CHAPTER III

CHEMISTRY OF CEMENT

3.1 Chemical Parameters

The essential components of Portland cement clinker are silica, alumina, iron and lime. Clinker manufactured from different raw materials using different processes generally contains the following essential compounds: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and Tetracalcium alumino ferrite (C_4AF).

The raw mix composition has a large influence on kiln performance and any change in the mix, even by 0.2% $CaCO_3$, can cause an upset in the rotary kiln.[14] There is no fixed composition for the raw mix or the clinker, but it is considered economical to keep $Fe_2O_3 + Al_2O_3$ (R_2O_3) at about 42% of SiO_2 and the CaO about three times that of the SiO_2.[14] In general, the kiln feed is divided into two categories:

1. Hard-burning mix: characterized by either high lime or high silica and low flux (iron, alumina, magnesia and alkalies) content. In some cases, raw mixes with high free silica are in this category. Such a raw mix does not promote the formation of coating in the kiln, this results in quick deterioration of the bricks and increases the costs per ton of clinker.

2. Easy-burning mix: characterized by high flux content and by relatively low lime. Such a raw mix promotes the formation of kiln

coating, decreases the kiln shell radiation, increases the service life of bricks, and reduces the cost per ton of clinker.

The hard-burning raw mix requires more heat, generally, heat requirement for drying process is about 850 kcal per kg of clinker,[21] and uses more fuel in order to form a clinker of good quality compared to the easy-burning mix. The former is less profitable because of higher energy consumption and brick replacement. Additionally, it is usually ground finer than easy-burning mix, which increases production costs. To improve the clinkerability of the hard-burning mix, a small percentage of iron should be added, but it may not be available in the vicinity of the plant and may have to be transported a long distance.

The following chemical parameters are used in order to obtain an easy-burning mix and economical cement plant operation.

On the basis of exhaustive investigations Michaelis[21] formulated a characteristic ratio for the composition of raw mixtures for the manufacture of Portland cement, namely:

$$\frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} = 1.7\text{-}2.2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

He called this ratio the hydraulic modulus (H.M.). For "natural" cements the hydraulic modulus is 1.7-2.4.

If the hydraulic modulus is too high, considerable volume changes (expansion) are liable to occur, which may have a disruptive effect on mortar or concrete made with such cement. In the other hand, if the hydraulic modulus is too low, the mortar will tend to be friable and will eventually disintegrate.

In order to achieve a closer definition of the raw mixture composition for Portland cement, Kühl[21] introduced the so-called silica modulus (or silica ratio):

$$\frac{SiO_2}{Al_2O_3 + Fe_2O_3} = 1.2\text{-}4.0^{21} \text{ (average 2.3-2.7)} \ldots\ldots\text{(3.2)}$$

The silica modulus (S.M.) is very important because it affects the behaviour of the raw mix in the kiln and the quality of the clinker. An increase of SiO_2 at the expense of Al_2O_3 and Fe_2O_3 produces a hard-burning mix, boosts fuel consumption[12] and requires a higher temperature for burning as the sintering of the raw mix becomes more difficult. Raw mix with a high S.M. also abrades and deteriorates the kiln linings, tends to produce a slow setting and hardening cement with slower strength-gaining (but a better progression with age), and-unless the silica content is ground finely (which increases production cost)-there may be a tendency to unsoundness (high free lime). All these factors affect the marketing of the produced cement.

Raw mixes with low S.M.'s sinter more easily, tend to form clinker rings, and produce rapid-hardening cement which develops its strength at an early age with little progression with increasing age. Raw mixes with very low S.M's may form a clinker ring which can block the kiln and lead to a serious reduction of clinker output.

There is practically no ideal figure for the S.M. but generally it should range between 2.3-2.7.[14] There are many cement plants burning their raw mixes economically with an S.M. lower or higher than these limits; this depends mainly on the mineralogical composition of the raw mix and the other chemical parameters.

The alumina-iron ratio (iron modulus or alumina modulus):

$$\frac{Al_2O_3}{Fe_2O_3} = 1.0\text{-}4.0 \text{ (average } 1.5\text{-}2.5) \ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

Low alumina modulus (A.M.) facilitates the formation of cement compounds at a lower temperature. A higher A.M. results in harder burning and higher fuel consumption. Iron, in general, has a favourable influence on the formation of the cement compounds, i.e., higher iron content leads to easier burning and cost reduction. A small percentage of iron oxide renders highly silicious raw materials easier to fuse. A large iron content produces a hard, dense clinker which requires more energy to grind in the finish mill, thus increasing the production cost.[13]

A raw mix with high alumina content tends to render cement quick setting and strong at early ages. Substitution of Fe_2O_3 for Al_2O_3, or an increase in Fe_2O_3 content, reduces the proportion of C_3A and increases C_4AF. Cement with low C_3A content have a higher resistance to sea-water and certain other destructive agencies with a low heat of hydration.

Raw mix with low alumina modulus reduces the clinkering temperature and the fuel consumption, increases the liquid phase and kiln production, and helps to produce high C_3S content without too much free lime.[12] If the A.M. is too low and the raw mix is without free silica, the probability of the clinker sticking and balling is high.

For raw mix or clinker calculation, lime Saturation Factor (L.S.F.) is:

$$\text{L.S.F.} = \frac{\text{CaO}}{2.80\text{SiO}_2 + 1.18\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3} \quad \cdots\cdots\cdots\cdots(3.4)$$

CaO should be carefully proportioned with reference to the other constituents of the raw mix. Kiln feed with high lime content is difficult to burn, tends to produce unsound, unacceptable cement, and shows slow setting with high strength at early ages. Raw mixes with low lime content will produce interior-strength cement with low C_3S content and either slow setting (if the mix is over-burned) or quick setting (if the mix is under-burned).

A change of 1.0% in the L.S.F. gives a change in burnability equal to a change of 0.1 S.M. of the same mix.[23]

Raw mixes with low L.S.F.'s correspond to a high C_2S, where all SiO_2 present in high L.S.F. corresponds to C_3S. Raw mixes with low L.S.F. also produce a poor quality cement containing excessive silica and alumina. A raw mix with a high percentage of L.S.F requires high temperature for burning and the resultant clinker will contain high free lime. Reducing CaO and increasing SiO_2 reduces the strength of the cement.

It is usually recommended to keep the L.S.F. of ordinary Portland cement clinker betweeen the range of 0.92 to 0.96[14] to obtain a high quality clinker. Generally, when the L.S.F. and/or S.M. increases and/or the content of MgO and alkalies decreases, the raw mix becomes harder to burn.

Magnesia (MgO) is usually found in cement raw materials in varying amounts and acts as a flux at the sintering temperatures which facilitates burning. A raw mix rich in MgO tends to ball easily in the burning zone, which affects the kiln operation and produces unsound cement unless the clinker is cooled with a grate cooler.

Cement with more than 6% MgO is not acceptable according to ASTM (American Society for Testing and Materials) specifications. Very little cement is sold having more than 5% MgO, as in this case the total silicates are lower than cements with about 2% MgO.

Alkalies (Na_2O and K_2O), sulphur, and chlorides. Alkalies are usually found in cement raw materials, they vary widely in different deposits throughout the world. Alkalies generally promote the formation of coating (rings, in some cases) in the kiln due to their high fluxing characteristics. A 1.0% change in the alkali or MgO content of the kiln feed will produce a change in the raw mix burnability similar to 3.0 multiplied by change in the L.S.F. percentage or to 0.3 multiplied by change in the S.M. of the same raw mix.[23]

Alkalies in cement are usually unfavourable when present in excessive quantities, and/or with unfavourable ratio to sulphur and especially in those countries which have alkali-reactive aggregates. Such countries usually specify that the total alkalies in cement (calculated as Na_2O) should not exceed 0.60%.

Liquid phase: The fluxes (alumina, iron, magnesia and alkalies) generally govern the amount of liquid present in the clinker. They promote fusion and are regarded as fluxes because they serve that purpose. It is known that the reaction, during formation of cement compounds, proceeds more easily with large quantities of flux. Raw mixes with low silica and alumina ratios:

a) Have high amounts of flux and liquid phase.

b) Easily form kiln coating, if the free silica in the raw mix is not high.

c) Are easy to sinter.

d) Produce clinker which is relatively dense.

However, if these ratios are too low, the amount of the flux produced is so large that the clinker is very viscous at the clinkering temperature and difficulties are encountered due to sticking and balling. Although such a raw mix can save fuel during the burning process, the resulting clinker requires more energy for grinding in the cement mills. Hence the saving in fuel is wasted in clinker grinding.

A raw mix with optimum liquid content has higher surface tension and is characterized by higher flowability, which promotes the sintering process and the reaction between the different grains. The clinker produced from such a raw mix and cooled rapidly in a grate cooler has a better clinker microstructure.

Generally speaking, a raw mix with about 25%[6,14] relative potential liquid phase in the clinker is considered an ideal raw mix for kiln lining, fuel savings and economical clinker grinding. The liquid phase is usually calculated by the Lea and Parker formula[16] which is: $2.95Al_2O_3 + 2.20Fe_2O_3 + K_2O + Na_2O + MgO$. This corresponds to the amount of the liquid phase which is formed at 1400°C. This formula is applied with an A.M. higher than 1.38. In the case of an A.M. lower than 1.38, the liquid phase is calculated by the formula: $8.5Al_2O_3 - 5.22Fe_2O_3 + K_2O + Na_2O + MgO$.

Lea[16] has shown that in the case of raw mixes in which the amount of liquid increases slowly with temperature, the clinker range may be fairly wide. In those mixes where the rates of increase of the liquid phase with temperature are rapid, the clinkering range will be small. Portland cement clinker with a rather high iron content is an example of the latter type.

3.2 Proportioning the Raw Materials for Portland Cement.

The first step in proportioning the raw mixture is to determine the silica modulus of the individual raw materials, i.e. the silica modulus of limestone, spent shale and clay. If the values of this modulus are outside the appropriate limits and if the resulting mixture also fails to comply with the requirements in this respect, then it will be necessary to add another material to compensate for the deficiency.

There are many different methods[21] to calculate the mix proportions for either two raw material components or three raw material components. Graphical Determination according to Grün and Kunze[21] is referred. The following is the detail of this determination.

3.2.1 Graphical Determination (according to Grün and Kunze)

A system of co-ordinate axes, as represented in Fig 3.1, is used for the purpose. On the basis of the ignited materials, the percentage of silica (SiO_2) from 0 to 100 is plotted on the horizontal axis (+ x-ordinate) and the percentage of residual lime (CaO) from 0 to 100 is plotted on the vertical axis (± y-ordinate). A line is drawn connecting the points corresponding to 100 percent of CaO and 100 percent of SiO_2 respectively. All conceivable cements must be located within the triangle thus obtained. The boundaries defining Portland cement are determined by the requirement that the cement should have the highest possible content of C_3S. The points corresponding to 100 percent of C_3S and 100 percent of C_2S are marked off on the hypotenuse of the triangle. These points are determined as follows:

3 x (Ca O)	(Si O_2)
3 x (40 + 16)	(28.4 + 32)
168 pts. CaO	60.4 pts. SiO_2
73.6% CaO	26.4% SiO_2
2 x (Ca O)	(Si O_2)
2 x (40 + 16)	(28.4 + 32)
112 pts. CaO	60.4 pts. SiO_2
65% CaO	35% SiO_2

These two points are represented by C_3S (73.6% CaO, 26.4% SiO_2) and C_2S (65% CaO, 35% SiO_2) which are on the hypotenuse of the triangle (Fig 3.1). Next, drawn the lines from the origin 0 to C_3S and C_2S respectively. The "Portland cement region" will then be bounded by O-C_3S, O-C_2S and by the 20 percent and 40 percent flux lines, (The fluxes: alumina, iron, magnesia and alkalies) which run parallel to the hypotenuse. The most favourable cements are those which are close to the C_3S line (O-C_3S). In choosing the distance of the point P from this line it takes into account the chemical composition of the received clinker.

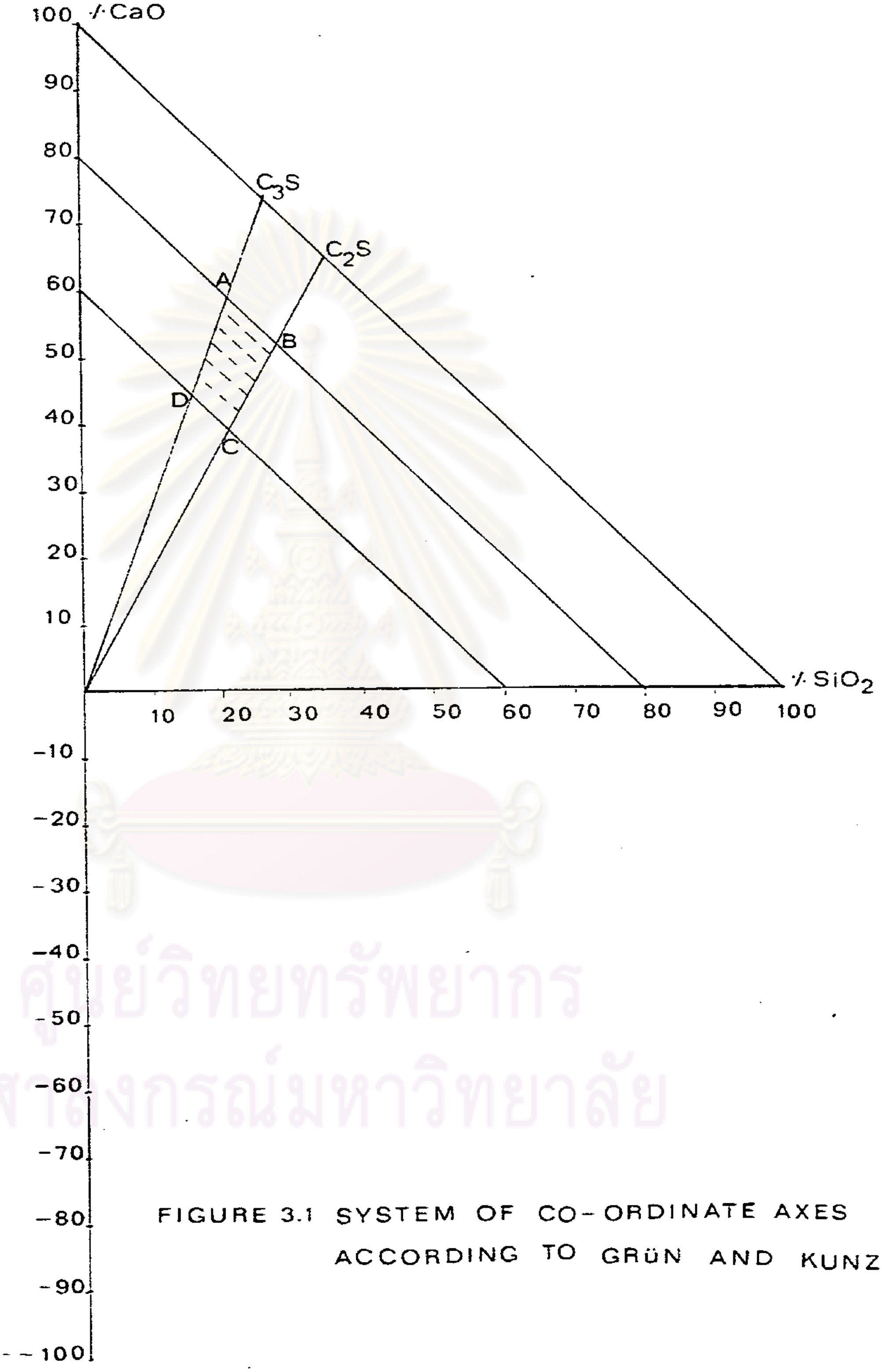

FIGURE 3.1 SYSTEM OF CO-ORDINATE AXES ACCORDING TO GRüN AND KUNZE

3.2.2 Determination of a three-component raw mixture.

This procedure may best be explained with the aid of an example. Ignited material will be considered.

Example: The raw materials are limestone, spent shale and clay which have the following chemical composition. (Appendix A).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI
limestone	1.78	0.65	0.40	53.70	0.91	0.10	trace	42.46
spent shale	41.77	14.67	3.90	17.16	7.78	2.32	1.21	11.19
clay	66.54	15.67	5.08	1.46	2.05	1.95	0.30	6.95

From equation 3.2; $S.M. = \dfrac{SiO_2}{Al_2O_3 + Fe_2O_3} = 1.2\text{-}4.0$

limestone: S.M. = 1.78/(0.65 + 0.4) = 1.695 = 1.70

spent shale: S.M. = 41.77/(14.67 + 3.90) = 2.249 = 2.25

clay: S.M. = 66.54/(15.67 + 5.08) = 3.207 = 3.21

Calculated on the ignited basis:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
limestone	3.09	1.13	0.70	93.33	1.58	0.17	trace
spent shale	47.03	16.52	4.39	19.32	8.76	2.62	1.36
clay	71.51	16.84	5.46	1.57	2.20	2.10	0.32

The values of the residual lime content of the raw materials are plotted in the system (calculated on the ignited basis). The residual lime is computed by deducting from the total lime content the lime that is combined with Al_2O_3 and Fe_2O_3. For determining the lime combined with Al_2O_3, the Al_2O_3 content should be multiplied by 1.65[21], similarly the lime combined with Fe_2O_3 is obtained by multiplying the Fe_2O_3 content by 0.7.[21]

Limestone:

Lime combined with Al_2O_3 = 1.65 x 1.13 = 1.87% CaO
Lime combined with Fe_2O_3 = 0.70 x 0.70 = <u>0.49% CaO</u>
<u>2.36% CaO</u>

Residual lime = 93.33 - 2.36 = 90.97% CaO

Spent Shale:

Lime combined with Al_2O_3 = 1.65 x 16.52 = 27.26% CaO
Lime combined with Fe_2O_3 = 0.70 x 4.39 = <u>3.07% CaO</u>
<u>30.33% CaO</u>

Residual lime = 19.32 - 30.33 = -11.01% CaO

Clay:

Lime combined with Al_2O_3 = 1.65 x 16.84 = 27.79% CaO
Lime combined with Fe_2O_3 = 0.70 x 5.46 = <u>3.82% CaO</u>
<u>31.61% CaO</u>

Residual lime = 1.57 - 31.61 = -30.04% CaO

From figure 3.2, The point K, corresponding to limestone component, is obtained by plotting +90.97 on the vertical axis (% CaO) and +3.09 on the horizontal axis (% SiO_2). The point T, corresponding to spent shale component, is obtained by plotting -11.01 on the vertical

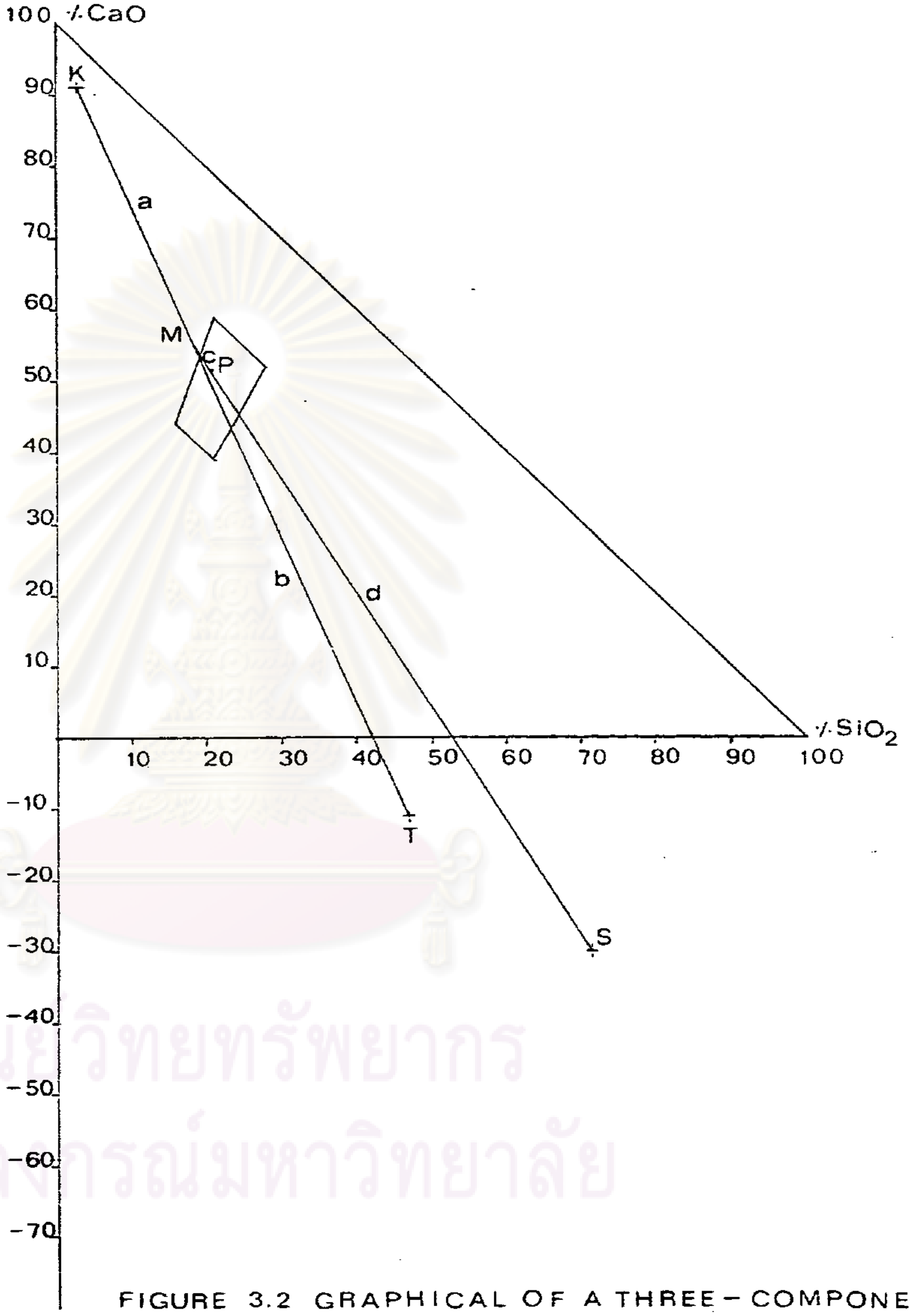

FIGURE 3.2 GRAPHICAL OF A THREE-COMPONENT RAW MIXTURE

axis and +47.03 on the horizontal axis. The point S, corresponding to clay component, is obtained by plotting -30.04 on the vertical axis and +71.51 on the horizontal axis. The lime K-T is drawn. Now the point P is chosen in Portland cement region (ABCD) which defines the envisaged clinker to be produced. Then the line S-P is drawn and extended beyond P until it intersects K-T at M.

Measuring the lines K-M (a), M-T (b), M-P (c) and S-P (d) which will give the proportions of the raw materials calculated on the ignited basis

a = 38.5 mm parts of spent shale

b = 72.0 mm parts of limestone

c = 4.0 mm parts of clay, referred to d

d = 96.0 mm parts of mixture limestone + spent shale

$$(a + b)\frac{c}{d} = 4.60 \text{ parts of clay}$$

Reduced to non-ignited material:

$$\frac{38.50 \times 100}{100 - 11.19} = 43.35 \text{ parts of spent shale}$$

$$\frac{72.00 \times 100}{100 - 42.46} = 125.13 \text{ parts of limestone}$$

$$\frac{4.60 \times 100}{100 - 6.95} = 4.94 \text{ parts of clay}$$

$$= 173.42$$

or in percent:

25.00% spent shale + 72.15% limestone + 2.85% clay

To see the percentage of chemical composition obtained in clinker. Multiply the percentage of each raw material above by their chemical composition

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	L.O.I.
25.00% spent shale	10.44	3.67	0.98	4.29	1.94	0.58	0.30	2.80
72.15% limestone	1.28	0.47	0.29	38.74	0.66	0.07	trace	30.64
2.85% clay	1.90	0.45	0.14	0.04	0.06	0.05	0.01	0.20
Raw meal	13.62	4.59	1.41	43.07	2.66	0.70	0.31	33.64
clinker	20.52	6.90	2.12	64.91	4.01	1.07	0.47	-

3.3 Reaction occurring in cement burning

The raw materials fed to a cement kiln contain calcium carbonate, a little magnesium carbonate, clay or shale and water. The reactions which occur during burning may be classified simply as follows:

1. Evaporation of free water
2. Release of the combined water from the clay
3. Dissociation of magnesium carbonate
4. Dissociation of calcium carbonate
5. Combination of lime and clay

It will be seen that these reactions do not all occur separately, but that 4 and 5 may often overlap and go on together. The essential reaction we shall have to consider in cement burning is 5, but the preliminary actions may first be considered.

Evaporation of free water takes place at, or below, 100°C, but release of combined water from the clay only becomes appreciable above about 500°C.[21] Clays are composed of a number of different hydrated aluminosilicates with ratios of $SiO_2:Al_2O_3$ varying from 2:1 to 4-5:1, some clays also contain ferric oxide as an essential constituent, but attention may be restricted here to one of the simplest of the clay compounds, kaolinite, $2SiO_2.Al_2O_3.2H_2O$. On furthur heating an exothermic reaction occurs at about 970°C variously attributed to the formation of a silicon spinel phase approximating to $2Al_2O_3.3SiO_2$ which converts to mullite above 1000°C by splitting off silica, or to the crystallisation of γAl_2O_3 from amorphous alumina. Mullite is formed at higher temperatures, but in cement burning the reaction with lime takes place before this stage is reached and indeed commences before the exothermic reaction of kaolinite at 970°C.

Magnesium carbonate decomposes at about 600-700°C but the temperatures reported vary considerably with the source of the material used. The decomposition pressure of calcium carbonate, when heated alone, reaches atmospheric pressure at 894°C.

In mixes of calcium carbonate and finely divided quartz reaction occurs very faintly at as low a temperature as 600°C; proceeds very slowly at 800°C, at an appreciable speed at 1100°C, and rapidly at 1400°C. Dicalcium silicate, probably as the α' form, is first formed whatever the ratio of lime to silica in the mix for the formation of the monosilicate is normally slow and is generally a secondary reaction between the disilicate and silica. In mixes of sufficient lime content all the combined silica is present as C_2S by 1200°C. Though the formation of C_3S commences at about 1300°C to 1400°C it proceeds only very slowly even at 1500°C, but the addition of alumina and particularly ferric oxide to the lime-silica mix increases markedly the rate of its production.

When mixes of lime, alumina and silica are heated the first compounds formed are monocalcium aluminate and $\alpha' C_2S$. Products obtained from burning at 1150-1350°C dust down (i.e. crumble) on cooling owing to the formation of γC_2S. Initial melting commences at about 1400°C and at higher temperatures dusting ceases to occur unless the cooling is slow. This may be due to the formation of the relatively more stable αC_2S or to the formation of solid solutions in the C_2S. Formation of C_3A does not occur readily, nor that of C_3S commence, until a temperature of 1300°C is reached. In mixes of CaO, Al_2O_3 and Fe_2O_3 the first iron compound to form at about 800°C is C_2F, followed by a transient appearance of CF between 900°C and 1100°C. Formation of C_4AF spreads over a temperature range of 1100°C to 1250°C. Mixes of CaO, Al_2O_3, Fe_2O_3 and SiO_2 show some evidence of a transient appearance of C_2AS between 1000°C and 1100°C and formation of C_3A and C_4AF beginning at somewhat lower temperatures than in the ternary mixes. The free CaO rapidly decreases above 1330°C as C_3S is formed.

The compound $C_{12}A_7$ is observed between 900° and 1100°C and converts to C_3A at 1100°C upwards. C_3S starts to form between 1200°C and 1300°C and by 1400°C the reaction products are C_3S, C_2S, C_3A, C_4AF and any remaining uncombined lime.

The course of the reactions[21] can probably best be summarised as follows:

Table 3.1 The course of the reactions occurred in cement burning.

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

Table 3.1 can only be regarded as approximate, but it indicates broadly the mode of cement compound formation. Overlapping of some of the stages shown may well occur and any inhomogeneity in the raw mix will tend to increase it. Formation of C_3S does not occur to any appreciable extent until liquid is present in the mix at 1260°C and above. No formation of this compound, even by solid reaction, is indeed to be anticipated much below this temperature in view of its instability at lower temperatures. The formation of C_3S becomes complete about 1350°-1450°C when the free lime remaining is reduced to a small quantity. When the clinkering temperature is reached most, if not all, of the alumina, ferric oxide and minor components will have passed into the liquid and the only solids present are C_3S, C_2S and often, a little free calcium oxide.

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

3.4 Thermo-chemistry of cement formation

The basic thermo-chemical data in cement formation of heat is absorbed or evolved.

Table 3.2 Thermo-chemistry of cement formation.

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