption and Capillarity

Aerated concrete is a strong interaction between water, water vapour and the porous system. There exists various moisture transport mechanisms. The water vapour transfer can be described in terms of water vapour permeability and moisture diffusion coefficient. The moisture transport phenomena in porous materials, by absorbing and transmitting water by capillarity, can be identified by sorptivity, which shows the water transmission property.

- Thermal Conductivity

Conductivity is a function of density, moisture, the amount of pores, and their distribution and ingredients of the material. The finer pores offer better insulation. In moisture content, 1% by mass increase increases the thermal conductivity by about 42% [18]. Thermal performance is required in buildings as an optimum material design.

- Fire resistance

The fire resistance of aerated concrete is better than the ordinary dense concrete because the material in aerated concrete is relative homogeneous. In addition, its closed pore structure pays rich dividends, as heat transfer through radiation is an inverse function of the number of air-solid interfaces traversed.

2.3 Aluminium

Aluminium is the one of the most popular non-ferrous metals used for many applications, such as the production of automobiles and trucks, packing of food and beverages, construction of buildings and the transmission of electricity, because of its lightweight, high strength and resistance to corrosion. Currently , the world consumes aluminium at 24 million tons per year and about 75% of this total is primary aluminium [39]. However, the secondary metallurgy of aluminium (aluminium recycling) has a benefit to the economy and in saving energy. One metric ton of primary aluminium requires about 17,000 kWh of electricity, while the secondary aluminium consumes only 750 kWh [40]. In addition, it still benefits the environment because the one metric ton of primary aluminium production is from four metric tons of bauxite which produces approximately two metric tons of red mud and also releases fluorides, while aluminium recycling does not.

2.3.1 The Manufacture of Primary Aluminium

Primary aluminium production concerns two independent industrial processes for the transition from naturally occurring aluminium oxide ores to the extracted metal. The method to produce the aluminium can be divided into two main stages [39].

- The first stage consists of aluminium ores (bauxites) being converted to aluminium oxide (alumina), which can be done by different chemical methods. For example, the Bayer process, the combined method (Bayer process with agglomeration) and the Pechiney H-Plus process.
- The second stage consists of aluminium oxide being converted to primary aluminium by electrolysis in a molten bath of natural or synthetic cryolite (Na_3AlF_6), which supports an electrolyte and a solvent for the alumina.

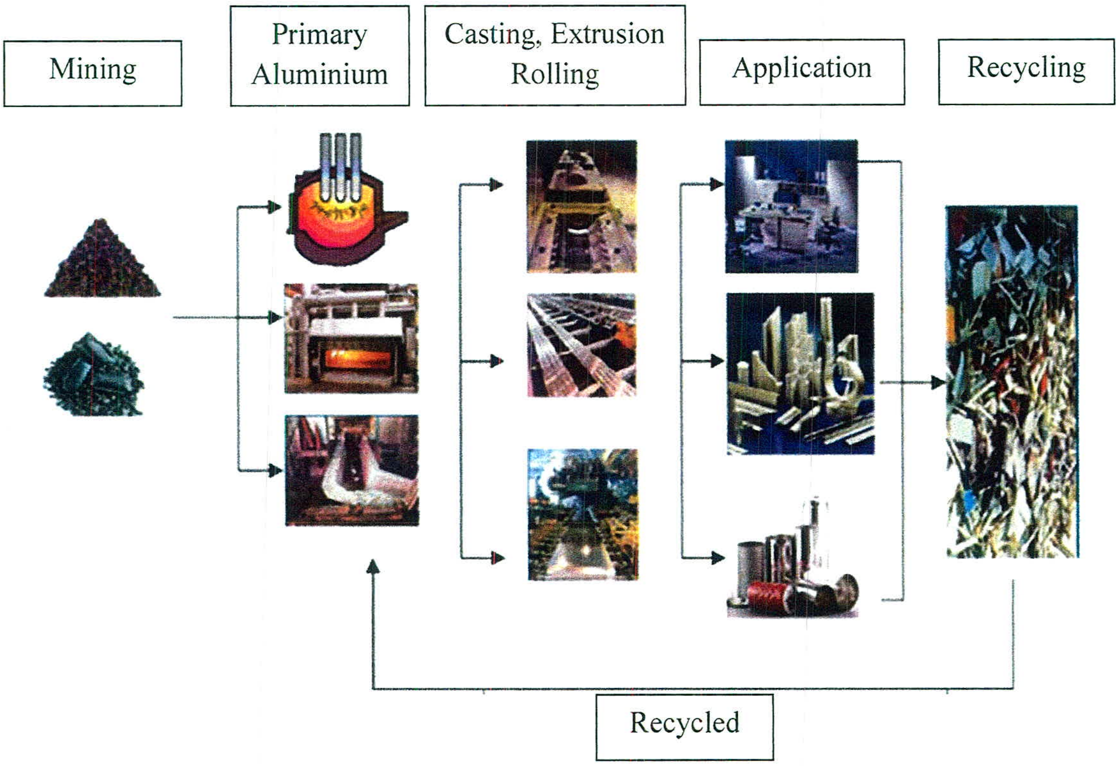

Figure 2.8 Aluminium processes [41].

Thailand cannot produce primary aluminium because it does not have the natural resources to produce it. However, Thailand imports primary aluminium for casting and extrusion rolling for the production of many applications.

2.3.2 The Casting Process

The Casting process, which has been done for many years, is classified by the types of mould. The sub-classifications are based on the type of compound used as the binder. The aluminium casting refers to the important advantage of being able to produce lightweight, highly complex function shapes quickly and easily. The aluminium casting process can be divided into 3 categories:

1. Sand Casting

Sand casting is one of the most versatile processes because it is an easy process to design in terms of size, shape and product quality [39]. The most common sands in the aluminium casting process are silicon and zircon. Sand casting processes are classified into bonded sand processes, resin binder processes, unbounded sand processes and sand reclamation.

2. Permanent Mould Casting

Permanent mould casting means gravity die casting, in which a metal mould is usually made of two or more parts, which are opened and closed during the operation [39]. This process is for high volume production of castings with a fairly uniform wall thickness and intricate internal coring, including producing more complex castings. However, the amount of production should be high because there is a high cost associated with metallic moulds. Permanent mould casting can be produced a high quality production better than a sand casting process.

3. Die Casting

The previous processes use gravity to fill the liquid metal into the different types of cavities, but this process uses pressure to push the liquid metal into the cavity, as shown in Figure 2.9 [39]. This process is called die casting, which can be divided into low and high pressure.

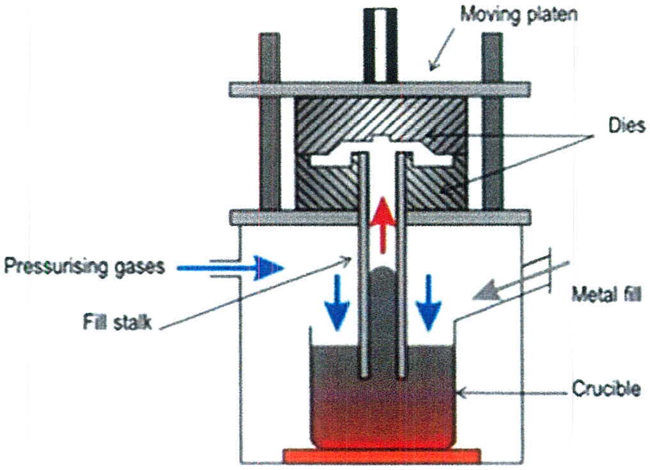

Figure 2.9 Schematic diagram of the low pressure process [39].

2.3.3 The Residue from the Casting of Aluminium

The dross is the slag from the melting of aluminium, which consists of aluminium oxide, carbides, nitrides and entrained aluminium. The amount of dross removed depends on the operator removing this dross from the surface of the bath after meltdown. Alloying and fluxing operations have been done. When the alloying elements, such as magnesium, silicon, zinc, copper, chromium and etc., have been used, some traces of those elements or their oxides are usually shown in the dross. Normally, the dross often contains as much as

50% entrained aluminium, so it is sent to a dross recycler and the metallic aluminium is recovered. In addition, the oxide fraction is recycled into abrasives, fiberglass or products that utilize aluminium oxide as a component [40].

Some melting furnace designs have an external well that is joined to the hearth by a submerged arch in the refractory wall. These are normally used to re-melt scrap. When scrap is charged into the furnace sidewall, the presence of oil, grease, etc. can produce a substantial amount of smoke. The smoke must be taken and passed through a bag house, which sometimes can contain adsorbed cadmium, chromium or other materials. The organics, such as PCBs from scrap sources, are also in the smoke particles. This collected bag house dust must to checked by the US EPA's Toxic Characteristic Procedure (TCLP) analysis, and then compared with the limits specified in EPAs list for Characteristics of Toxicity [40].

2.4 Rice Husk Ash

Billions of people around the world consume rice as a primary source of food, and approximately 600 million tons per year of rice paddy ash is produced. In the production of rice paddy, about 20% of rice husk is produced. This husk is usually disposed of by burning or dumping as waste. However, nowadays rice husk is used as a fuel resource in biomass power plants. The calorific value depends on the types of rice, moisture and bran content, where the typical value for husk is about 8-10% of moisture content and 15 MJ/kg of bran.

The production of rice husk is called rice husk ash (RHA). A 3 MW power plant requires 31000 tons of rice husk each year, if it operates at 90% of capacity [42]. This produces rice husk ash at about 5580 tons each year [42]. Normally, rice husk ash is disposed of in landfills, but nowadays RHA is used for many applications, such as in the production of refractory bricks, to absorb oil on hard surfaces and in the production of silicon chipboard. RHA contains over 90% silica (SiO_2), is highly porous, is lightweight and has a very high external surface area [43]. Therefore, its properties have many benefits, such as being an excellent insulation, absorbent and pozzolanic material. The transformation of silica in RHA depends on the temperature in the combustion stage. At 550-800°C amorphous silica is formed and at upper temperatures, crystalline silica is formed [44].

2.4.1 Enhanced Properties of Concrete

When Portland cement reacts with water, it produces calcium silicate hydrate (CSH) and an excess of calcium hydroxide ($Ca(OH)_2$). Adding a pozzolanic material, such as RHA, which reacts with $Ca(OH)_2$ to generate CSH is similar to Portland cement. This is stronger, less permeable and more resistant to chemical attack.

A wide variety of environmental circumstances, such as a reactive aggregate, high sulphate soils, freeze-thaw conditions, and exposure to salt water, de-icing chemicals, and acids are deleterious to concrete. Laboratory research and field experience has shown that careful use of pozzolanic materials is useful in countering all of these problems. The pozzolanic materials are not just a "filler", but a strength and performance enhancing additive. Pulverized fly ash and ground granulated blast furnace slag are the most common pozzolanic materials for concrete.

Many studies have been carried out to determine the efficiency of RHA as a pozzolanic material. These studies have concentrated on the quantity of ash in the mix and the improved characteristics resulting from its use.

- Comparison of setting time

Table 2.8 compares the setting characteristics of OPC and RHA cement paste. It can be seen that the addition of RHA speeds up the setting time, although the water requirement is greater than for OPC.

Table 2.8 Influence of RHA on setting times of cement at a replacement rate of 35% [44].

Type of mortar	Water requirement	Initial setting time	Final setting time
OPC	29 liters	105 minutes	225 minutes
RHA	36 liters	113 minutes	180 minutes

- Compressive strength

Figure 2.10 compares the compressive strengths of OPC and RHA mortars. At 35% replacement, the RHA cement had improved early strength, and due to its higher percentage of silica, the RHA cement also had a higher compressive strength later. Other studies have also shown that at 28 days RHA cement had significantly greater rates of compressive strength compared with OPC. The highest compressive strength has been obtained when 35% of Portland cement was replaced with RHA. If 50% is replaced then the strength is considerably reduced.

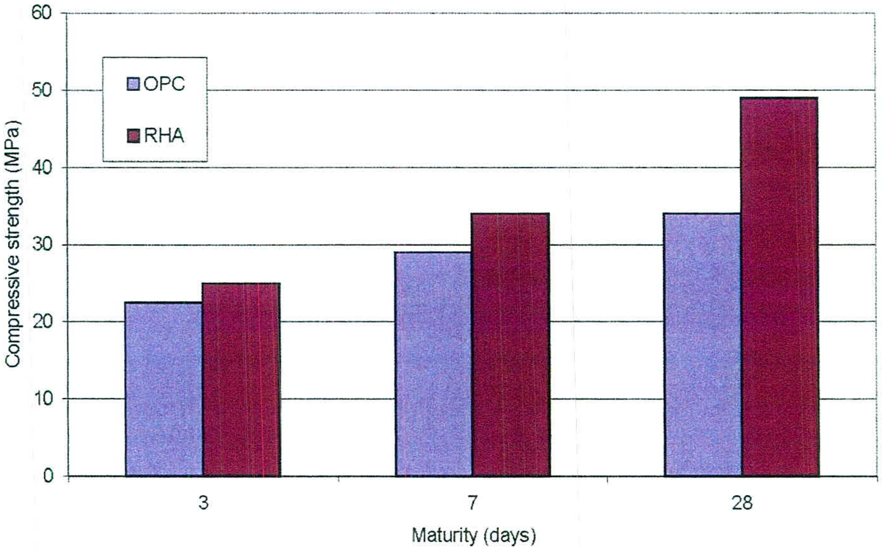

Figure 2.10 Compressive strengths of RHA and OPC [44].

- Resistance against acid attack

RHA cement was exposed to a mixture of 10% Hydrochloric Acid and 10% Sulphuric Acid and was found to have more resistance than did OPC. It is the silica present in the RHA that combines with the calcium hydroxide and reduces the amount susceptible to acid attack as well as reducing permeability.

- Resistance against chlorine

More recent studies have that shown RHA has uses in the manufacture of concrete for marine environments. Replacing 10% Portland cement with RHA can improve resistance to chloride penetration. Capillary suction and accelerated chloride diffusity are also improved by the addition of RHA, as given in Table 2.9.

Table 2.9 Effect of RHA on the resistance of concrete against chloride penetration after one year of exposure to seawater [44].

W/B ratio	Accelerated chloride diffusity ($m^2/s\ 10^{-12}$)		Electrical resistivity (Ohm m)		Effective chloride diffusity ($m^2/s\ 10^{-12}$)	
	Control	RHA	Control	RHA	Control	RHA
0.6	2.4	1.0	31	63	63	2.4
0.5	1.7	0.3	44	107	2.5	1.5
0.4	1.3	0.1	53	172	3.6	1.4

Remark: W/B is Water/ binder.

2.5 Phase Transformations in $CaO\text{-}SiO_2\text{-}H_2O$ System

In cement-based materials, calcium silicate hydrate (CSH) phases are mainly considered to be hydration products in the normal curing process, which are produced from di-calcium silicate (C_2S) and tri-calcium silicate (C_3S). This is because CSH phases are related to the development of compressive strength in cement-based materials. The verities of CSH phases are dependent on the Ca\Si ratio, ranging from 0.8-2.0 [19], and conditions, which have been reported to be highly complex with over 30 crystalline calcium silicate hydrates [45], such as CSH(I), CSH(II), jennite and 1.4 nm tobermorite. 1.4 nm tobermorite is remarkable in that it can be converted to 1.1 nm phases upon heating to 80-100°C; subsequent heating at 300°C for a few hours results in 0.9 nm tobermorite [46]. Nevertheless, it is well known that these products are mostly amorphous and unstable at all temperatures. Under hydrothermal treatment, the metastable CSH gels of appropriate compositions can convert rapidly to crystalline structures, such as 1.1 nm tobermorite ($Ca_5(Si_6O_{16})(OH)_2\cdot 4H_2O$) and xonotlie ($Ca_6(Si_6O_{17})(OH)_2$.

The mechanism of the $CaO\text{-}SiO_2\text{-}H_2O$ system in a hydrothermal reaction was described by Taylor [21]. If there is an absence of reactive silica or if the compound contains a small amount of quartz leads the bulk Ca/Si ratio to be 2.0 and then CSH tends to transform to α-C2S hydrate at above 150°C. This phase is relatively dense and crystallizes as rectangular tablets, however the crystalline material is porous and weak. With larger amounts of quartz or the presence of pozzolanic materials, the calcium hydroxide is consumed and consequently, α-C_2S hydrate is avoided and replaced by a crystalline CSH of low Ca/Si ratio. The other phases revealed under hydrothermal treatment were demonstrated by Hong and Glasser (2004) [19], and are summarized in Fig. 2.11. They synthesized the crystalline CSH phases from $Ca(OH)_2$ and amorphous silica. The optimised preparative conditions are given in Table 2.10.

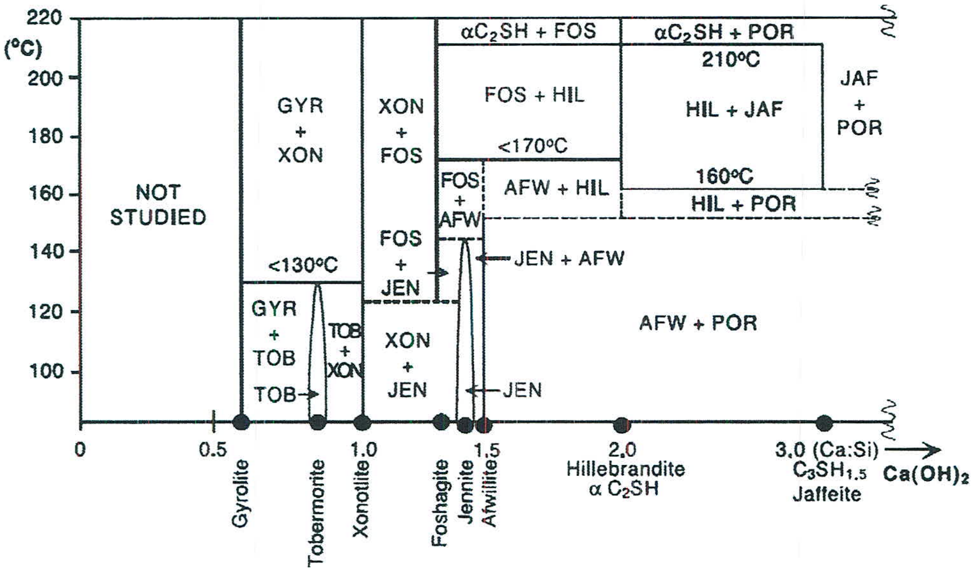

Figure 2.11 Phases relations of hydrated calcium silicates under hydrothermal treatment [19].

Tobermorite, while apparently stable indefinitely at 120°C, begins to break down at temperatures ≥ 130°C, is mainly xonotlite. This phase is relatively weaker than crystalline tobermorite. However, tobermorite is readily synthesised at temperatures well in excess of their stability limit. For example, commercial processes for tobermorite production are often produced at 160-180°C with 12-24 h autoclaving cycles. This reaction product relates with the ingredients in the system, which has own optimum times and temperatures for autoclaving. If these times and temperatures are exceeded, this leads to a decrease in strength. Moreover, Taylor [21] suggested that neither 1.1 nm tobermorite nor α-C_2S hydrate is an equilibrium product in a pure system at 180°C under hydrothermal treatment. In this condition, truscottite, gyrolite, xonotlite, hillebrandite and jaffeite can be formed, which are dependent on compositions. Of these phases, only xonotlite forms readily under autoclaving conditions from mixtures in which the SiO_2 is supplied partly as quartz. This phase shows good thermal stability in air and can be used as autoclaved thermal insulation materials. If amorphous silica is used, such as diatomaceous earth, gyrolite is formed and followed by truscottite at high temperatures while, 1.1 nm tobermorite is formed at Ca/Si ratio of 0.8-1.0.

Table 2.10 Preferred conditions for synthesis of crystalline CSH phases from $Ca(OH)_2$ and amorphous silica [19].

Phase/formula	Ca/Si ratio	Temperature (°C)	Curing time (days)	Pressure
1.1 nm tobermorite/ $Ca_5(Si_6O_{16})(OH)_2{\cdot}4H_2O$	~0.83	140	90	Saturated steam
Xonotlite/ $Ca_5(Si_6O_{17})(OH)_2$	1.0	200	90	Saturated steam
Foshagite/ $Ca_4(Si_3O_9)(OH)_2$	1.33	180	56	Saturated steam
Jennite/ $Ca_9H_2Si_6O_{18}(OH)_8{\cdot}6H_2O$	1.45	85	540	-
Afwillite/ $Ca_3(SiO_3)_2(OH)_2{\cdot}2H_2O$	1.5	85	240	-
Hillebrandite/ $Ca_2SiO_3(OH)_2$	2.0	180	56	Saturated steam
α-C_2S hydrate/ $Ca_2(HSiO_4)OH$	2.0	170	35	Saturated steam
Tricalcium silicate hydrate/ $Ca_6Si_2O_7(OH)_6$	3.0	200	28	Saturated steam