DU TOIT, PIETER

EXAMINATION AND INTERPRETATION OF PORTLAND CEMENT CLINKERS BY MICROSCOPY AS AN AID TO PROCESS CONTROL

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Examination and interpretation of Portland cement clinkers by microscopy as an aid to process control

by

Pieter du Toit

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SUMMARY

Examination and interpretation of Portland cement clinkers by microscopy as an aid to process control

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Pieter du Toit

Promoter: Prof E B Förtsch
Geology Department

Presented in part fulfillment of the requirements for the degree Philosophiae Doctor

Microscopy has proven to be a relevant method in the elucidation of problems that occur during Portland cement clinker manufacture. In addition to describing the basic Portland cement clinker manufacturing processes, the thesis sets out the laboratory methods for sample preparation and microscopic examination.

The raw materials and cement clinkers were examined using a variety of microscope techniques and the features observed described. Microscopy of Portland cement clinker has only been used in South Africa to a limited extent and this was the first systematic investigation to characterise both the raw materials and the resultant Portland cement clinker by microscopy means. The advantage to the manufacturing industry is that the quality of the end product can be improved.

The quality of the cement clinker is determined by various factors such as the raw feed composition, fineness and homogeneity, and the kiln burning and cooling conditions. Microscopic examination was carried out to analyse the kiln feed, to

evaluate powder mounts of cement clinker according to the Ono method and to interpret the microstructures observed in polished sections. The quality of the cement clinker can be improved in many instances if attention is paid to details of the microscopic examination and appropriate action taken to change the manufacturing process based on the results of the examination.

Two case studies are discussed to demonstrate the practical application of cement clinker microscopy. In the one study, the quality of cement clinker can be improved by carefully controlling the fineness of the kiln feed. In the other study, microscopy assisted in the selection of alternative raw materials for cement clinker manufacture.

The case studies have shown that theoretical knowledge gained in the study of South African cement clinkers and numerous overseas samples has been used in a practical environment to improve the quality and consistency of cement clinker.

Cement clinker microscopy has a major role to play in the quality control of the cement manufacturing process. Cost savings can also be effected through clinker microscopy. For it to be used to optimal benefit, microscopic examination should take place on a regular basis, i.e. daily or on a shift basis.

OPSOMMING

Ondersoek en interpretasie van Portlandsementklinker ter ondersteuning van prosesbeheer met behulp van die mikroskoop

deur

Pieter du Toit

Studieleier: Prof E B Förtsch
Department Geologie

Voorgelê ter gedeeltelike vervulling van die vereistes vir die graad Philosophiae Doctor

Dit is bewys dat die mikroskoop met welslae gebruik kan word in die verklaring van probleme wat voorkom tydens die vervaardiging van Portlandsementklinker. Basiese sementklinkervervaardigingsprosesse word in die proefskrif beskryf. ’n Uiteensetting van laboratoriummetodes wat gevolg is vir monstervoorbereiding en -ondersoek met behulp van ’n mikroskoop, word ook gegee.

Die grondstowwe en sementklinker is ondersoek deur middel van ’n verskeidenheid mikroskooptegnieke en die kenmerke daarvan word beskryf. Mikroskopie is nog net in baie beperkte mate in Suid-Afrika gebruik om sementgrondstowwe en sementklinker te ondersoek. Hierdie is die eerste sistematiese poging om beide die grondstowwe wat gebruik word in die vervaardigingsproses en die klinker wat daaruit voortvloei te karakteriseer met behulp van die mikroskoop. Die voordeel van hierdie toepassing vir die sementbedryf is dat die gehalte van die eindproduk verbeter kan word.

Die gehalte van die Portlandsementklinker word bepaal deur verskeie faktore soos die samestelling, fynheid en homogeniteit van die grondstof, en die brand- en afkoeltoestande van die oond. Mikroskopiese ondersoek is uitgevoer om die grondstof te ontleed, om poeiermonterings van die sementklinker volgens Ono se metode te evalueer, en die mikrostrukture waargeneem in gepoleerde stukke te interpreteer. Die gehalte van die sementklinker kan in baie gevalle verbeter word indien ag geslaan word op die bevindings van die ondersoek met behulp van 'n mikroskoop. Tydige stappe kan dan gedoen word om die vervaardigingsproses aan te pas.

Twee gevallestudies word bespreek om die praktiese toepassing van sementmikroskopie te demonstreer. In die een studie kan die gehalte van sementklinker verbeter word deur die fynheid van die grondstof noukeurig te beheer. In die ander studie het mikroskopie bygedra tot die selektering van alternatiewe grondstowwe vir Portlandsementklinkervervaardiging.

Die gevallestudies het getoon dat die teoretiese kennis opgedoen in die ondersoek van Suid-Afrikaanse sementklinkers en verskeie buitelandse monsters prakties toegepas kan word om die gehalte en bestendigheid in vervaardiging van Portlandsementklinker te verbeter.

Portlandsementklinkermikroskopie kan 'n betekenisvolle rol vervul in die gehaltebeheer van die sementklinkervervaardigingsproses. Kostebesparings kan ook teweeggebring word deur die gebruik van klinkermikroskopie. Om dit optimaal te benut, behoort mikroskoopondersoeke op 'n gereelde grondslag plaas te vind, dit wil sê, daagliks of tydens elke skof.

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1. INTRODUCTION

A problem often encountered in the South African cement industry is the production of Portland cement clinker of inconsistent quality. If the quality of the resultant cement is inconsistent, then problems could arise in the use of the cement in concrete manufacture. Variations in cement quality could also arise due to changes in raw material quality. The quality of the Portland cement clinker could also be dependent on the type of process or kiln in which it is manufactured.

This thesis sets out to show that microscopy can be used to make improvements in most stages of Portland cement clinker manufacture, from raw material preparation to clinkering. This would result in the production of a more consistent and better quality Portland cement clinker. By manufacturing Portland cement clinker under optimum conditions, cost savings in the manufacturing process can be achieved, from more efficient material preparation, to savings on refractory life in the kiln.

In order to interpret microscopic findings in Portland cement clinker manufacture, one needs to have a good understanding of each stage in the manufacturing process of Portland cement clinker. The manufacturing process is described in terms of raw material preparation, heat treatment and cooling.

A brief historical review is given of the development of kiln systems, from the original wet process to the modern pre-calciner process. Each stage in the manufacturing process is described.

All the analytical techniques available for the analysis of raw materials and Portland cement clinker need to be understood to be able to know which technique is best suited for the required purpose. The most common analytical and laboratory techniques used worldwide are described. Of these, the Bogue calculation, wet chemistry, chemical separation and microscopy have been used in this study.

Sampling and various preparation techniques are discussed with particular emphasis on selective chemical dissolution of kiln feed and polishing of epoxy-impregnated Portland cement clinker for microscopic examination.

Samples of raw materials (kiln feed) and Portland cement clinker from 5 South African plants and 6 overseas plants have been examined using transmitted and incident light microscopy. The characteristics of the Portland cement clinker phases and the relationship between microstructures observed and manufacturing processes are described.

The knowledge gained from the examination of raw materials and Portland cement clinkers was used in practice to examine materials from two South African plants. Recommendations to alter and/or modify process parameters were made.

Four publications are recommended for reading on the subject of Portland cement clinker microscopy. These are by Gille et al. (1965), Hofmänner (1973), Fundal (1980) and Campbell (1986).

2. NOMENCLATURE

2.1 INTRODUCTION

Cement chemists use an abbreviated notation to express chemical formulae. The notation is a simplification of the actual formulae as used by earth scientists. For example, in cement chemistry Ca_2SiO_4 can be written as $2CaO.SiO_2$ and is further abbreviated to C_2S. The original formulae and abbreviations are given in Table 1.

Portland cement clinker phase names used by cement chemists may not be recognised by earth scientists. However, Portland cement clinker terminology developed over the last century as a result of greater understanding of the chemistry and formation of the phases and the development of microscopic techniques. The history of Portland cement clinker terminology is discussed in Section 2.3. For ease of reference the names of the equivalent geological mineral species (if found in nature) are given in Table 1.

2.2 NOMENCLATURE

Set out in Table 1 are the chemical formulae, clinker phase name, abbreviations and names of the equivalent mineral species. In some instances, there is debate as to the mineral equivalent of the Portland cement clinker phase, and for this reason, a reference is given as to where the mineral equivalent is mentioned in literature.

Table 1. Portland cement clinker nomenclature

	Formula	Clinker phase name	Abbreviation	Mineral/Group Name	Reference
Major clinker phases	$3CaO.SiO_2$	Alite	C_3S	Hatrurite	Kolodny, 1979.
	$2CaO.SiO_2$	Belite	β C_2S	Larnite	Nurse, 1952.
	$2CaO.SiO_2$	Alpha belite	α C_2S	Nagelschmidtite	Taylor, 1990.
	$2CaO.SiO_2$	Alpha prime belite	α' C_2S	Bredigite	Nurse, 1952.
	$2CaO.SiO_2$	Gamma belite	γ C_2S	Calcio-olivine group	Nurse, 1952.
	$3CaO.Al_2O_3$	Calcium aluminate	C_3A	No equivalent	Nurse, 1952.
	$4CaO.Al_2O_3.Fe_2O_3$	Ferrite	C_4AF	Brownmillerite	Hansen et al, 1928, cited by Lea, 1956.
	MgO	Periclase	M	Periclase	Taylor, 1990.
	CaO	Free lime	C	Lime	Taylor, 1990.
Minor clinker phases	K_2SO_4	Arcanite	$K\bar{S}$	Arcanite	McGinnety, 1972 cited by Taylor, 1990.
	$K_2Ca_2(SO_4)_3$	Ca-Langbeinite	$K_2C_2\bar{S}_3$	Ca-Langbeinite	Swanson et al, 1969 cited by Taylor, 1990.
	$(Na,K)_2SO_4$	Aphthitalite	$(N,K)\bar{S}$	Aphthitalite	Okada and Ossaka, 1980 cited by Taylor, 1990.
	Na_2SO_4	Thenardite	$N\bar{S}$	Thenardite	Newkirk, 1952.

2.3 HISTORY

The nomenclature used in the literature with regard to Portland cement clinker terminology has a long history.

Lea (1956) points out that clinker microscopy probably has its origins as far back as 1883 with the publication of the first paper by Le Chatelier (1883). In later work by Le Chatelier (1905) and Törnebohm (1897), both cited by Lea (1956), the former identified four and the latter five phases in Portland cement clinker. These phases were named alite, belite, celite, felite and isotropic residue (Insley and Frechette, 1955).

In the period 1910 to 1940, several workers including Rankin and Wright (1915), Assarsson and Sundius (1929), Guttmann and Gille (1931), all cited by Lea (1956), and Schwiete and Büssem (1932), and Brownmiller and Bogue (1930) cited by Campbell (1986), identified Törnebohm's minerals as follows:

Alite	C_3S
Belite	C_2S
Felite	C_2S
Celite	C_4AF
Isotropic residue	C_3A

Tavasci (1934), cited by Campbell (1986), was largely responsible for developing the techniques for the examination of polished sections and the use of etching solutions, and classified the various forms of belite.

Insley (1936), improved on Tavasci's classification of the morphology of belite (dicalcium silicate) and this classification is still used today. Insley's work on clinker phases forms the basis for many other people's work in this field.

Other workers (according to Insley and Frechette, 1955 and Campbell, 1986) who made significant contributions to the techniques and results of microscopic observation of Portland cement clinker were Brown (1937), Bates and Klein (1916-1917), Parker and Nurse (1939), Radczewski and Schwiete (1938) and Ward (1941), all cited by Insley and Frechette, 1955, and Taylor (1943), Gille (1955), Krämer (1969) and Midgley (1964), all cited by Campbell (1986).

3. PORTLAND CEMENT CLINKER MANUFACTURE

3.1 GENERAL

John Smeaton can be credited with the discovery in 1756 of why some limes were hydraulic and others not (cited by Bogue, 1955). He understood that a hydraulic cement must contain a mixture of limestone and clayey material. However, he did not patent this material. Many attempts were made to improve the material of Smeaton during the following 68 years, and in 1824 Joseph Aspdin patented Portland Cement. Aspdin's product did not differ significantly from that produced by Smeaton and other workers. The name Portland cement was derived from its resemblance to Portland stone used for building purposes.

The Portland cement developed by Aspdin and others was manufactured in vertical bottle or shaft kilns. After grinding the limestone/clay mixture in a slurry, brick size pieces were cut from the dried material and stacked with layers of coke in the vertical kiln for burning. The burnt material was then ground to a powder for use.

Although economical in fuel, vertical kilns were very labour intensive and operated on a batch basis. To save labour costs, experimentation in continuous vertical and horizontal kilns took place. This eventually led to the patenting of the first successful rotary kiln by Frederick Ransome in 1885 (Peray, 1986). Portland cement was produced in this horizontal kiln at Grays in the United Kingdom in 1885 and approximately 10 years later at Coplay in the United States of America (Bogue 1955). Portland cement clinker produced during this time was almost exclusively by the wet process, in which the raw materials were ground in a slurry form and fed into the kiln in a slurry, the water being required for pumping, mixing and blending. All the water added in the preparation of the kiln feed had to be removed (evaporated) during the manufacturing process. The dry process, in which all the grinding and mixing was done in the dry state, was developed later and used less energy (fuel consumption) to manufacture Portland cement clinker.

The rotary kiln is a cylindrical, refractory-lined, steel shell which rotates slowly about an axis which is inclined a few degrees from the horizontal.

The prepared raw material feed is introduced at the upper "back" end, from which it is transported by the slope and rotation of the kiln to the lower, hotter, end. Here a flame is maintained by injecting pulverised coal, liquid fuel or gas through a burner pipe in the nose of the kiln. During the heating-up and burning processes there occur decomposition reactions, phase transformations and the formation of the Portland cement clinker minerals from the raw materials. The Portland cement clinker is then cooled in a special cooler where air is drawn across or through the Portland cement clinker. From the cooler the Portland cement clinker is transported to storage. A small amount of gypsum (natural or synthetic) is ground together with the Portland cement clinker to make cement, which is stored in silos prior to despatch either as bulk or in bags. Figure 1 shows a flow diagramme of a typical dry process Portland cement manufacturing plant (KHD Humboldt Wedag trade literature). The schematic diagramme shows the quarrying operation and the preparation of the raw materials (top left), before storage in silos (middle right). The raw material is processed in the kiln (centre) before being stored in a clinker store (bottom left). The

Portland cement clinker is ground with gypsum to produced Portland cement and stored in silos before being despatched (bottom right).

3.2 RAW MATERIALS

3.2.1 TYPES OF MATERIAL

The starting materials for Portland cement clinker manufacture are those which contain lime (CaO), silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3). These components are seldom found in one raw material and therefore, most Portland cement manufacturing plants use a mixture of one calcareous and one argillaceous material for Portland cement clinker manufacture. The most common rock types containing the calcium oxide required for Portland cement clinker manufacture are limestone, marl and chalk. In the raw material (of correct composition for Portland cement clinker manufacture), the CaO content is generally between 70 and 80 per cent, thus a wide range of composition of limestone, chalk and marl may be used to manufacture Portland cement clinker. Texturally, limestones and marls are predominantly fine-grained crystalline rocks while chalk, being of organic origin, is usually a soft material. Argillaceous material (normally clay or shale) is the other major raw component for Portland cement clinker manufacture and can occur as many different mineral phases.

In both the major clay mineral groups (two-layer and three-layer types) however, the main oxides present are alumina and silica.

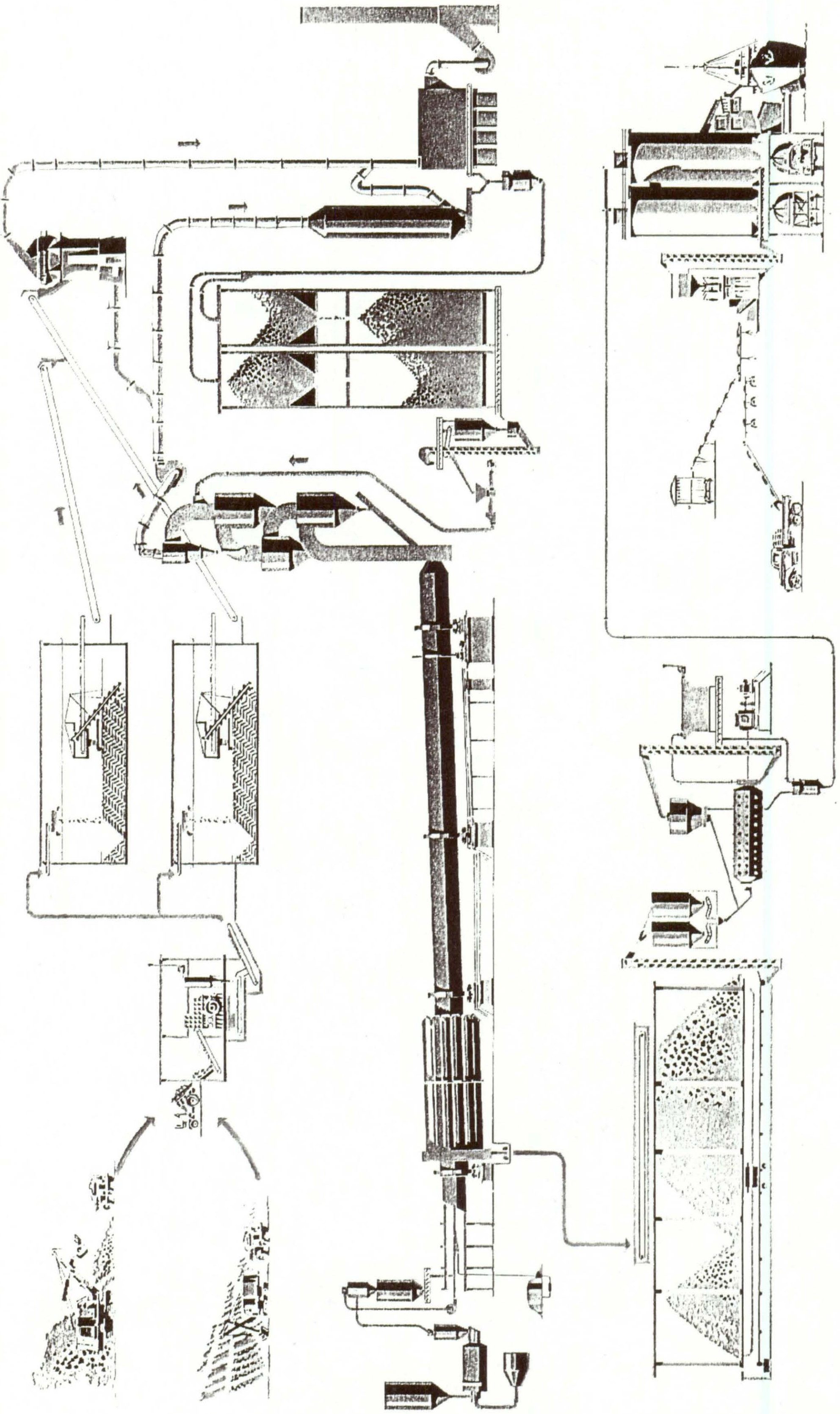


Figure 1. Schematic flow diagramme of a dry process cement plant

Several components that may be deleterious both in the manufacturing process and in the manufactured product are naturally present in the raw materials. These include magnesium oxide, potassium oxide, sodium oxide, sulphur and chlorine. In addition to the quantities of MgO and C_3A being specified in the finished product, the quantities of deleterious chemical components, eg. alkalis, are also controlled by specification.

The fuel used in the Portland cement clinker manufacturing process can be either solid, liquid or gaseous. Of the three, solid fuel requires the most preparation before it can be used.

Generally, the South African cement industry uses secondary limestones as the source of lime (CaO) for Portland cement clinker production. The other oxides (SiO_2, Al_2O_3 and Fe_2O_3) are usually derived from impure limestones or argillaceous materials. Sand (SiO_2), bottom ash (Al_2O_3) and magnetite or mill scale (Fe_2O_3) can be used to adjust the composition of the raw materials to produce a kiln feed of suitable composition.

3.2.2 PREPARATION

The raw materials are usually blasted in the quarry operation and then crushed down to a size range where they can be transported to the cement plant and ground down to the size required for blending and further processing.

The machinery used for the crushing operation can utilise two principles viz. compression (jaw crushers or gyratory crushers), or impact (hammer mills or impact crushers). The crushing operation can take place in one single pass or may be a closed circuit operation in which the oversized material is returned to the crusher.

The grinding operation is usually carried out at the cement plant and again a variety of machinery is used, viz. ball mills, tube mills and bowl mills. Both open circuit (one pass) and closed circuit grinding is used. The fineness of the raw materials, which are somewhat dependent on the type of kiln system, are usually ground so that 97 to 99 per cent passes through a 300-μm sieve and 88 to 90 per cent passes through a 90-μm sieve. If solid fuel, normally coal, is used for firing the kiln, it is ground so that about 90 per cent passes through a 90-μm sieve. These fineness parameters for raw materials and coal are generally used in the South African cement industry.

3.2.3 COMPOSITION

The chief constituents of the raw mix are limestone, sand (quartz) and clay minerals and their relative proportions must be calculated in order to produce a Portland cement clinker with the correct chemical and mineralogical composition. The chemical composition of a typical kiln feed from a South African cement plant (Blue Circle, Lichtenburg), is given in Table 2.

Table 2. Chemical composition of a typical kiln feed

Oxide	Per cent
CaO	44,38
SiO_2	14,30
Al_2O_3	3,03
Fe_2O_3	1,11
MgO	0,59
SO_3	0,07
K_2O	0,52
Na_2O	0,13
LOI	35,86
Total	99,99

Apart from the importance of the composition of the raw materials and their correct proportioning, an important consideration is the composition of the coal because coal ash is absorbed by the Portland cement clinker in the case of coal fired kilns (Duda, 1976). Generally, coal ash is high in SiO_2, and the absorption of the coal ash into the Portland cement clinker will effectively decrease the lime saturation factor and increase the silica ratio (see section 3.2.4 for further explanation of these control moduli). The composition of the kiln feed is adjusted accordingly to take into account the composition of the coal ash.

3.2.4 CHEMICAL CONTROL PARAMETERS (MODULI)

Several parameters are used to control the chemical composition of the kiln feed, the most common being based on the calculation of the lime saturation factor (LSF), silica ratio (SR) and alumina ratio (AR). Conventionally, LSF is expressed as a percentage whilst SR and AR are presented as ratios. The sensitivity of LSF as a controlling parameter necessitates this convention. The percentage of liquid at 1 450 °C and the burnability index are other parameters which give an indication of how easily the raw materials will convert to Portland cement clinker (i.e. the burnability of the kiln feed).

Although these formulae only take into account the four major oxides (CaO, SiO_2, Fe_2O_3 and Al_2O_3), minor oxides also play a role in the burnability of the kiln feed and the formation of the clinker phases. The effects of some common non-volatile compounds are given in Table 3 (after Chatterjee, 1991). Volatile compounds which may also have an effect on the formation of the Portland cement clinker phases include alkalies (potassium and sodium), sulphur compounds, phosphorous pentoxide, fluoride and chloride.

The theoretical LSF formula, which is an approximate method to calculate the maximum amount of CaO required to combine with the acidic oxides to form the phases C_3S, C_3A and C_4AF and disregards the proportions of each phase, is represented as a percentage ratio.

$$LSF\ (\%) = \frac{100\ CaO}{2{,}8(SiO_2) + 1{,}65(Al_2O_3) + 1{,}4(Fe_2O_3)}$$

where $3CaO.SiO_2 : 3CaO/SiO_2 = 168{,}24/60{,}08 = 2{,}80$
$3CaO.Al_2O_3 : 3CaO/Al_2O_3 = 168{,}24/101{,}96 = 1{,}65$
$4CaO.Fe_2O_3 : 4CaO/Fe_2O_3 = 224{,}32/159{,}70 = 1{,}4$

In practice however, this would result in free CaO existing in equilibrium with the liquid. Lea and Parker (1935), cited by Lea (1970), have derived an empirical formula based on their own experimental work, while numerous other workers, including Guttmann and Gille (1929), Kühl (1929) and Hendrickx (1922), all cited by Lea (1970), have derived their own empirical formula which attempt to address the balance of phases in Portland cement clinker.

Table 3. Role of non-volatile compounds on clinker formation

Oxide	Limiting range	Preferred limit	Effect of high content
SiO_2 (free quartz)	0 - 3%	As low as possible	Increased power and fuel consumption Difficult coating formation Deterioration of coating formation Increased radiation of heat from kiln shell Increased kiln exit-gas temperature
MgO	0 - 5%	0 - 2%	Reduced viscosity of liquid C_3S formed more quickly Increases C_3S and melt Clinker balls easily in burning zone Periclase formed when M > 2%
TiO_2	0 - 4%	1,5 - 2%	Reduction in C_3S content Reduced viscosity and surface tension of melt Grain size of C_3S and C_2S reduced Slower setting times and lower strength in cement Forms darker colour clinker
Mn_2O_3	0 - 4%	1,5 - 2%	Viscosity of melt reduced C_3S crystal size reduced Early strength of cement reduced

The proportions of the acidic oxides have therefore been reduced and the empirical formula gives the maximum CaO content that can be present in equilibrium with the liquid without free CaO present (Lea, 1970).

$$LSF\ (\%) = \frac{100\ CaO}{2{,}8(SiO_2) + 1{,}2(Al_2O_3) + 0{,}65(Fe_2O_3)}$$

The LSF may be calculated for both the raw material and the clinker. Usually, the LSF is calculated on the Portland cement clinker and if deviations occur, the proportions of the raw materials are adjusted to correct the LSF. The ideal range for LSF on the clinker is between 92 and 96 per cent. Generally, an increase in the LSF makes the material more difficult to burn since there is more CaO to combine, although it also increases the amount of C_3S in the clinker.

The SR is calculated as follows :

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

The AR is calculated as follows :

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

The influence of the SR and AR on clinker formation is closely related, and generally controls the amount of liquid phase present during clinker formation. The SR can give an indication of the "quality" of the liquid phase, while the AR gives an indication of the "quantity" of the liquid phase. Raw materials which produce about 25 per cent liquid phase in the clinker are considered an ideal raw mix in terms of kiln lining, fuel saving, rapid C_3S formation (through the dissolution of C_2S and free CaO), and economical clinker grinding (Chatterjee, 1991).

Generally, a higher SR results in harder burning and higher fuel consumption and causes difficulty in coating formation. A high AR increases the proportion of C_3A and reduces the C_4AF.

3.2.5 FINENESS AND HOMOGENEITY

The fineness of the kiln feed is important because the temperature at which the minerals will satisfactorily combine is a function of the maximum size of the particles - the larger the particles, the higher the temperature required for total combination. Typically, the size range of particles in the raw feed varies from 1 to 200 μm (Chatterjee 1979). Heilmann (1952) indicated that the upper limit for raw feed size is approximately 100 μm and that no more than 1 per cent quartz and 6 per cent calcite (or limestone) should be coarser than this.

Work done by Dorn (1978) has shown that the upper limit for the size of the raw feed should be 45 μm for quartz and 125 μm for calcite. Burnability problems (i.e. the inability of the components to combine completely) can occur if the material is coarser than these limits.

The lower limits for material fineness are normally dependent on the type of kiln system, because too fine a raw mix will cause material flow problems in pre-calciner kiln systems. Generally, the raw mix is only ground as fine as is required because it is costly to grind too fine when it is unnecessary to do so. The limits for coarseness of specific components as given by Heilmann (1952) and Dorn (1978) are theoretical, whereas those given in section 3.2.2 Preparation, are those generally used in practice in modern cement plants in South Africa.

The importance of the fineness of the raw mix is discussed under Section 3.2.6 Burnability, below.

Homogeneity of the raw feed is important because if segregation of the quartz and calcite occurs, there will be portions in the clinker that will be rich in either silica or calcium. The Portland cement clinker minerals cannot be formed in the burning zone of the kiln due to this segregation, and the resulting clinker will be of inferior quality (Dorn, 1987).

3.2.6 BURNABILITY

Burnability is the ability of a cement raw mix to produce a good quality clinker. The process as a whole depends not only on the physical, chemical and mineralogical characteristics of the raw material, but also on the implied burning and cooling conditions (Kiesser et al., 1979). It is also an indication of how much fuel is required to burn the kiln feed into a good quality clinker.

The reactions which take place in the kiln and cooler are primarily a function of temperature and time of residence of the material in the processing system. These reactions are also influenced by the density, volume and motion of the material in the kiln.

Many papers have been written on the influence of mineralogy and chemistry on burnability and there are a number of ways to determine the burnability of a raw mix.

The burnability index (BI) according to Peray and Waddell (1972) is based on the potential clinker compounds as follows:

$$BI = \frac{\% C_3S}{\% C_4AF + \% C_3A}$$

The higher the content of C_3S with corresponding lower C_3A and C_4AF contents, the harder the burnability. Typically, for the South African cement industry a BI of between 3,5 and 5,0 would indicate a good burnability.

Theissen (1992) defines the raw mix burnability as the content of free lime remaining in the clinker for a particular raw mix after a specific heat treatment, obtained through either chemical or optical methods, compared with the free lime content in clinker resulting from a standard raw mix treated in exactly the same way. In Theissen's formula, the chemistry and three groups of minerals (limestone >125 μm, quartz >45 μm and acid insoluble minerals >45 μm), are important.

The parameters determined are used in the following burnability formula:

$$Free\ CaO = 0{,}343(LSF-93) + 2{,}74(SR-2{,}3) + 0{,}10C_{125} + 0{,}83Q_{45} + 0{,}39Aq$$

Where LSF = Lime saturation factor
SR = Silica modulus
C_{125} = per cent limestone $>125\ \mu m$
Q_{45} = per cent quartz $>45\ \mu m$
Aq = per cent acid-insoluble residue $>45\ \mu m$

Miller (1981) uses the same parameters but in different proportions in the following formula:

$$\%\,Free\,CaO = 0{,}31(LSF-100) + 2{,}18(SR-1{,}8) + 0{,}73Q_{45} + 0{,}33C_{125} + 0{,}34Aq$$

In both Theissen's and Miller's formulae, the higher the free lime content, the more difficult it will be to burn the raw mix.

The burnability of a raw mix can also be evaluated by estimating the amount of liquid phase present at 1 470 °C. One formula is given by Peray (1986) as follows:

$$\%\ Liquid = 1{,}13C_3A + 1{,}35C_4AF + MgO\ (\max 2\%) + alkalies$$

For the South African industry, a liquid content of between 20 and 24 per cent would indicate a good burnability.

Krupp Polysius, who are process engineers and equipment suppliers to the cement industry, determine a Burnability Index (BI) where the actual amount of free CaO is determined in laboratory burnt pellets at different temperatures. The values for free CaO are put into the formula:

$$BI = \frac{\Sigma\ \%FrCaO@1350°C + 1400°C + 1450°C + 1500°C}{(\%FrCaO@1350°C/\%FrCaO@1500°C)^{0,25}}\ x\ 3{,}73$$

The assessment of the raw meal burnability on the basis of the BI is set out in Table 4.

Table 4. Classification of burnability

BI	Burnability	Symbol
< 60	Very easy	VE
60 - 80	Easy	E
80 - 100	Normal	N
100 - 120	Somewhat difficult	SD
120 - 140	Difficult	D
140 - 160	Very difficult	VD
> 160	Extremely difficult	ED

Blue Circle Industries PLC refer to a combinability temperature to determine the ease with which a raw mix will combine to form clinker. Values of free CaO determined from laboratory burnt pellets are plotted on a graph. From the resulting curve, the temperature is read off at which the free CaO content is 2 per cent, and this is defined as the Combinability Temperature.

3.3 HEAT TREATMENT

3.3.1 ENERGY REQUIREMENTS

According to Taylor (1990), "the theoretical amount of heat needed to produce one kilogram of clinker from typical raw materials is approximately 1 750 kJ". Of course, additional heat is required because heat is retained in the clinker, kiln dust and exit gases leaving the system. Heat is also lost from the plant by radiation from the kiln shell.

The dry process of clinker manufacture requires less energy than the wet process because there is less water to be evaporated.

Table 5 shows typical values for the energy requirement for wet- and dry-process kilns (Taylor, 1990).

Table 5. Heat requirement in dry and wet process kilns

Process	Dry (kJ/kg)	Wet (kJ/kg)
Theoretical heat requirement	1 807	1 741
Evaporation of water	13	2 364
Heat lost in exit gases and dust	623	753
Heat lost in clinker	88	59
Heat lost from cooler	427	100
Heat lost by radiation and convection	348	682
Total	**3 306**	**5 699**

The heat requirements given in Table 5 do not include the energy requirement for grinding the Portland cement clinker to produce cement.

3.3.2 ENTHALPY REQUIREMENTS

The section on enthalpy requirements is based on Taylor (1990) and Taylor (1995).

To calculate the enthalpy of formation for Portland cement clinker it is necessary to know the standard enthalpies of two sets of reactions, namely, those in which the oxides are formed from the raw materials, and those in which the products are formed from the oxides.

The standard enthalpy change for the formation of 1 kg of each component (raw material or product) is given in Table 6 (modified from Taylor, 1990).

Table 6. Standard enthalpies of reaction

Raw materials to oxides	ΔH (kJ)	For 1 kg of
$CaCO_3 \rightarrow CaO + CO_2$	+ 1 782	$CaCO_3$
$OH_2Al_2Si_4O_{10}$ (pyrophyllite) $\rightarrow \alpha\text{-}Al_2O_3 + 4SiO_2 + H_2O$	+ 224	AS_4H
$OH_4Al_2Si_2O_5$ (kaolinite) $\rightarrow \alpha\text{-}Al_2O_3 + 2SiO_2 + 2H_2O$	+ 538	AS_2H_2
$2FeO.OH$ (goethite) $\rightarrow \alpha\text{-}Fe_2O_3 + H_2O$	+ 254	$FeO.OH$
Oxides to products	**ΔH (kJ)**	**For 1 kg of**
$2CaO + SiO_2 \rightarrow \beta\text{-}C_2S$	- 734	C_2S
$3CaO + SiO_2 \rightarrow C_3S$	- 495	C_3S
$3CaO + \alpha\text{-}Al_2O_3 \rightarrow C_3A$	- 27	C_3A
$6CaO + 2\alpha\text{-}Al_2O_3 + \alpha\text{-}Fe_2O_3 \rightarrow C_6A_2F$	- 157	C_6A_2F

The quantities of the theoretical raw materials and theoretical products needed to produce 1 kg of Portland cement clinker are given in the top section of Table 7. In order to calculate the enthalpy of formation of 1 kg of Portland cement clinker, the ΔH (kJ) values for the standard reactions (Table 6) are multiplied by the amount of material required.

The total enthalpy change (bottom section of Table 7) is the difference between the enthalpy change for the "raw materials to oxide" value and the "oxides to products" value. For example, 1,2 kg of calcite is needed for CaO, giving an enthalpy change for the theoretical formation of the crystalline oxide of +2 138 kJ (1,2 kg x 1 782 kJ = 2 138 kJ). Similarly, 0,637 kg of C_3S is formed from crystalline oxides, giving the enthalpy change of formation of -333 kJ (0,637 kg x -495 kJ = -333 kJ).

The enthalpy requirements given in Table 7 are calculated at 25 °C and 0,1 MPa. At the temperature of formation in the kiln, however, the enthalpy changes are different because the specific heats of reaction and products are different (Taylor, 1990).

3.3.3 REACTIONS - GENERAL CONSIDERATIONS

There is a lack of clarity in the understanding of the reaction sequences which take place in the kiln due to the practical difficulty in taking samples from the kiln for analysis (Chatterjee, 1991).

Chatterjee (1991) has, however, defined a number of zones by temperature range and reaction profile which give an idea of the reaction sequences which occur in the burning of the cement raw mix in the kiln. These are shown in Table 8.

Table 7. Enthalpy of formation of 1 kg of Portland cement clinker

Theoretical raw materials for 1 kg clinker	Amount
Calcite	1,20 kg
Quartz	0,10 kg
Pyrophillite	0,15 kg
Kaolinite	0,04 kg
Goethite	0,03 kg
Theoretical products for 1 kg clinker	Amount
C_3S	0,673 kg
β-C_2S	0,133 kg
C_3A	0,118 kg
C_6A_2F	0,064 kg
CaO	0,010 kg
Raw materials to oxides	ΔH (kJ)
$CaCO_3 \rightarrow CaO + CO_2$	+ 2 138
Quartz	0
$OH_2Al_2Si_4O_{10}$ (pyrophyllite) $\rightarrow \alpha$-$Al_2O_3 + 4SiO_2 + H_2O$	+ 34
$OH_4Al_2Si_2O_5$ (kaolinite) $\rightarrow \alpha$-$Al_2O_3 + 2SiO_2 + 2H_2O$	+ 22
2FeO.OH (goethite) $\rightarrow \alpha$-$Fe_2O_3 + H_2O$	+ 8
Sub total	+ 2 202
Oxides to products	ΔH (kJ)
$3CaO + SiO_2 \rightarrow C_3S$	-333
$2CaO + SiO_2 \rightarrow \beta$-$C_2S$	- 98
$3CaO + \alpha$-$Al_2O_3 \rightarrow C_3A$	- 3
$6CaO + 2\alpha$-$Al_2O_3 + \alpha$-$Fe_2O_3 \rightarrow C_6A_2F$	- 10
CaO	0
Sub total	- 444
Total enthalpy change	+ 1 758

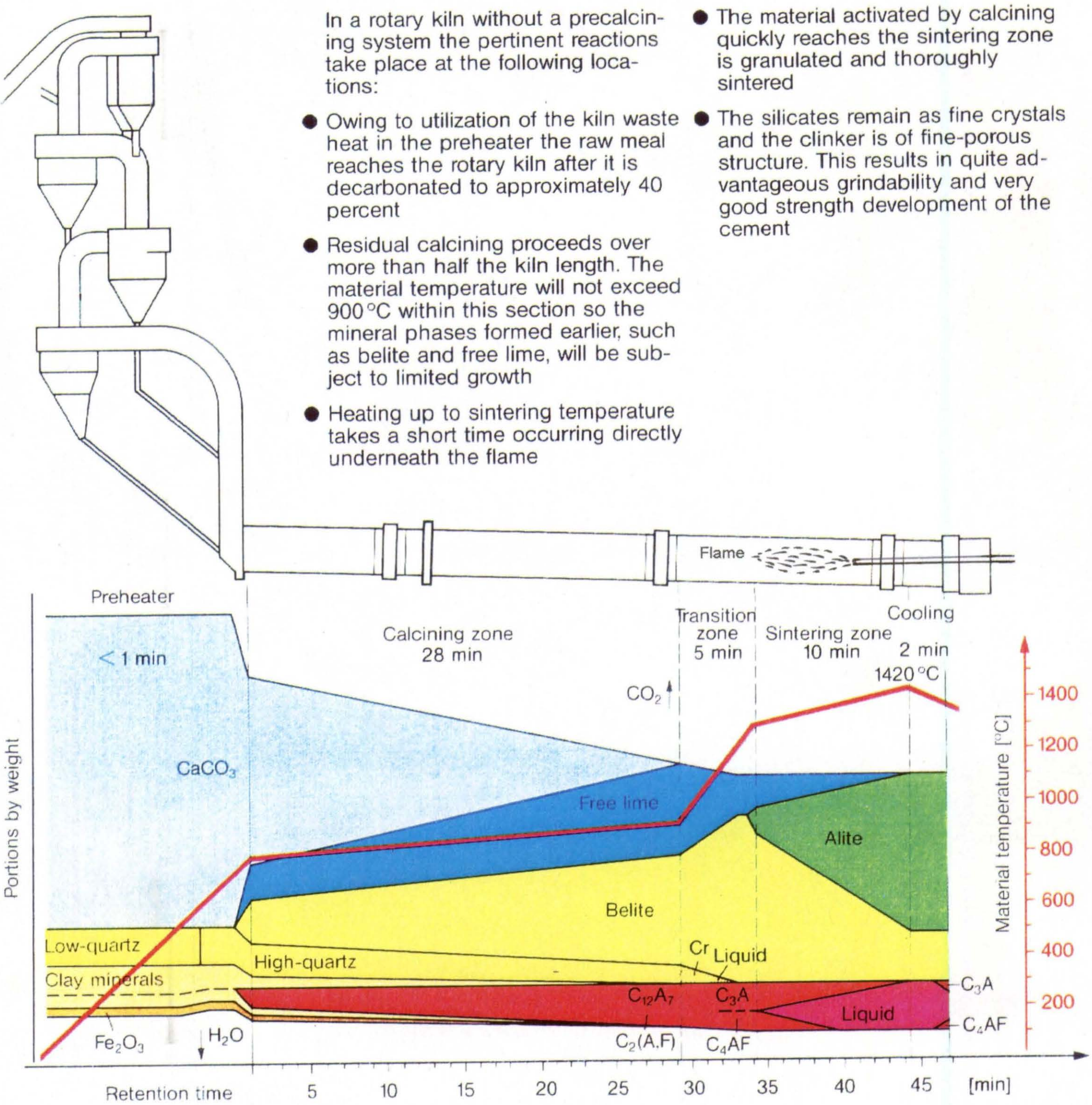
Table 8. Zones defined by temperature range and reaction profile

Zone	Temperature range (°C)	Reaction profile
I	Up to 200	Evaporation (slurry drying)
II	200-800	Preheating (dehydration,dehydroxylation, and first appearance of new phases)
III	800-1 100	Decarbonation (calcination)
IV	1 100-1 300	Exothermic reactions
V	1 300-1 450-1 300	Sintering
VI	1 300-1 000	Cooling

The position of these zones in relation to a kiln is shown in Figure 2 (KHD Humboldt Wedag trade literature). Zone I, which applies to wet process kilns is not shown in the diagramme. The preheating of the material (Zone II) occurs in the preheater cyclones and takes place rapidly, usually in less than a minute. Zones III and IV occur in the kiln in the calcining and transition zones respectively. Zone V occurs in the sintering zone below the flame and Zone VI occurs in the cooling zone behind the flame before the material enters the cooler.

There are many types of reactions occurring in the kiln. Unfortunately, no single kinetic theory exists whereby all types of reactions may be treated. Imlach (1976) investigated the kinetics of the reactions occurring during Portland cement clinker formation. He concluded that there were "phase boundary" controlled stages, for example the decomposition of calcite and the formation of C_2S. These were followed by "diffusion" controlled stages, where the Ca^{2+} diffusion controlled the rate of reaction. Initially, the diffusion controlled reactions took place in the solid state, while above

1 325 °C the reactions occurred through a liquid medium. Table 9 summarises the reactions described by Imlach (1976).



In a rotary kiln without a precalcining system the pertinent reactions take place at the following locations:

- Owing to utilization of the kiln waste heat in the preheater the raw meal reaches the rotary kiln after it is decarbonated to approximately 40 percent
- Residual calcining proceeds over more than half the kiln length. The material temperature will not exceed 900 °C within this section so the mineral phases formed earlier, such as belite and free lime, will be subject to limited growth
- Heating up to sintering temperature takes a short time occurring directly underneath the flame
- The material activated by calcining quickly reaches the sintering zone is granulated and thoroughly sintered
- The silicates remain as fine crystals and the clinker is of fine-porous structure. This results in quite advantageous grindability and very good strength development of the cement

Figure 2. Reaction zones in a rotary kiln with cyclone preheater.

Table 9. Reactions taking place in the kiln

Stage	Reaction	Mechanism	Temperature
1	Calcite decomposition	Phase boundary controlled	570-890 °C
2	Solid state reaction I	Phase-boundary controlled	600-800 °C
3	Solid state reaction II	Diffusion controlled	1 000-1 250 °C
4	Solid liquid reaction	Diffusion controlled	1 325-1 450 °C

Taylor (1990) confirms that reactions below about 1 200 °C occur largely in the solid state, the first visible effect in the cement raw mix being the appearance of reaction rims around quartz grains.

Table 10 (after Glasser, 1979) classifies a few phase changes taking place at higher temperatures during clinkering.

Table 10. Phase changes during clinkering

Example	Type
$CaCO_{3\,s} \rightarrow CaO_{\,s} + CO_{2\,g}$	Solid → gas
$K_2SO_{4\,l} \rightarrow [K_2SO_4]_{\,g}$	Liquid → gas
$CaO_{\,s} \rightarrow (CaO)_{\,l}$	Solid → melt
$(CaO)_{\,l} + (SiO_2)_{\,l} \rightarrow Ca_3SiO_{5\,s}$	Melt → solid
$(C,A,F,S)_{\,l} \rightarrow 2CaO.SiO_{2\,s} + 3CaO.Al_2O_{3\,s}$	Nucleation, crystallisation
( ) = species dissolved in melt [ ] = dissociation products	s = solid g = gas l = liquid

3.3.4 REACTIONS BELOW ABOUT 1 300 °C

Numerous workers have studied the reactions taking place during Portland cement clinker manufacture. A brief summary of the work done by Lea (1971), Ludwig and Ruekensteiner (1974), Weyer (1931) and Locher (1976), cited by both Ghosh (1991), and Taylor (1990) reveals that:

On heating, the decomposition of clay minerals is dependent on their structure. Interlayer and adsorbed water is lost between 100 and 250 °C, dehydroxylation begins between 300 and 400 °C and is rapid by 500 to 600 °C.

The decarbonation of calcite (which is highly endothermic - see Section 3.3.2) becomes significant from 500 to 600 °C if sufficiently low partial pressure of CO_2 is maintained or if the calcite is intimately mixed with quartz or clay minerals. The CaO formed during the decarbonation reacts with other components simultaneously (up to 17 per cent however remains unreacted at temperatures as high as 1 000 °C).

Quartz undergoes a minor, rapid and reversible phase transition to α-quartz at 573 °C. It is unstable relative to tridymite at 867 to 1 470 °C and to cristobalite above 1 470 °C.

The first detectable phases $CA + C_{12}A_7 + C_2S$ are noticed at 700 °C. The amount of these phases increases with temperatures up to 900 to 1 000 °C, when poorly detectable C_3S and some C_4AF/C_2F are found.

3.3.5 REACTIONS AT 1 300 TO 1 450 ˚C

The solid state reactions are almost complete at a temperature of about 1 300 ˚C and the melt phase appears.

Klemm (1979) has found that the temperature of liquid formation is determined by the composition of the raw mix and that the quaternary eutectic temperature for the system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$ is 1 338 ˚C. However in the presence of other oxides and elements (Na_2O, MgO and F), the liquid phase formation can be as low as 1 280 ˚C. The optimum liquid content is generally considered to be between 23 and 28 per cent. Too little liquid leads to difficult burnability of the raw mix, while an excess of liquid leads to the formation of sticky clinker, a dense coating and kiln rings.

The quality of the liquid phase is also important and is influenced by small additions of minor oxides, for example, the viscosity of the liquid is increased by SiO_2, Al_2O_3 and alkalies, and decreased by MnO, Fe_2O_3 and MgO. The change in viscosity and surface tension of the liquid will affect the reaction kinetics and diffusion parameters.

The liquid phase is essential for the formation of C_3S as CaO, C_2S and silica dissolve in the melt, diffuse together, react and crystallise.

The formation of nodules occurs through the sticking together of solid particles by liquid. Nodulisation requires an adequate proportion of liquid and is favoured by low viscosity and high surface tension of the liquid and small particle size of the solid material (Timashev, 1980).

It is in the nodulisation process that there is intimate mixing of the components to form C_3S. Chromy (1982) recognised three stages in the reaction at clinkering temperature. In the first, the melt and C_2S are formed. In the second, C_2S continues to form together with a material consisting of lime crystals with C_3S coatings. These crystals are dispersed in a matrix of C_2S crystals and liquid. The third stage consists of the lime clusters reacting with the C_2S to give C_3S. This mechanism is based on the diffusion of CaO through the liquid.

The reaction sequence can perhaps best be summarised in Figure 3 (Chatterjee, 1991).

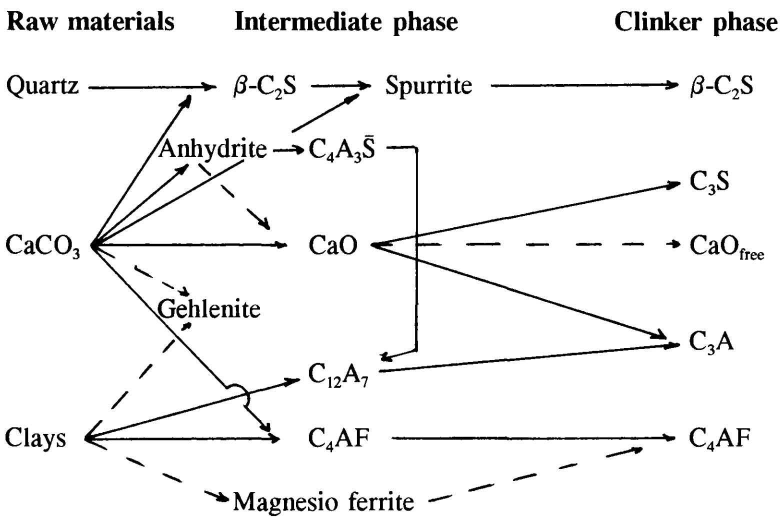


Figure 3. Reaction sequence for clinker phases

Lea (1956) explains the crystallisation of the major phases by means of the ternary diagramme shown in Figure 4. This shows an enlarged portion of the $CaO-Al_2O_3-SiO_2$ system.

A Portland cement clinker of composition **M** will consist of solid C_3S and a liquid of composition **V**. On cooling C_3S will separate from the liquid and the composition of the liquid will move along the line **MV** until the C_3S-C_3A boundary is reached at point **R**. C_3A will crystallise and the liquid composition will follow the line **RY**, until point **Y** is reached. C_2S now crystallises and the last of the liquid will solidify.

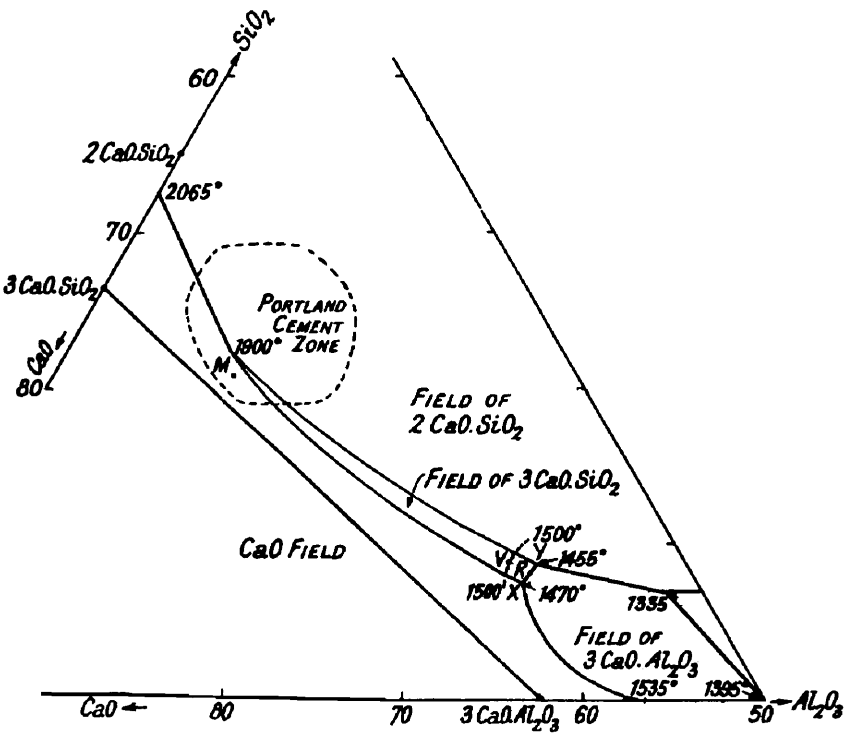


Figure 4. The $3CaO.SiO_2$ field in the system CaO-Al_2O_3-SiO_2

3.3.6 OXIDISING AND REDUCING CONDITIONS

An oxidising kiln atmosphere is generally required for burning Portland cement clinker (Locher, 1979). However for reasons of fuel economy, the amount of oxygen in the fuel gases must be kept as low as possible, usually between 1 and 2 per cent. Even with excess oxygen, a reducing atmosphere can develop in the Portland cement clinker if the raw materials contain oxidisable components such as carbon or sulphur compounds.

Oxidising burning conditions are required in order to sinter the iron contained in the raw mix as far as possible into ferric oxide for it to be bound into the molecular structure of C_4AF.

Ferrous oxide, formed under reducing conditions is undesirable because it promotes the breakdown of C_3S during Portland cement clinker cooling. The C_3A content is also increased at the expense of the C_4AF. Finally, the colour of the Portland cement clinker changes from greyish-green to brown.

Long (1983) summarised the effects of a reducing atmosphere in the burning zone. The decomposition of C_3S is promoted and more C_3A forms at the expense of the C_4AF. Some of the Fe^{2+} that is formed replaces Ca^{2+} in the solid phases, making burning more difficult and decreasing reactivity towards water.

3.3.7 REACTIONS ON COOLING

After reaching maximum temperature in the burning zone, the Portland cement clinker starts cooling in the kiln (behind the flame) before further cooling in a cooler (see section 3.4 for detailed description of coolers).

The Portland cement clinker phases, as well as the liquid formed during clinkering are affected by the rate of cooling. The best Portland cement clinker is obtained by cooling slowly to 1 250 °C followed by rapid cooling (Chatterjee, 1991). A cooling rate of 18 to 20 °C per minute has been suggested as a good cooling rate.

During the cooling period, the C_3A and C_4AF crystallise from the liquid phase. Composition of the C_3A and C_4AF phases is, therefore, controlled by the that of the clinker liquid and the conditions under which the latter crystallises (Taylor, 1990). Slow cooling produces relatively large crystals of each phase, while fast cooling produces close intergrowths.

The effects of slow cooling are also seen on the C_3S and C_2S. At slow cooling rates, the liquid can re-absorb part of the C_3S to form C_2S and C_3A instead. At a temperature below 1 250 °C, the C_3S becomes unstable and breaks down to form C_2S and free CaO. This breakdown is strongly enhanced if ferrous oxide is present as a result of reducing conditions. The C_2S transitions are also affected by slow cooling, with the breakdown of the C_2S and re-absorption into the liquid phase. The edges of the C_2S crystals become more ragged as the cooling rate decreases. The polymorphic transformations of alite and belite which occur on cooling are discussed more thoroughly in Chapter 6, Sections 6.2.1.1 and 6.2.2.1.

The behaviour of the MgO in Portland cement clinker formation depends on the cooling rate. A Portland cement clinker which is burned at high temperatures ($>$1 500 °C) can contain a relatively high MgO content in the liquid phase which will remain in the C_3A and C_4AF phases if quickly cooled. On slow cooling however, only about 1,5 per cent of the MgO is taken into solid solution, the balance of the MgO crystallising as periclase.

At lower burning temperatures (< 1 450 °C), even less of the MgO is taken into solution, and more periclase can result.

Most of the SO_3 is present at clinkering temperatures as an immiscible liquid phase. The alkali cations are distributed between the two liquids and the C_3S and C_2S (Taylor, 1990). During cooling, the sulphate liquid solidifies below 900 °C, to form potassium calcium sulphates. For most normal Portland cement clinker compositions, the major sulphate phase will be $(Na,K)\bar{S}$ (aphthitalite) with minor amounts of $K\bar{S}$ (arcanite) and $K_2C_2\bar{S}_3$ (calcium langbeinite).

All the effects described above indicate that rapid cooling is desirable. The C_3A phase reacts more slowly with water when it occurs as a finely grained intergrowth with C_4AF. The amount of C_3S is not reduced by reactions involving the interstitial material or by decomposition and high levels of MgO are not found as periclase.

3.4 COOLING

The cooling of the Portland cement clinker is very important as it affects the mineralogical composition and ultimately the quality of the cement.

The process of Portland cement clinker formation is not complete when the material has been exposed to the hottest temperature in the kiln (the burning zone) because some of the Portland cement clinker phases are in the liquid state. Thus the cooling of the Portland cement clinker behind the flame before being discharged into the cooler is very important. During this "pre-cooling" stage the melt (liquid phase) crystallises in the cooling process to form two phases, namely C_3A and C_4AF and the silicate phases are partly retained in a metastable condition in their high-temperature modifications as described in Section 3.3.7.

The length of this "precooling zone" in the kiln will depend on the position of the flame, burner setting, secondary air temperature and type of cooler.

A brief description of the various types of coolers is however pertinent to illustrate the effects that each have on the cooling rate of the Portland cement clinker.

The rotary cooler is the oldest type of cooler and operates in conjunction with the rotary kiln. The slope of the rotary cooler is between 4 and 7° from the horizontal and the cooler rotates at 1 to 8 rpm. The cooling of the Portland cement clinker takes place by the movement of cool air across the clinker i.e. counter-current.

The satellite cooler consists of a number of steel cylinders, normally refractory lined for some of their length, attached at the discharge end of the kiln. The satellite coolers revolve together with the kiln. Cooling also occurs as a counter-current movement of air.

The grate cooler works on a slightly different principle, i.e. utilising both cross- and counter-cooling. It consists of alternating mobile and immobile grates.

The Portland cement clinker is discharged from the kiln onto a sloping grate (typically about 5° from the horizontal) and then onto a short horizontal grate. The air used to cool the Portland cement clinker moves up through the bed of clinker.

After passing through the cooler, the Portland cement clinker is transported to storage areas, where it is allowed to cool before being ground together with a small quantity of gypsum to produce cement.

3.5 DEVELOPMENT OF KILN SYSTEMS

Throughout the world today, there are many varying kiln designs which are in use for the manufacture of ordinary Portland cement clinker.

Through the years, there has been a progression from the wet process to the semi-wet and finally the dry process for Portland cement clinker manufacture. These changes have come about as a result of, amongst others, the need to reduce energy costs, to promote stable kiln operation and as a result of new technology becoming available.

3.5.1 WET PROCESS KILNS

In the wet process, the raw materials are wet-ground as a slurry with a water content of about 18 to 45 per cent (Duda, 1976). Depending on the method by which the raw materials are prepared, a number of kiln combinations can be used.

A long wet-process kiln is used where there are internal heat exchangers such as chains to dry the slurry.

3.5.2 SEMI-WET PROCESS KILNS

A semi-wet process would typically utilise a short wet-process kiln together with a slurry dryer or concentrator. A medium long wet-process kiln with a mechanical dewatering device (pressure filters) and a short chain section is another semi-wet combination. A short wet-process kiln where the feed is pressed into a filter cake and then pelletised and presented in the form of nodules is another example of the semi-wet process.

3.5.3 DRY PROCESS KILNS

The most recent development is the dry process kiln and even this has gone through an evolutionary cycle.

When first installed, the dry-process used a long kiln without internal heat exchangers, and the raw material was introduced into the back end of the kiln at room temperature. The hot gases from the flame were required to heat the material from this low temperature to the burning zone temperature.

A later development in the dry process kiln saw the use of internal heat exchangers such as chains and refractory bridges to heat up the raw materials.

Where chains are used, they may occur in two predominant patterns, in a chain curtain or a chain garland, depending on the kiln design. Dry-process kilns normally have chain curtains while wet-process kilns normally have both types of chain.

The short dry-process kiln is used in conjunction with up to five stages of pre-heaters to heat the raw materials to approximately 700 °C before being introduced into the kiln. Figure 5 (Peray, 1986) illustrates the flow of raw material and gases through a four stage pre-heater cyclone before being introduced into the kiln.

The four-stage pre-heater kiln was only introduced into the cement manufacturing industry in 1951 (Duda, 1976).

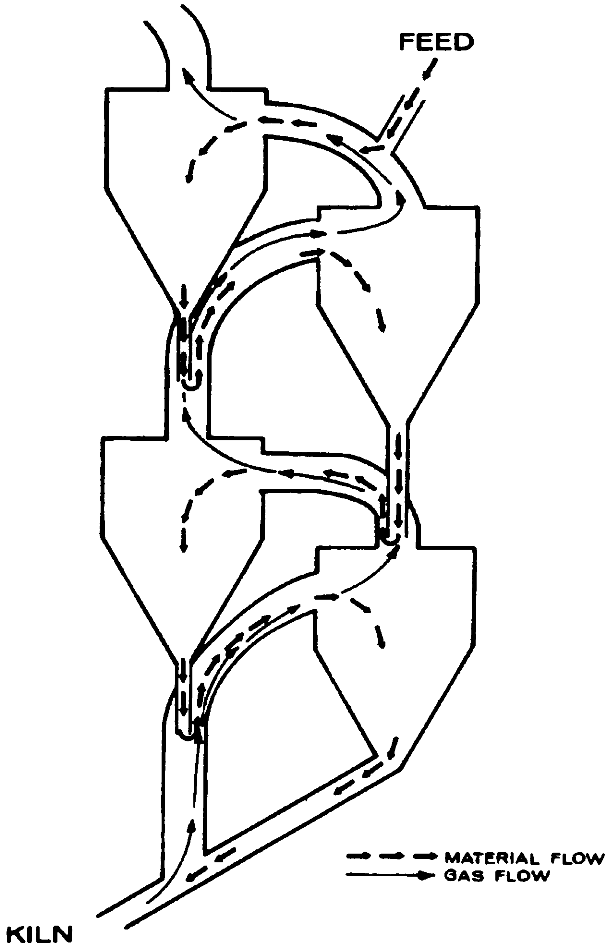


Figure 5. Diagramme of a four stage pre-heater showing the material and gas flow.

The use of pre-heater kiln systems however, had a bad side effect in that alkalies (Na_2O and K_2O) were concentrated both in the kiln system and in the Portland cement clinker. Alkalies within the kiln, at relatively high levels, can cause excessive coating and ring formation in some sections of the kiln. Alkalies concentrated in the Portland cement clinker can lead to the development of alkali-aggregate reaction products and ultimately to damage to the concrete structures built using this cement.

Alkalies are quite reactive chemically and combine with chlorine and sulphur in the kiln, forming chlorides and sulphates. The chloride content is generally low in the raw materials, and the alkalies are therefore, present mainly as sulphates. The alkalies have low vapour pressures and are thus volatilised from the raw materials in the high temperature of the burning zone and are picked up in the gas stream and swept back in the kiln to the cooler areas where they condense at the bottom of the pre-heater.

In the pre-heater, where the kiln gas and incoming raw materials mix, virtually all the vaporised alkali compounds are returned to the kiln, so concentrating in the Portland cement clinker.

The removal of the alkalies is accomplished by the installation of a by-pass system at the bottom of the pre-heater in the area where the raw mix is just entering the kiln. In this area much of the alkali is in the vapour state and this vapour, together with fine dust, is pulled out of the system before it has chance to mix with the raw mix. The by-passed gas is quickly cooled and the alkali dust separated in cyclones. The alkali-rich dust is wasted in order to reduce the alkali content of the system. Variable degrees of bypass are available through the use of dampers and valves, depending on the degree of alkali removal required.

The latest development includes the use of pre-calciners to drive-off the CO_2 from the limestone and introduce the raw material into the back end of the kiln at about 900 °C and the clinkering of the mix is done in a relatively short kiln.

The advantage of the dry process method over the wet is lower specific heat consumption for Portland cement clinker manufacturing. Previously, the raw materials were more easily mixed in the form of a slurry, but recently the use of sophisticated equipment utilising pneumatic machinery has made the homogenisation of dry raw materials possible.

3.6 SOUTH AFRICAN KILN SYSTEMS

Portland cement clinker is produced in South Africa by three companies, Blue Circle Cement (Pty) Ltd (BCC), Pretoria Portland Cement Co. Ltd (PPC) and Anglo Alpha (Pty) Ltd (AA). PPC was founded in 1892 in Pretoria as "Eerste Cement Fabrieken Beperkt". BCC started producing Portland cement clinker in 1914 at Hennenman as Whites South African Cement Co. Ltd. AA started producing cement at Roodepoort on the Witwatersrand in 1935 as Anglovaal Portland Cement Co. Ltd. (Hodgkiss, 1993). For many years the three companies had an "Industry agreement" covering production and selling. This agreement is being phased out and more emphasis will be placed on quality and price.

There are ten active Portland cement clinker producing plants, one plant under commissioning and a number of milling facilities and depots. In 1992, total Portland cement clinker manufacturing capacity was 10 933 000 tpa (Hodgkiss, 1993). Because of reduced demand for cement, the operating units are producing Portland cement clinker at an average utilisation of approximately 65 per cent. Rather than focussing on creating capacity, technical improvements were aimed at efficient production of Portland cement clinker of consistent quality. For example, computer control is being used on a few of the more recently installed kilns.

Table 11 (Hodgkiss, 1993) indicates the kiln types installed in South Africa.

Table 11. Installed kiln lines

Kiln types	Number
Wet process kiln	5
Straight dry kiln	5
Single stage preheater kiln	3
Two stage preheater kiln	2
Four stage preheater kiln	9
Four stage precalciner kiln	2

4. ANALYSIS OF PORTLAND CEMENT CLINKER

4.1 GENERAL CONSIDERATIONS

Portland cement clinkers are composed mainly of calcium silicates, calcium aluminates and calcium alumino ferrites.

The chemical composition of a typical Portland cement clinker (from Blue Circle Cement, Lichtenburg) is given in Table 12.

Table 12. Chemical composition of Portland cement clinker

Component	Per cent
CaO	63,84
SiO_2	21,94
Al_2O_3	4,27
Fe_2O_3	3,05
MgO	2,46
TiO_2	0,45
Mn_2O_3	0,22
Na_2O	0,12
K_2O	0,11
SO_3	0,14
LOI	2,52
Total	99,12

Even though the manufacture of Portland cement clinker has been carried out for approximately 170 years, there are numerous ways to analyse the Portland clinker phases, and each method only reveals certain aspects about the phases.

For the quantitative determination of the phases in Portland clinker, three methods have proved effective, namely calculation from bulk chemical analysis, X-ray diffraction and light microscopy (see comparison in Section 4.10). These methods, as well as other techniques for analysing Portland clinkers, are examined.

4.2 BOGUE CALCULATION

From a bulk chemical analysis of Portland clinker obtained either by X-ray fluorescence analysis (see Section 4.3) or classical wet chemical methods (see Section 4.4), the quantitative phase composition can be calculated using a method developed by Bogue (1929). Several assumptions are made when using the Bogue calculation as follows:

> The compositions of the four major phases are C_3S, C_2S, C_3A and C_4AF.
> All the Fe_2O_3 occurs as C_4AF (together with Al_2O_3.)
> The remaining Al_2O_3 occurs as C_3A.
> The remaining CaO is apportioned to the SiO_2 to give C_3S and C_2S.

In the following equations, it is assumed that the CaO has been corrected for free CaO.

$$C_3S = 4{,}0710\,CaO - 7{,}6024\,SiO_2 - 6{,}787\,Al_2O_3 - 1{,}4297\,Fe_2O_3$$

$$C_2S = -3{,}0710\,CaO + 8{,}6024\,SiO_2 + 5{,}0683\,Al_2O_3 + 1{,}0785\,Fe_2O_3$$

$$C_3A = 2{,}6504\,Al_2O_3 - 1{,}6920\,Fe_2O_3$$

$$C_4AF = 3{,}0432\,Fe_2O_3$$

Because minor oxide components are not taken into account, the total for the four main phases will not add up to 100 per cent. It is also assumed that all the MgO occurs as periclase. Therefore, the results of the Bogue calculation are often called the potential phase composition. When this method was devised, it was generally considered that the principal source of error was the failure of the Portland clinker phases to reach equilibrium during cooling. However the direct source of error is that the compositions of the clinker phases differ considerably from those of the pure compounds (one of the Bogue assumptions).

The results of the Bogue composition differ from the true phase composition, especially in underestimating the C_3S and overestimating the C_2S (Spohn et al, 1968). According to Krämer and zur Strassen (1960), the MgO content is a predominant factor in controlling the deviation of the alite content from the potential C_3S value.

Lea (1970) has modified the procedure of Bogue slightly to account for different Al_2O_3/Fe_2O_3 ratios. If the $Al_2O_3{:}Fe_2O_3$ ratio of the ferrite phase has been determined by X-ray fluorescence, the Bogue calculation can be made using the content of Fe_2O_3 corresponding to the ferrite composition (this result is sometimes called the "modified Bogue calculation").

Taylor (1990) has more recently developed a method of quantifying the phases in clinker which takes into account the substitution of ions into the clinker phases and the subsequent variation in composition from the pure phases. The method first estimates the sulphate phases and then calculates the percentages of the major phases using four linear simultaneous equations.

4.3 X-RAY FLUORESCENCE ANALYSIS

X-ray fluorescence spectrometry provides the means for the identification of an element by measurement of its characteristic secondary X-ray emission wavelength or energy. The method allows the quantification of a given element by first measuring the emitted characteristic line intensity and then relating this intensity to elemental concentration (Jenkins, 1988). X-ray fluorescence is used almost exclusively in modern cement plants to analyse the raw materials, kiln feed and Portland clinker for process control purposes.

Several different types of source have been used for the excitation of characteristic X-ray radiation. By far the most common source is the X-ray photon source. Most conventional wavelength dispersive X-ray spectrometers use a high power (2 to 4 kW) X-ray source. The primary source unit consists of a very stable high voltage generator (typically 40 to 100 kW) and a sealed X-ray tube.

The most common X-ray tube for Portland analysis has an anode of Rhodium and delivers intense, continuous and characteristic radiation. The X-rays impinge on the analyses specimen, where characteristic secondary X-ray radiation is generated.

In the wavelength dispersive spectrometer, a single crystal of known interplanar spacing is used to disperse the polychromatic beam of characteristic wavelengths coming from the specimen, so that each wavelength will diffract at a discrete angle. Typical analysing crystals used in wavelength dispersive spectrometers are LiF, PET and Ovonix. Each crystal is used to analyse a specific atomic number range of elements.

The X-ray detector is a transducer for converting X-ray photon energy into voltage pulses. The detector works through a process of photoionisation in which interaction between entering X-ray photon and the active detector material produces a number of electrons. The current produced by these electrons is converted to a voltage pulse by a capacitor and resistor, such that one digital voltage pulse is produced for each entering X-ray photon. Typical X-ray detectors are either gas flow proportional counters, scintillation counters, sealed gas detectors or Si(Li) detectors, the latter being used almost exclusively for energy dispersive X-ray spectrometry.

There are many forms of sample suitable for X-ray fluorescence analysis, for example, bulk solids, liquids and gases. For Portland clinker samples, the common sample presentation form is as a heterogeneous bulk solid or powder.

The method of preparing powder samples is first to grind the samples to less than 20 μm and then to pelletise at high pressure. By far the greatest potential problem in the analysis of such powders is that of local heterogeneity. The emmision of the secondary X-ray radiation from the sample of long wavelengths takes place only from a shallow depth and is known as the critical depth. In the case of Portland, the critical depth for the lighter elements is about 5 μm. If the specimen is heterogeneous over the same range as the critical depth, the analysis will not be representative of the whole specimen. The problem in specimen preparation is to ensure that the relatively thin surface layer actually analysed is representative of the bulk of the sample.

Probably the most effective way of presenting sample to overcome this heterogeneity is the fusion method. It involves fusion of the sample with a lithium tetraborate and casting into a solid bead. Chemical reaction in the melt converts the phases present in the sample into glasslike borates, giving a homogeneous bead.

For the quantitative analysis of multi element samples such as Portland clinker using X-ray fluorescence, the most common method used is the close match standardisation method (Type standardisation).

The close match standardisation is probably the oldest of the quantitative analytical methods used, and the method is usually evaluated by taking data from a well characterised set of standards, and, by inspection, establishing whether a linear relationship exists between the analyte concentration and the measured characteristic line intensity. This method is extremely useful for quality control applications where the finished product is compared with a desired product but only works well if mineral species are the same in the sample and reference specimens (applicable for powder samples and not fused beads).

4.4 WET CHEMICAL METHODS

The methods for determining the chemical composition of Portland clinker phases differ from country to country. The analysis is usually carried out on a dry basis (dried at 110 °C) and after the loss on ignition has been determined (Aldridge, 1975a). A brief description of the procedures for analysing the major elements occurring in Portland clinker is given (ASTM C-114-69, reapproved 1976).

The classical gravimetric method of analysing calcium is to double precipitate the calcium as oxalate and ignite this to CaO. Volumetric methods are also used, where the calcium oxalate is redissolved and the oxalate titrated by $KMnO_4$ (EDTA can also be used for titration).

The usual gravimetric procedure for the analysis of silica is to precipitate gelatinous silicic acid from solution in the presence of a dehydrating agent. The silica is separated by filtration, ignited at about 1100 °C, weighed, volatilised by treatment with HF and then the mass determined of the residue.

The ammonium hydroxide group (R_2O_3) includes Al_2O_3, Fe_2O_3, TiO_2, and P_2O_5. The classical method for analysing alumina is to precipitate the R_2O_3 from the silica. The standard method requires that the amount of alumina be calculated by subtracting the Fe_2O_3, TiO_2 and P_2O_5 from the amount of R_2O_3. The other oxides in the R_2O_3 group are calculated on separate samples. The method for analysing for Fe_2O_3 is to reduce it to the ferrous state with stannous chloride ($SnCl_2$) and then titrate with a standard solution of potassium dichromate ($K_2Cr_2O_7$). The TiO_2 and P_2O_5 are determined colorimetrically using a Tiron reagent (disodium-1, 2-dihydroxybenzene-3, 5 disulphonate) and an ammonium molybdate solution respectively.

To analyse for MgO gravimetrically, the magnesium is precipitated as magnesium ammonium phosphate which is ignited to form $Mg_2P_2O_7$. Volumetrically, magnesium oxyquinolate can be titrated (EDTA can also be used).

The Mn_2O_3 is determined volumetrically by titration with sodium arsenite solution ($NaAsO_2$) after oxidising the manganese with sodium metabismuthate ($NaBiO_3$).

The amounts of Na_2O and K_2O are determined by flame photometry using the direct intensity procedure.

The sulphate is precipitated from an acid solution with barium chloride ($BaCl_2$). The precipitate is ignited and weighed as barium sulphate ($BaSO_4$) and the SO_3 equivalent is calculated.

The free CaO is usually determined by the Franke Method (Pressler et al., 1956).

To calculate the Loss on ignition, the Portland cement clinker is ignited in a muffle furnace at a controlled temperature of 950 ± 50 °C. The loss is assumed to represent the total moisture and CO_2 in the cement.

4.5 X-RAY DIFFRACTION ANALYSIS

Many workers have used X-ray diffraction to characterise the phases occurring in Portland clinker.

Yamaguchi and Takagi (1968) have reviewed much of the work that has been carried out using X-ray diffraction on both pure Portland clinker phases (synthesised in the laboratory) and commercial Portland clinkers.

Midgley et al. (1960) state that the only suitable way to determine the ferrite composition in clinker is by X-ray diffraction.

Sehlke (1963) developed a method based on direct quantitative X-ray diffraction for determining the four main constituents of Portland cement clinker.

Gutteridge (1984) has developed a method to quantitatively determine the four major phases in Portland clinker by X-ray diffraction, and uses some of the chemical dissolution techniques described in Section 4.6.

Aldridge (1975b) carried out an inter-laboratory study using X-ray diffraction to quantify the four major Portland clinker phases. He concludes that the errors in X-ray diffraction can be caused by:

Errors caused by measuring the diffraction pattern (e.g. incorrect alignment of peaks with known values).
Errors caused by the incomplete separation of the diffraction peaks.
Errors in standardisation.
Crystallite size and orientation.

More recently, advances in X-ray diffraction software, for example, SIROQUANT have made it possible to quantify the phases occurring in Portland cement clinker very accurately.

4.6 CHEMICAL SEPARATION

Numerous methods exist for the chemical separation of the various Portland clinker phases, but most use the principle of selective dissolution to dissolve out one or other phase.

Gutteridge (1979) has established chemical selective dissolution techniques to separate the silicate and interstitial phases, and has characterised the minerals by X-ray diffraction. Gutteridge uses a salicylic acid-methanol solution to dissolve out the aluminate and ferrite phases, and a KOH-sugar solution to dissolve out the silicate phases.

Adams and Larkin (1983) have developed a chemical dissolution technique to obtain a residue rich in ferrite and periclase, and use microscopy to determine the size of the periclase crystals. This method uses maleic acid-methanol, acetic acid-water and acetic acid-potassium fluoride-water solutions to dissolve out the various components.

4.7 ELECTRON MICROSCOPIC OBSERVATION AND ELECTRON PROBE MICRO ANALYSIS

The scanning electron microscope (SEM) is usually used in combination with energy dispersive X-ray analysis (EDXA), wavelength dispersive X-ray analysis (WDXA), or image analysis, to investigate Portland clinkers. Skalny and Maycock (1974) have used the (SEM) and (EDXA) to study the fracture surfaces of industrial clinkers. This method of investigation has been successful in locating clinker components that are too small to detect by other methods such as X-ray diffraction and optical microscopy. Skalny et al. (1975) have used the SEM, combined with EDXA to good effect to study partially and selectively dissolved Portland clinkers, in particular to study the interstitial phases.

Harrison (1988) describes the procedures used to examine Portland clinker by SEM and EDXA which provides additional information on the chemical composition of the phases in the clinker when compared with optical analysis. This is accomplished using a combination of image analysis using back-scattered electrons, quantitative EDXA and digital elemental mapping.

Ghose and Barnes (1979) have used modern electron microprobe techniques to obtain the composition of all the major phases in Portland cement clinker. They have studied the incorporation of minor elements into alite and belite and note that potassium is found preferentially in belite. Their study of the interstitial phases in Portland cement clinker revealed that there is a solid solution between the C_3A and the C_4AF phases (caution is expressed, however, because of the effect of electron beam spread, which usually limits the microprobe analysis to crystals larger than about 5 μm).

Sarkar and Roy (1985) have obtained accurate results using electron probe micro analysis for alite and belite in a number of Nigerian clinkers, though the level of accuracy dropped appreciably for the interstitial phases owing to the limitation of probe analyses of minute grains (<5 μm). Distinction between the interstitial phases from electron probe micro analysis is extremely difficult (Sarkar and Roy, 1984) because of the size of these phases between the calcium-silicate phases (<1 μm).

Most of the analyses carried out by microprobe have concentrated on the composition of the alite and belite phases in Portland cement clinkers, and the amount and type of substitution which takes place in these phases. Analyses of the interstitial phases have always presented problems because of the limitations of the size of the electron beam due to spread.

The use of electron microscopes, together with their analysis capabilities, is limited by the high cost involved in operating such instruments, and thus this type of examination is not usually carried out on a routine basis. Its use to date has also been limited by the relative scarcity of facilities and expertise available. It is, however, more commonly used by research institutions and universities to carry out investigations in material science.

4.8 DIFFERENTIAL THERMAL ANALYSIS

The DTA of Portland cement clinker has been used mainly to characterise the phase transformations which take place in synthesized Portland cement clinker. Guinier and Regourd (1968) describe in detail the characteristics of the polymorphic transformations of C_3S and C_2S by DTA.

4.9 TRANSMITTED AND INCIDENT LIGHT MICROSCOPIC OBSERVATION

Transmitted light microscopic examination is mainly used to determine the optical properties of the Portland cement clinker phases, and may be carried out in both thin-section or powder mount. Both Rigby (1948) and Insley and Frechette (1955) have carried out comprehensive studies on the optical properties of Portland cement clinker phases. Ono (1957) and Ono et al. (1968) give more details of the examination of Portland cement clinker phases by transmitted light microscopic observation. Transmitted light may also be used to examine the raw materials (mainly the raw mix and kiln feed) to determine both the mineralogy and granulometry. Centurione (1993) gives details on the examination of raw mixes and kiln feeds to determine the properties used to evaluate the combinability of the raw materials.

Incident light microscopic observation is used to determine the microstructural relationships between the Portland cement clinker phases, the crystal sizes occurring in the clinker and to determine the quantitative phase composition.

This thesis focuses on both transmitted and incident optical techniques to improve the quality of Portland cement clinker manufacturing in the industrial environment. From a cost point of view, optical microscopes offer a more economical alternative to the other types of instrumentation described above, to examine Portland cement clinkers. The operator does not have to have the specialist skills level required for SEM operation, and the optical microscopes can be moved from one plant to another.

The other techniques used for analysing Portland cement clinkers as described above are not discussed in any further detail.

4.10 COMPARISON OF QUANTITATIVE TECHNIQUES

Harrison et al. (1985) have analysed the four major Portland cement clinker phases (by X-ray diffraction and incident light microscopy) and have attempted to relate these results to the bulk chemical composition and quantitative phase composition determined by the Bogue calculation.

Aldridge (1978) also carried out a comparison of phase composition calculations using the Bogue calculation, X-ray diffraction and optical microscopy. He (Aldridge, 1982) concluded that light microscopy gave accurate results for the quantitative determination of phases in clinker, assuming an experienced operator and adequate sampling. The results obtained using quantitative X-ray diffraction analysis (QXRDA) were widely varied. When compared with microscopy, the Bogue calculation always gave low results for C_3S.

Odler et al. (1981) established that the alite content determined by microscopy or QXRDA was always greater than that calculated by the Bogue formula.

Kristmann (1977) found that alite and belite were more easily determined by microscopy than QXRDA. Aluminate and ferrite were difficult to determine microscopically (due to their crypto-crystalline nature), and were better determined by QXRDA.

Taylor (1990) summarised these findings by stating that all four major phases can be satisfactorily determined by QXRDA if an adequate experimental procedure is employed. Alite, belite and the total content of the interstitial material can be determined by microscopy. With any of these methods, the absolute accuracy is probably 2 to 5 per cent for alite and belite, and 1 to 2 per cent for aluminate and ferrite.

5. SAMPLING AND PREPARATION OF KILN FEED AND PORTLAND CEMENT CLINKER

5.1 GENERAL

Portland cement clinker from a dry process kiln forms rounded pellets and from a wet process kiln irregular lumps (Taylor, 1990). A lot of information can be obtained by visual examination of the Portland cement clinker without any preparation (visual examination of kiln feed is not usually carried out). If the kiln is running satisfactorily, the Portland cement clinker should be black. Under reducing conditions, the Portland cement clinker will be reddish brown, and if the Portland cement clinker is under-burnt, it will show light or whitish patches (Midgley, 1964).

For a detailed examination of kiln feed and Portland cement clinker, the petrographic microscope provides an ideal tool and for this examination, the material must be sampled and prepared.

5.2 SAMPLING

There is no recommended method for taking kiln feed and Portland cement clinker samples for microscopical examination. The object however is to take a representative sample from which meaningful conclusions can be drawn.

Depending on the object of the examination, the samples can either be spot or grab samples, or they may be composite samples. If it is thought that the problem with a Portland cement clinker may be related to a kiln feed problem, then samples of both materials must be taken. Due consideration must be given to the residence time in the kiln, and the Portland cement clinker sample must be taken after the correct time following the collection of the kiln feed sample so that any features noted in the Portland cement clinker can be related back to the examination of the kiln feed.

Long (1982) points out that a spot sample is best to study a Portland cement clinker quality problem, whereas a composite sample is best to examine process variations over numerous days.

The kiln feed sample may be collected from the conveyer belt supplying the riser pipe to the kiln or in cases where this is not possible, from the belt between the raw material storage silos and the kiln feed storage bins. A sample size of approximately 5 kg is sufficient to carry out all examinations on the kiln feed. The frequency of sampling and the type of sample (spot versus composite) for the kiln feed is similar to that described below for taking Portland cement clinker samples.

The Portland cement clinker sample is usually taken from the belt transporting it from the cooler to storage.

Campbell (1986) has summarised the views of a number of workers with respect to sampling of Portland cement clinker as follows:

> Ono (1981) recommends a grab sample every eight hour shift during clinker production.
>
> Hicks and Dorn (1982) recommend a polished section examination once a week, if the Ono method is carried out once per day.

> Long (1982) recommends taking a 15 kg sample, crushing it to less than 6 mm, and then sieving out the 2 mm to 4 mm fraction. A representative portion (by quartering or riffling) of the 2 mm to 4 mm fraction is examined.

Campbell (1986) restricts the microscope investigation to Portland cement clinker from the modal-size class. A number of nodules are selected for examination. The modal-size class is presumed to represent that part of the Portland cement clinker size population that volumetrically supplies most of the Portland cement.

Centurione (1993), recommends the collection of 15 kg of clinker which is quartered to 2,5 kg. This sample is then sieved through a number of sieves and the percentage retained of each fraction calculated. A proportionate amount is taken from each sieve so that a representative sample is prepared for examination. A simplified diagram of this sampling procedure is shown in Figure 6 (from Centurione, 1993).

Opinion is divided as to whether to study whole nodules or crushed fractions of nodules. One advantage of studying a crushed fraction is that a large number of particles are examined and this increases the probability of studying most of the original clinker sample. A disadvantage, however is that porosity and phase abundances can not be studied as well as in whole nodules. The best method then, is to collect nodules and study both whole nodules as well as a crushed fraction of the nodules.

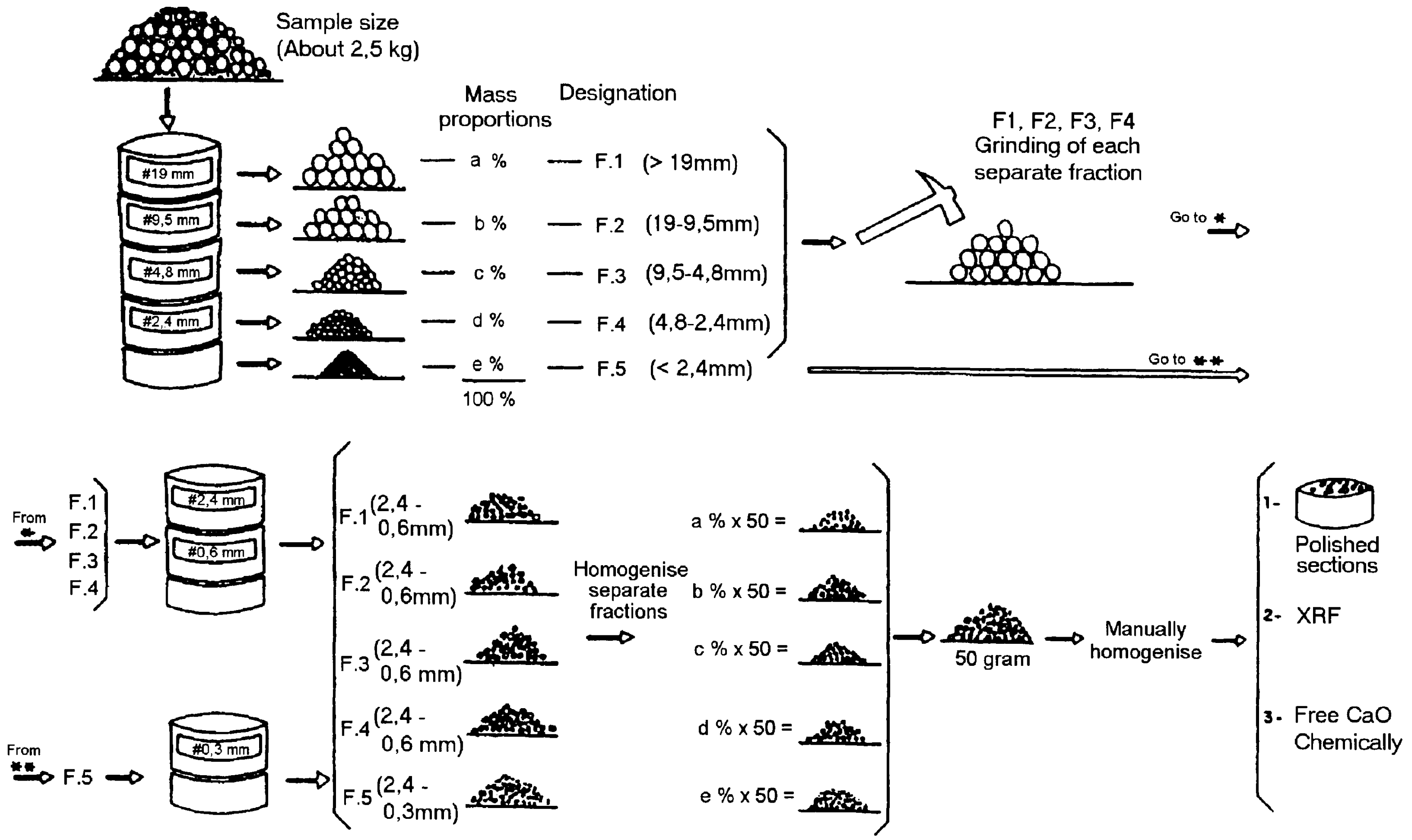


Figure 6. Schematic diagramme of sampling procedure

5.3 SAMPLE PREPARATION

5.3.1 KILN FEED

The kiln feed may be investigated using three techniques, namely XRDA, XRF and transmitted light microscopic examination.

The XRDA will give the mineralogical composition of the kiln feed, while XRF will give the oxide composition of the kiln feed. Transmitted light microscopic examination together with selective dissolution techniques can be used to assess the coarseness of the material.

5.3.1.1 XRF

The preparation of samples for XRF analysis has been discussed in detail in Chapter 4, Section 4.3. Results of the XRF analysis are presented in oxide form, similar to those shown in Table 12, Chapter 4, Section 4.1. Na_2O is usually determined by XRF on a pressed pellet and not a fused bead.

5.3.1.2 XRDA

For XRDA, a representative sample of the kiln feed is crushed to minus 53 μm. This sample is then presented to the X-ray diffractometer in the form of a pressed powder mount, either back loaded or side loaded. The analysis is carried out on the X-ray diffractometer, usually using Cu Kα or Co Kα radiation and a graphite monochromator. From the resulting X-ray diffractogram, the minerals present in the kiln feed are determined, either by a manual or computer assisted search through the Powder Diffraction

File (PDS-2 data base) compiled by the International Center for Diffraction Data (ICDD).

5.3.1.3 TRANSMITTED LIGHT MICROSCOPY

For transmitted-light examination of kiln feed, different size fractions can be examined, depending on the requirements of the examination. As the plus 125 μm fraction is important in assessing the burnability of the kiln feed, this fraction is usually the maximum which is examined. A representative sample of the selected size fraction of kiln feed powder is mounted on a glass slide in liquid with a refractive index (RI) of 1,540 and covered with a cover-glass in preparation for microscopic examination.

In order to assess the coarseness of the kiln feed, a combination of selective dissolution techniques and microscopy are used. Samples of the kiln feed are first wet-sieved through a 125-μm and a 45-μm sieve, using iso-propyl alcohol, and the fractions retained on these sieves calculated (see Appendix 1 for a worked example).

The percentage of carbonate minerals (mainly calcite and dolomite) in the plus 125 μm fraction is determined by selective dissolution in 10 per cent HCl (Centurione, 1993).

The percentage of quartz in the plus 45 μm fraction is calculated by microscopic point counting of this fraction after dissolution in 10 per cent HCl.

The coarseness of the kiln feed is then assessed according to the criteria as discussed by Centurione (1993) (see discussion in section 9.4).

5.3.2 PORTLAND CEMENT CLINKER

Preparation of the clinker sample can be divided into two sections, preparation of clinker samples for examination under transmitted light and under incident light.

5.3.2.1 TRANSMITTED LIGHT MICROSCOPY

Samples of clinker are usually crushed and wet-sieved using iso-propyl alcohol to obtain a fraction which is most suitable for examination i.e. minus 75 μm plus 45 μm. The sample is mounted on a glass slide in liquid with a RI of 1,715 and covered with a thin cover-glass.

Examination under transmitted light is carried out to identify Portland cement clinker phases and measure optical properties such as birefringence and colour as well as the size of the Portland cement clinker phases. These parameters may be used to infer the burning and cooling conditions in the kiln according to the technique developed by Ono et al. (1968). The "Ono Technique" was explained in greater detail at the third ICMA conference in Houston by Ono (1981) and is discussed in Chapter 7.

5.3.2.2 INCIDENT LIGHT MICROSCOPY

Numerous methods exist for the preparation of clinker for examination using reflected light. Clinker nodules and crushed clinker particles are usually mounted in an epoxy resin and polished to obtain a smooth surface which is then etched and/or stained (see Appendix I for a detailed description of equipment and methods required to produce high quality specimens).

Impregnation should be done under vacuum to ensure complete penetration of the embedding medium into the voids of the Portland cement clinker nodule or particle. This is particularly pertinent if whole nodules of clinker are being prepared. Epoxy resins have various setting times and it is not advisable to heat samples too much for quick curing as this induces strain in the epoxy.

For this investigation Cieba Geigy "M-resin", together with "HY-956" hardening agent was used for impregnation. The impregnation was carried out using Buehler Vacuum Impregnation equipment. Moulds can be made of "non-stick" PTFE (polytetrafluoroethylene) and this eliminates the use of mould release agents. Once hard, the mounts can be cut using a diamond blade to expose the sample for subsequent grinding. This is not essential because the hardened mounts can be ground using coarse abrasives to expose the sample.

The initial grinding by hand to obtain a flat surface can be carried out on glass plates using SiC 600- and 1200-sized grinding media and iso-propyl alcohol as lubricant. Alternatively, specialised equipment can be used. These include using diamond-cup wheels, metal-bonded diamond discs, and cast iron discs using oil- or alcohol-based abrasive slurries.

The equipment employed for this study for trimming the epoxy mount was a Buehler Isomet low speed saw with a diamond wafering blade (0,5 mm thick). The initial grinding was carried out on a Buehler Metaserve 2000 Polisher/Grinder with a variable speed 200-mm wheel. Metal-bonded diamond discs are attached to the wheel by means of a magnetic disc. A 50:50 mixture of iso-propyl alcohol and propylene glycol is used for lubricant. The diamond grain sizes on the discs are 60 μm, 15 μm and

6 μm. The epoxy mount is ground on each diamond disc for approximately 2 minutes. Between stages of grinding, the epoxy mount is cleaned in an ultra-sonic bath.

Polishing is carried out on synthetic cloths using non-water based lubricants and a number of different sized polishing media. The most popular medium is diamond grit, varying in size from 15 μm to 0,25 μm. Alumina powder is also widely used as a polishing media.

After evaluating numerous polishing methods, hard, synthetic cloths of low nap (typically Texmet^R), alumina powder of various sizes (5 μm, 3 μm, 1 μm and 0,3 μm) and a mixture of propylene glycol and iso-propyl alcohol as lubricant was used to obtain flat polished surfaces for microscopical examination. A Buehler Minimet^R Polishing machine is used for polishing the epoxy-impregnated mounts. After each polishing stage, the polished specimen is cleaned in an ultra-sonic bath and examined under incident light to establish if that particular stage of polishing is sufficient. This is usually determined by looking for scratches remaining from the previous stage of polishing. If no scratches are seen, the next stage of polishing is started.

Producing flat surfaces for incident light examination also has disadvantages in that certain phases are not easily identifiable, for example, periclase. For this reason, "relief polishing" may be used to overcome this difficulty. Highly polished samples are usually polished on a napped cloth using alumina abrasives (typically 0,05 μm) for a very short period (in the order of 20 seconds) to produce relief of the clinker phases.

The method of relief polishing is to use Buehler Microcloth^R polishing cloth together with 0,05 μm alumina powder. The epoxy mount is held against the polishing cloth for approximately 30 seconds, using the 50:50 mixture of iso-propyl alcohol and propylene glycol for lubricant. This method is used to identify periclase crystals in clinker samples.

The highly polished surface may be etched and/or stained using a variety of chemical solutions to aid in the identification of the clinker minerals.

Observations using incident light include the measurement of crystal sizes and the microstructural features of the Portland cement clinker phases.

5.4 ETCHING AND STAINING

5.4.1 GENERAL

There are many chemical solutions that can be used to preferentially colour the various phases present in Portland cement clinker for identification purposes. Stains are used to colour phases preferentially and etches are used to bring out certain microstructural details.

According to Bogue (1955), etched polished sections for microscopic examination by reflected light were used at the turn of the century by Stern (1907) and later by Wetzel (1913). However, it was Tavasci (1934), Insley (1936) and Insley and McMurdie (1938) who examined both thin- and polished-sections of clinker and made significant advances on the staining and etching techniques.

Both Tavasci (1934) and Insley (1936) found that a solution of 1 per cent nitric acid in alcohol was the most useful for differentiating the silicate phases in Portland cement clinker. The C_3A phase was best etched with an oxalic acid-alcohol solution (10 ml *N*-oxalic acid in 90 ml 95 per cent ethyl alcohol), while the C_4AF phase was etched by HF as well as a $NaOH$-Na_2HPO_4 solution (8 ml 10 per cent NaOH + 2 ml 10 per cent $Na_2HPO_{4)}$. HF was also very useful for etching the silicate phases.

According to Campbell (1986), the most thorough work carried out on the subject of stains and etches is that of Ellson and Weymouth (1968), which lists 43 reagent solutions and their effects on phases occurring in cement and blast furnace slags.

Campbell (1986), however lists many stains and etches used by Marlin (1978) to study Portland cement clinkers.

A few of the solutions have been selected from the above range in this study of the Portland cement clinker specimens. A combination of solutions is used to colour all the phases simultaneously. These are listed in the relevant sections below.

There are a number of methods that can be used to apply the solutions to the specimen.

> *Exposure of the specimen to the vapour of the etchant.* This is usually carried out with HF, where the specimen is held face down over a platinum crucible containing HF. This method is difficult as the quality of the etch depends on the time of etching as well as the temperature of the specimen.
>
> *Selected area etching.* This technique is difficult to apply because the solution runs across the grains that are not to be etched.

Flooding the surface with etchant solution. This method is usually used for epoxy-impregnated specimens and a dropper is used to apply the solution to the surface of the specimen.

Immersion in etchant solution. This method works well for polished thin sections where the thin section is immersed in a watch glass containing the required solution. Impregnated specimens can also be immersed up-side down in the etchant.

In applying the techniques to clinker minerals, care must be taken to stop the effect of the stain or etch solution by rinsing the surface of the specimen with iso-propyl alcohol and drying under warm air. Over-etching will destroy the highly polished surface and the clinker phases will not be identifiable.

Most of the solutions have both etching and staining effects, and are used at room temperature.

5.4.2 ALITE AND BELITE

5.4.2.1 NITAL

Nital is a solution of 1 ml nitric acid (HNO_3) in 99 ml anhydrous iso-propyl alcohol (Campbell, 1986). The prepared polished section is usually flooded with the Nital solution, or the impregnated epoxy mount immersed in the solution. The Nital solution reacts with alite and belite within 6 to 10 seconds. After this period, the surface is rinsed with iso-propyl alcohol and dried under warm air.

The colours produced by this etch are dependent on the reactivity of the silicate minerals and the time for which it is applied. Alite crystals usually turn blue to green and belite brown to blue.

Care must be taken not to over-etch with Nital as this destroys the highly polished surface and the structure of the lamellae of the belite crystals is lost.

5.4.2.2 HYDROFLUORIC ACID (HF) VAPOUR

Almost all the clinker phases can be identified with this etch, but alite and belite are the most brightly coloured. The HF used for etching is poured into a platinum crucible (about 20 ml). The etching is carried out at room temperature (20°C) and the polished surface is held for 5 to 10 seconds in the HF vapour.

No rinsing and drying are necessary after the etch has been applied (because the sample does not come into direct contact with the HF liquid) but care must be taken to allow the excess vapour to leave the surface before examination under the microscope, otherwise the objective lenses may be damaged. This is best achieved by placing a clean glass slide on top of the etched polished surface (Long, personal communication, 1992). Suitable precautions such as gloves and the use of a fume cupboard are recommended.

Alite crystals are coloured straw-yellow to brown and belite blue to orange to red, depending on the length of etch time.

5.4.3 ALUMINATES

5.4.3.1 KOH (0.1 MOLAR AQUEOUS)

The prepared polished section is usually flooded or immersed with the KOH solution for a period of approximately 15 seconds. The specimen is then rinsed with iso-propyl alcohol and dried under warm air. The C_3A stains blue, alkali sulphate darkens and free lime turns brown (Campbell, 1986).

5.4.4 FERRITE PHASE

The ferrite phase in Portland cement clinker is not readily etched by any of the more common solutions and remains white in polished specimen. The reflectivity of the ferrite phase will decrease, however, if reducing conditions are present in the kiln.

5.4.5 FREE CaO

5.4.5.1 DISTILLED WATER

This is best used for the identification of free lime.

There are two popular methods of applying the distilled water etch. The water can be applied to the polished surface by a dropper, or the water can be squirted onto a synthetic polishing cloth while the sample is held lightly against the cloth. Using either method, the time for which the sample is etched is usually 10 seconds. The surface is rinsed with iso-propyl alcohol and dried under warm air.

When applied for approximately 10 seconds, the free lime etches bright iridescent colours (red, green, blue and yellow).

With careful polishing techniques, the free lime can be identified before etching as small rounded grains with a "pearly" colour and texture. Etching with distilled water, however, verifies the presence of free lime.

5.4.6 PERICLASE

5.4.6.1 RELIEF POLISHING

Periclase is not detected by staining or etching, but by relief polishing. As discussed in section 5.3.2.2. highly polished samples are polished on a napped cloth using alumina abrasives for a very short period to produce relief of the clinker phases.

5.4.7 ALKALI SULPHATES

5.4.7.1 KOH (0.1 MOLAR AQUEOUS)

This solution can also be used to detect the presence of alkali suphates. When etched for approximately 15 seconds, alkali sulphates occurring in voids will darken.

5.5 RECORDING OF DATA

An important aspect of Portland cement clinker microscopy is the recording of data. This includes keeping records of samples received and techniques used to prepare the samples of kiln feed and Portland cement clinker. The records on the polishing techniques are especially useful as this ensures that good polished surfaces can be easily reproduced at a later stage.

Comments on the visual examination of Portland cement clinker nodules are useful once the Portland cement clinker particles have been impregnated. Features seen in nodules (such as brown or yellow centres) cannot always be seen after the Portland cement clinker has been prepared as a polished specimen.

Recording of all optical and microstructural parameters is essential and a photographic record of the Portland cement clinker sample is probably the most important.

For the latter a Nikon Optiphot-Pol polarising microscope (utilising both transmitted and incident light) which has a fully automatic Nikon Microflex HFX-IIA camera system attached to the trinocular tube, was used in this investigation.

6. CHARACTERISTICS OF PORTLAND CEMENT CLINKER PHASES AND INTERPRETATION OF MICROSTRUCTURES

6.1 GENERAL

Microscopy can be used as a diagnostic and evaluation tool in all the stages of Portland cement clinker manufacture. To derive maximum benefit, microscopy should be carried out daily or on a shift basis.

During exploration to source raw materials for Portland cement clinker manufacture, the rock types can be characterised by microscopy. For example, the use of alternative raw materials for Portland cement clinker manufacture were identified as described in Section 9.

The microscopical evaluation of the kiln feed raw materials can indicate deficiencies in grinding and mixing. This is done by an assessment of the coarseness of the raw materials. The relationship between the different phases in the Portland cement clinker is important and can confirm whether the proportioning and mixing of the raw materials was correct. This is explained in Section 6.3.2.

The burnability of the raw materials can also be calculated according to the criteria of various workers. For example, Centurione's method is discussed in Section 9.4.

Characteristics of individual Portland cement clinker phases can give an indication of the burning and cooling conditions in the kiln. Features of the phases can be identified by using both transmitted and incident light microscopy. The former evaluation is normally carried out according to the Ono method as explained in Section 7, while the latter uses polished specimens. Ono's method is quick and the burning and cooling conditions in the kiln can be evaluated within 30 minutes of taking a sample. Examination of polished specimens take longer but give more detailed information.

The size of the belite crystals indicate the length of the burning zone, while ragged edges indicate slow cooling behind the flame.

The size and optical properties (birefringence) of alite crystals give an indication of the heating rate of material in the kiln and the maximum temperature in the burning zone.

The interstitial phases of C_3A and C_4AF indicate the rate of cooling and whether reducing conditions are present. This is explained in Sections 6.3.4 and 6.3.5.

A description of the occurrence of the pure mineral phases and the typical Portland cement clinker phases are given in Section 6.2. Examples of many of the microstructural relationships between the phases and the associated manufacturing process are described in Section 6.3.

The characteristic formation of the Portland cement clinker phases are taken from several references and the phases described in this Chapter do not necessarily occur in the Portland cement clinker samples examined in this study.

6.2 CHARACTERISTICS OF PORTLAND CEMENT CLINKER PHASES

6.2.1 ALITE

6.2.1.1 POLYMORPHISM AND SOLID SOLUTION

Guinier and Regourd (1968) have shown by DTA, high temperature XRD and microscopy that on heating, pure C_3S undergoes a series of reversible phase transformations from triclinic, through monoclinic to rhombohedral (trigonal) as illustrated below.

$$T_I \overset{600\ ^{\circ}\mathrm{C}}{\rightleftharpoons} T_{II} \overset{920\ ^{\circ}\mathrm{C}}{\rightleftharpoons} T_{III} \overset{980\ ^{\circ}\mathrm{C}}{\rightleftharpoons} M_I \overset{990\ ^{\circ}\mathrm{C}}{\rightleftharpoons} M_{II} \overset{1\,050\ ^{\circ}\mathrm{C}}{\rightleftharpoons} R$$

Pure C_3S is therefore triclinic (Jeffery, 1952) but impurities cause a solid solution and the usual form of the alite in Portland cement clinker is monoclinic (occurring as pseudo-hexagonal sections) or triclinic where it occurs as elongated prismatic crystals (Taylor, 1964).

Hahn et al. (1968) researched the levels of the substitution into the C_3S crystal by various oxides, both alone and in combination. Taylor (1990) summarises their results as follows:

The limits of solid solution of MgO and ZnO are strongly dependent on temperature, e.g. at 1 550 ˚C up to 2,0 per cent MgO and at 1 400 ˚C up to 5,0 per cent ZnO can be incorporated into C_3S. At 1 420 °C, only 1,5 per cent MgO can be substituted in the C_3S. Al_2O_3 can only substitute up to a limit of 1,0 per cent, irrespective of temperature.

The occurrence of other oxides in impure alite as well as the typical composition of the pure C_3S phase in Portland cement clinker is given in Table 13, page 102.

Incorporation of these oxides into the C_3S causes a higher temperature polymorph to persist on cooling to room temperature. An increase in the amount of oxide substituted leads to a successively higher temperature polymorph being present. In the system $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$, total substitution of 1 per cent causes T_I to be replaced by T_{II}, whereas at 2% substitution, T_{II} is replaced by M_I.

The polymorphic forms of alite which occur in Portland cement clinker are M_{III}, M_I and occasionally T_{II} (Taylor, 1990). C_3S is stable between 1 250 and 2 070 °C, the temperature at which it melts to form CaO and a liquid phase. Below 1 250 °C, pure C_3S does not decompose, but in Portland cement clinkers, in the presence of potassium, alite will decompose into belite and free lime (Welch and Gutt, 1959).

Alite will crystallise from the melt in the R polymorphic form, and invert to the other forms on cooling. At higher temperatures, relatively small crystals high in foreign ions are formed, while at lower temperature, larger crystals with lower levels of substitution are found.

6.2.1.2 OPTICAL CHARACTERISTICS

The optical characteristics of alite are given in Table 14, page 103, (modified from Bogue, 1955).

6.2.1.3 IDENTIFICATION OF ALITE IN CLINKER

In transmitted plane-polarised light, alite crystals generally appear as elongated pseudo-hexagonal crystals which are colourless to slightly coloured. In cross-polarised light the alite interference colour (in a section 20 to 30 μm thick) is low first order grey to yellow with wavy to straight extinction. Plate 1 (A) shows the typical colour and shape of an alite crystal viewed under transmitted plane-polarised light.

In incident light, alite crystals are seen as relatively large euhedral crystals which may be pseudo-hexagonal in shape. When etched with Nital for approximately 20 seconds, the crystals are usually coloured tan to orange to blue. The etch colour is a function of the time of the etch, temperature and reactivity of the crystal.

Plate 1 (B) is a photograph of a polished section of clinker (etched with Nital) showing the typical form of alite crystals. Inclusions of belite frequently occur. Twinning and zonation are often seen in etched sections and are the result of polymorphic transformations which take place on cooling. Alite can account for up to 70 per cent of a Portland cement clinker.

Plate 1 (C) shows another form of alite where the egdes of the alite are rimmed with belite as a result of slow cooling. These are traditionally referred to as transformational boundaries.

6.2.2 BELITE

6.2.2.1 POLYMORPHISM AND SOLID SOLUTION

Belite, or C_2S, occurs in at least five polymorphic forms depending on the heat treatment it has undergone. These are α (alpha), α'_H (alpha prime high), α'_L (alpha prime low), β (beta) and γ (gamma), in descending temperature order. α-C_2S exists between 1 425 °C and its melting point, at 2 130 °C (Guinier and Regourd, 1968). α'-C_2S exists in two forms, a high and a low form, stable between 1 420 to 1 160 °C and 1 160 to 675 °C respectively. The β phase is stable below 650 °C. As with C_3S, the higher temperature polymorphs cannot exist on cooling unless stabilised with foreign ions. The quantity of foreign ions required to stabilise the higher temperature form (e.g. α-C_2S) is high, and decreases with temperature until the lower temperature polymorphic form (e.g. β-C_2S) is found.

The transformation from one polymorph to another follows a different sequence on heating and cooling. On heating, starting with either γ-C_2S or β-C_2S, the transformation is;

$$\gamma\text{-}C_2S \rightarrow \alpha'_L\text{-}C_2S \rightarrow \alpha'_H\text{-}C_2S \rightarrow \alpha\text{-}C_2S$$

Note that β-C_2S does not form.

$$\beta\text{-}C_2S \rightarrow \alpha'_{L}\text{-}C_2S \rightarrow \alpha'_{H}\text{-}C_2S \rightarrow \alpha\text{-}C_2S$$

On cooling, the transformation is as follows;

$$\alpha\text{-}C_2S \rightarrow \alpha'_{H}\text{-}C_2S \rightarrow \alpha'_{L}\text{-}C_2S \rightarrow \beta\text{-}C_2S \rightarrow \gamma\text{-}C_2S$$

While the transformations from α-C_2S to β-C_2S are accompanied only by a decrease in the symmetry, the β-C_2S to γ-C_2S transformation is accompanied by a volume increase and the phenomena of dusting is found. The polymorphic forms of belite most commonly found in production Portland cement clinkers is discussed in Section 6.2.2.3.

The typical composition of pure C_2S and impure belite in Portland cement clinker is given in Table 13, page 102.

6.2.2.2 OPTICAL CHARACTERISTICS

The optical characteristics of belite are given in Table 14, page 103 (modified from Bogue, 1955).

6.2.2.3 IDENTIFICATION OF BELITE IN CLINKER

In transmitted plane-polarised light, belite crystals appear as rounded grains showing a multidirectional lamellar structure. The crystals can range in colour from colourless to yellow or amber. In cross-polarised light, the interference colour (in a section 20 to 30 μm thick) is first order white to yellow. Plate 1 (D) shows a typical belite crystal viewed under transmitted plane-polarised light. The multi-directional lamellae are clearly visible.

In incident light the rounded shape is characteristic for belite, but occasionally a polygonal shape may be evident. The edges of the belite crystals may vary from smooth to ragged, depending on the degree of cooling.

Belite normally etches brown to blue with Nital, and again the colour is dependent on time of etch, temperature and reactivity of the crystal. Plate 1 (E) shows the rounded shape of belite crystals with lamellae present, while Plate 1 (F) shows ragged-edged belite crystals associated with slow cooling. Plate 2 (A) shows that belite can also occur as "blebs" in the matrix of aluminate and ferrite and Plate 2 (B) shows scalloped shaped belite crystals between alite crystals.

Belite crystals generally show characteristic lamellar textures (striations), and these are formed as a result of belite undergoing transformations from one phase to another on cooling. The incorporation of foreign ions into the belite structure will result in the stabilisation of a high temperature form.

Insley (1936) classified the different types of belite, and this has become an industry standard (Campbell 1986). Four types of belite, characterised by their lamellar structure, have been distinguished, and are listed below:

Type I - two or more sets of intersecting lamellae

Type Ia - discrete particles along traces of intersecting lamellae

Type II - one set of parallel lamellae

Type III - no lamellae

PLATE 1 CAPTIONS

A. Typical pseudo-hexagonal shape of alite crystal (A) in a powder mount.
Clinker from BCC - Lichtenburg
Powder mount in refractive index liquid of 1,715
Field of view = 150 μm x 110 μm

B. Large euhedral blue/brown alite crystals (A) together with golden/tan belite (B). The white interstitial matrix (I) consists of cryptocrystalline aluminate and ferrite.
Clinker from BCC - Lichtenburg
Polished specimen with 20 second Nital etch
Field of view = 150 μm x 110 μm

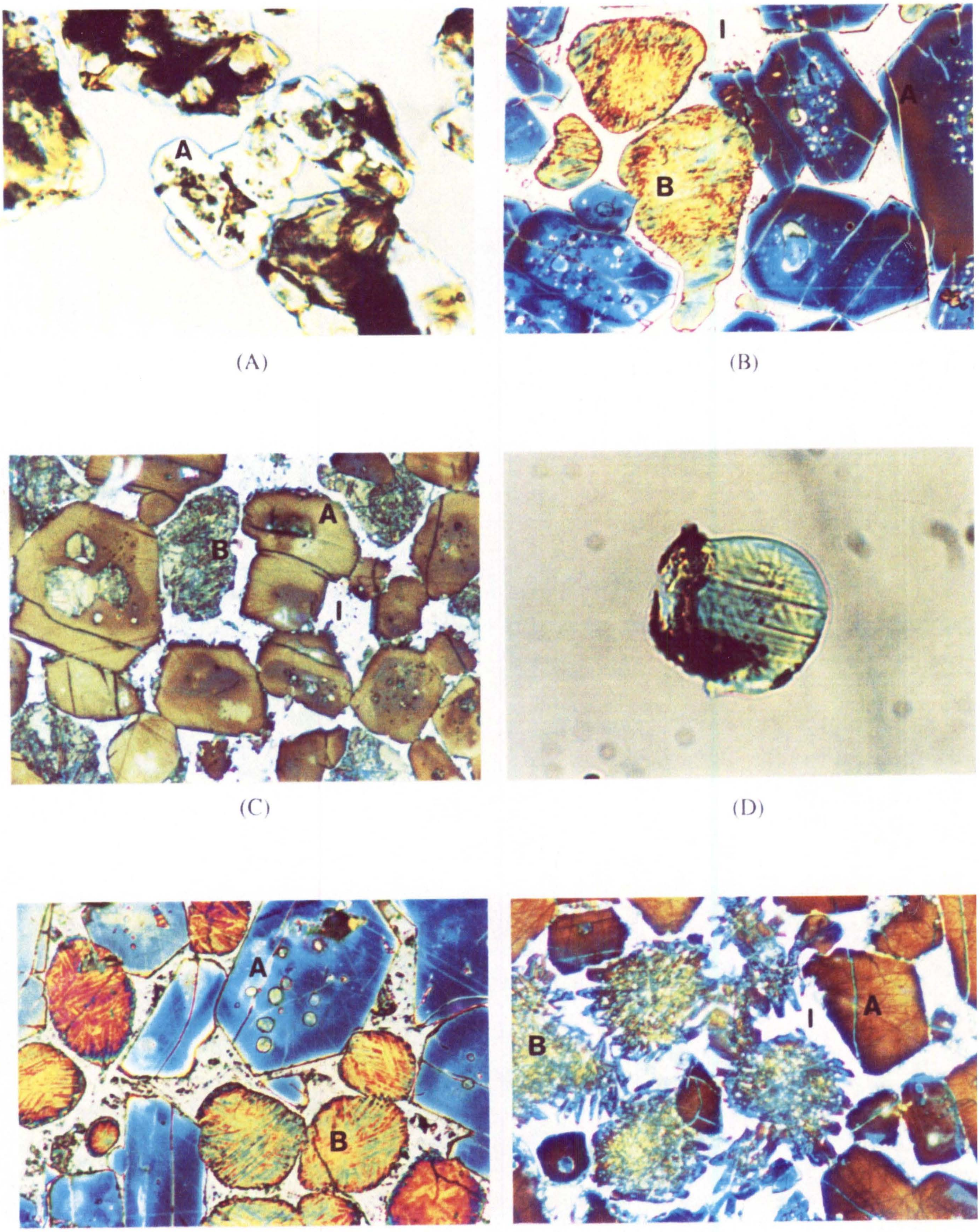
C. Large subhedral brown/tan alite crystals (A) which show transformational boundaries (consisting of belite). The multi-coloured belite (B) in the matrix is not well rounded. The aluminate and ferrite form a cryptocrystalline white matrix (I) to the alite and belite crystals.
Clinker from PPC - Jupiter
Polished specimen with 20 second Nital etch
Field of view = 150 μm x 110 μm

D. Round belite crystal showing multi-directional lamellae.
Clinker from PPC - Jupiter
Powder mount in refractive index liquid 1,715
Field of view = 150 μm x 110 μm

E. Rounded golden brown belite crystals (B) together with euhedral blue alite crystals (A).
Clinker from BCC - Lichtenburg
Polished specimen with 20 second Nital etch
Field of view = 150 μm x 110 μm

F. Ragged turquoise/yellow belite and subhedral brown/tan alite crystals in a white matrix of cryptocrystalline aluminate and ferrite.
Clinker from BCC - Lichtenburg
Polished specimen with 20 second Nital etch
Field of view = 150 μm x 110 μm

PLATE 1



(A) (B)

(C) (D)

(E) (F)

Campbell (1986) and Taylor (1990) discuss the lamellar structures and the origin of Type I, II and III in detail.

The Type I belite crystals are those formed above 1 420 °C and have crystallised in the α-C_2S form. The primary striations are due to the $\alpha \rightarrow \alpha'_H$ transition (the symmetry decreases from hexagonal to orthorhombic). The secondary set of striations is caused by the $\alpha'_L \rightarrow \beta$ transition in which the symmetry decreases from orthorhombic to monoclinic. Type I belites are the most common form found in production Portland cement clinkers.

Type II belites originate from belite which crystallises below the $\alpha \rightarrow \alpha'_H$ transition. The single set of striations are a result of the $\alpha'_{L\rightarrow} \beta$ transition. This form of belite is rare in production Portland cement clinkers.

Type III belite, also rare in production Portland cement clinkers, is a single crystal with a uniform internal microstructure.

The usual form of belite in Portland cement clinker is the β-C_2S polymorphic form, and as discussed earlier, it is usually stabilised by the incorporation of foreign ions. Nurse (1952) has shown that in the lattice of the β-C_2S crystal, the Ca^{2+} can be substituted by Mg^{2+}, K^+, Na^+, Ba^{2+}, Cr^{3+} and Mn^{2+}, while the $(SiO_4)^{4-}$ group can incorporate $(PO_4)^{3-}$ and $(SO_4)^{2-}$.

6.2.3 ALUMINATE

6.2.3.1 MODIFICATIONS

Pure C_3A does not exhibit polymorphism (Taylor 1990).

The C_3A may be cubic, orthorhombic, tetragonal or monoclinic and melts at 1 542 °C to form CaO and a liquid phase (Guinier and Regourd, 1968).

C_3A can incorporate a number of foreign ions into its structure. The Ca^{2+} can be substituted by Na^+ up to a level of about 1 per cent (Taylor, 1990), while the Al^{3+} can be substituted by Fe^{3+} or Si^{4+}. Lea et al. (1982) found that under equilibrium conditions, the level of substitution by Fe^{3+} was 3 per cent to 4 per cent and by Si^{4+} about 2 per cent. Higher levels of substitution were possible in slowly-cooled Portland cement clinkers.

Typical composition of pure C_3A and orthorhombic and cubic aluminate occurring in Portland cement clinker is given in Table 13, page 102.

6.2.3.2 OPTICAL CHARACTERISTICS

The optical characteristics of aluminate are given in Table 14, page 103 (modified from Bogue, 1955).

6.2.3.3 IDENTIFICATION OF ALUMINATE IN CLINKER

In transmitted plane-polarised light, the aluminate phase is colourless to tan or brown, while in cross-polarised light, it is usually isotropic.

In incident light, the aluminate is etched grey with water and appears as long prismatic crystals when present as the orthorhombic variety, which occurs if sufficient alkali is present (Taylor, 1990). Pollitt and Brown (1968) have established that the orthorhombic form of C_3A is formed with a minimum alkali content of 2,8 per cent equivalent potash or 1,8 per cent equivalent soda. The formation of the alkali aluminate is also favoured by rapid cooling. Plate 2 (C) shows long lath-like crystals of alkali aluminate. In low-alkali or alkali-free clinker, the aluminate crystallises in the cubic form. It occurs as a dark interstitial phase intermixed with the dendritic ferrite phase (Campbell, 1986). Plate 2 (D) shows cubic C_3A crystals intergrown with C_4AF. Plate 2 (E) show the appearance of aluminate formed under reducing conditions.

The rate of cooling of the clinker also determines the crystal size of the aluminate.

6.2.4 FERRITE

6.2.4.1 POLYMORPHISM AND SOLID SOLUTION

The ferrite phase C_4AF is one point in a solid solution series which ranges from C_2F to hypothetical C_2A. The one end member of the series, C_2F, shows three polymorphic forms (Woermann et al, 1968), but all experiments carried out indicate that the differences between the three polymorphic forms are very small.

C_4AF can incorporate about 10 per cent of foreign ions into its lattice (Taylor, 1990). These can include Si^{4+}, Mg^{2+}, Ti^{4+}, Mn^{3+}, and Cr^{3+}.

The typical composition of C_4AF and ferrite occurring in Portland cement clinker is given in Table 13, page 102.

6.2.4.2 OPTICAL CHARACTERISTICS

The optical characteristics are given in Table 14, page 103.

PLATE 4 CAPTIONS

A. Large areas of K_2SO_4 (K) - dark speckled material - in voids between light brown alite and rounded tan belite crystals. The Na_2O of the clinker was approximately 1,2 per cent, resulting in the crystallisation of the alkali sulphate in the voids.
Clinker from Blue Circle (UK) - Plymstock
Polished specimen with HF vapour etch
Field of view = 150 μm x 110 μm

B. Small areas of dark alkali sulphate (K) which show a characteristic "halo" of light grey in the normally brown surrounding alite. Ill-formed, speckled blue belite and white ferrite are also visible.
Clinker from Blue Circle (UK) - Aberthaw
Polished specimen with HF vapour etch
Field of view = 150 μm x 110 μm

C. Large alite crystals (A) which are fused together. The belite (B) occurs predominantly as clusters in the clinker.
Clinker from BCC - Lichtenburg
Polished specimen with 20-second Nital etch
Field of view = 600 μm x 435 μm

D. A clinker microstructure showing the alite and belite crystals well distributed through the clinker.
Clinker from BCC - Lichtenburg
Polished specimen with 20-second Nital etch
Field of view = 300 μm x 215 μm

E. A large, pore-centered, grey/blue belite cluster (B) resulting from a large quartz particle in the kiln feed. The green/brown epoxy impregnation media (E) is visible surrounding the clinker.
Clinker from PPC - Riebeeck Wes
Polished specimen with 20-second Nital etch
Field of view = 300 μm x 215 μm

F. A large particle of dolomite in the kiln feed which has not combined totally, resulting in a cluster of free lime (L) and periclase (P), surrounded by blue/green alite crystals.
Clinker from PPC - Hercules
Polished specimen with 10-second distilled water + 20-second Nital etch
Field of view = 150 μm x 110 μm

PLATE 2 CAPTIONS

A. Belite (B) occurring as "blebs" in a matrix of aluminate and ferrite. Belite also occurs on the edges of the alite crystals (A) which show blue interior and yellow borders.

Clinker from BCC - Lichtenburg
Polished specimen with 20 second Nital etch
Field of view = 150 μm x 110 μm

B. Belite occuring as yellowish scallop shaped crystals (B) in between large blue alite crystals (A). The matrix of aluminate and ferrite (I) is cryptocrystaline.

Clinker from BCC - Lichtenburg
Polished specimen with 20 second Nital etch
Field of view = 150 μm x 110 μm

C. Unetched grey/brown alite (A) and belite crystals (B) surround brown, lath-like crystals (C) of alkali aluminate (C_3A). Creme C_4AF (F) is also present.

Clinker from ICMA #32 sample
Polished specimen with 10 second KOH etch.
Field of view = 150 μm x 110 μm

D. Unetched grey/brown alite and belite. The well differentiated matrix consists of dark brown C_3A (C) in the cubic form and creme C_4AF (F).

Clinker from ICMA #32 sample
Polished specimen with 10 second KOH etch.
Field of view = 150 μm x 110 μm

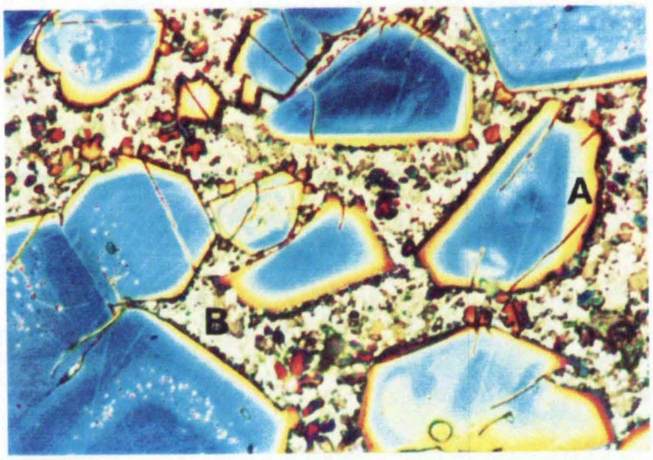
E. Extensive formation of large, dark creme C_3A crystals (C) possibly as a result of reducing conditions in the kiln. Other phases include poorly shaped blue alite and slightly ragged multi-coloured belite crystals.

Clinker from BCC - Lichtenburg
Polished specimen with 20 second Nital etch
Filed of view = 150 μm x 110 μm

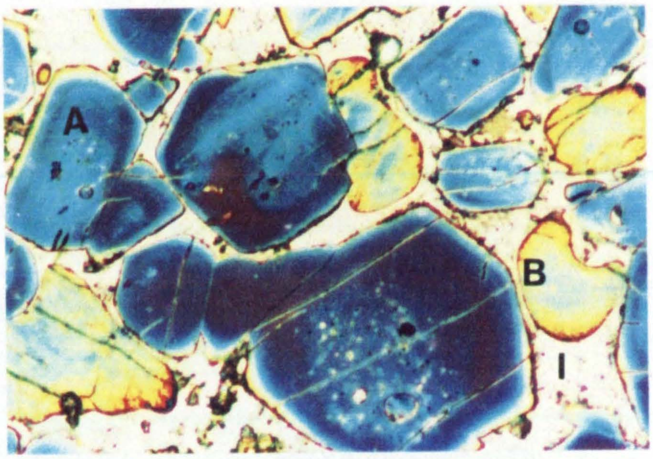
F. Brown/tan and dark blue euhedral alite crystals occur together with rounded greenish blue belite. The white, cryptocrystalline matrix (I) consists of C_3A and C_4AF.

Clinker from BCC - Lichtenburg
Polished specimen with 20 second Nital etch
Field of view = 150 μm x 110 μm

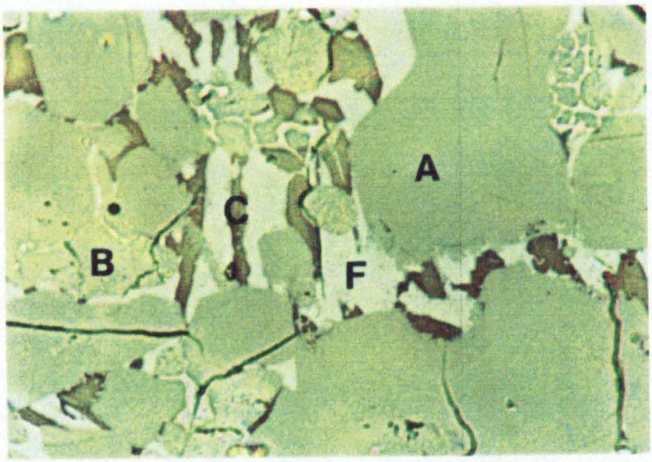
PLATE 2



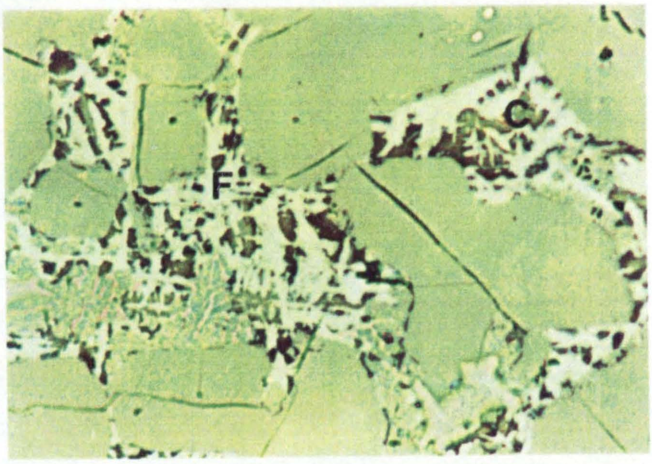
(A)



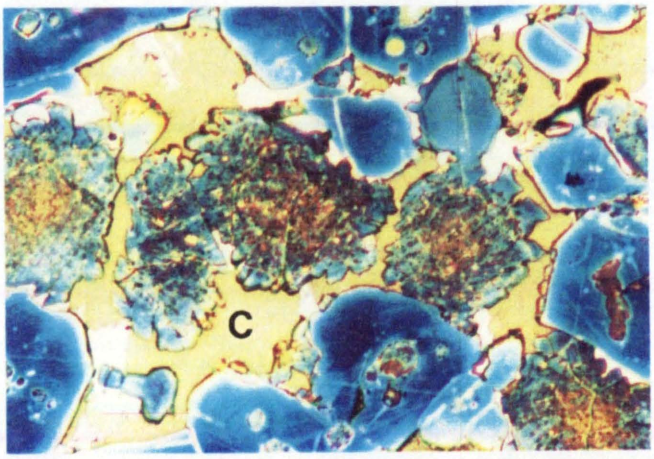
(B)



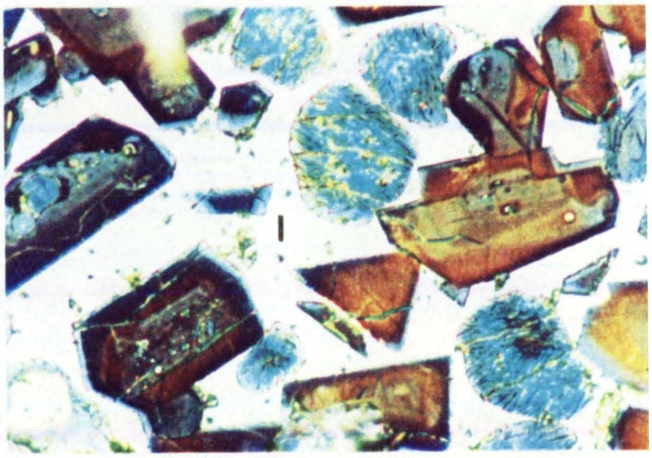
(C)



(D)



(E)



(F)

6.2.5 FREE CaO

6.2.5.1 IDENTIFICATION OF FREE CaO IN CLINKER

Free CaO, almost always present in clinker, can occur in two predominant forms. As small, white, rounded crystals in the matrix (as clusters or distributed throughout the clinker), or as fringes around alite crystals (as a result of the decomposition of alite to belite and free CaO).

Table 14, page 103 gives the optical properties of free CaO.

Free CaO etches rapidly with water to produce iridescent colours. Plate 3 (B) shows a cluster of free CaO crystals etched with distilled water for 10 seconds, while Plate 3 (C) shows free lime distributed throughout the clinker nodule. Plate 3 (D) shows free lime and belite occurring as a fringe around alite crystals.

6.2.6 PERICLASE

6.2.6.1 IDENTIFICATION OF PERICLASE IN CLINKER

Periclase is cubic magnesium oxide and occurs as small colourless triangular, octahedral, rectangular, or rounded grains, or as dendritic crystals (Campbell, 1986). Although MgO can be incorporated into most of the Portland cement clinker phases, if it is present in amounts in excess of 2 per cent (Kurdowski, 1991), it will crystallise as individual periclase crystals on cooling. The form of the periclase will depend on the rate of cooling of the clinker and may be either euhedral or dendritic.

Table 14 (page 103) gives the optical properties of periclase.

In incident light, periclase is seen as pinkish, light grey crystals of high relief (because of its hardness). It is not easily etched by any of the more common etching media.

Plate 3 (E) shows euhedral periclase while Plate 3 (F) shows dendritic periclase.

6.2.7 MINOR PHASES

6.2.7.1 ALKALI SULPHATES

Sodium and potassium sulphates occur in various crystal forms and are the last phases to crystallise in the Portland cement clinker. They are typically found as small crystals in voids in Portland cement clinker or as deposits on alite crystals. Plates 4 (A) and 4 (B) show the typical appearance of alkali sulphates in polished section.

In incident light, alkali sulphates are recognised as dark crystals when etched with hydrofluoric acid or potassium hydroxide (0,1 Molar aqueous). Table 14, page 103 gives optical properties of the more common alkali sulphates.

The most common alkali sulphates are arcanite ($K\bar{S}$), calcium langbeinite ($K_2C_2\bar{S}_3$) and aphthitalite ($K_3N\bar{S}_4$).

PLATE 3 CAPTIONS

A. Coarse crystallisation of dark brown C_3A (C) and creme C_4AF (F) in a moderately slow-cooled clinker. The alite crystals are blue/yellow and the belite multi-coloured.
Clinker from ICMA #32 sample
Polished specimen with 10 second KOH + 20 second Nital etch
Field of view = 150 μm x 110 μm

B. A cluster of multicoloured free lime crystals (L) is surrounded by unetched grey/brown alite and belite. The white matrix consisting predominantly of C_4AF is visible. The green/brown colour of the epoxy impregnating medium (E) is also seen.
Clinker from ICMA #31 sample
Water etch, 10 seconds
Field of view = 300 μm x 215 μm

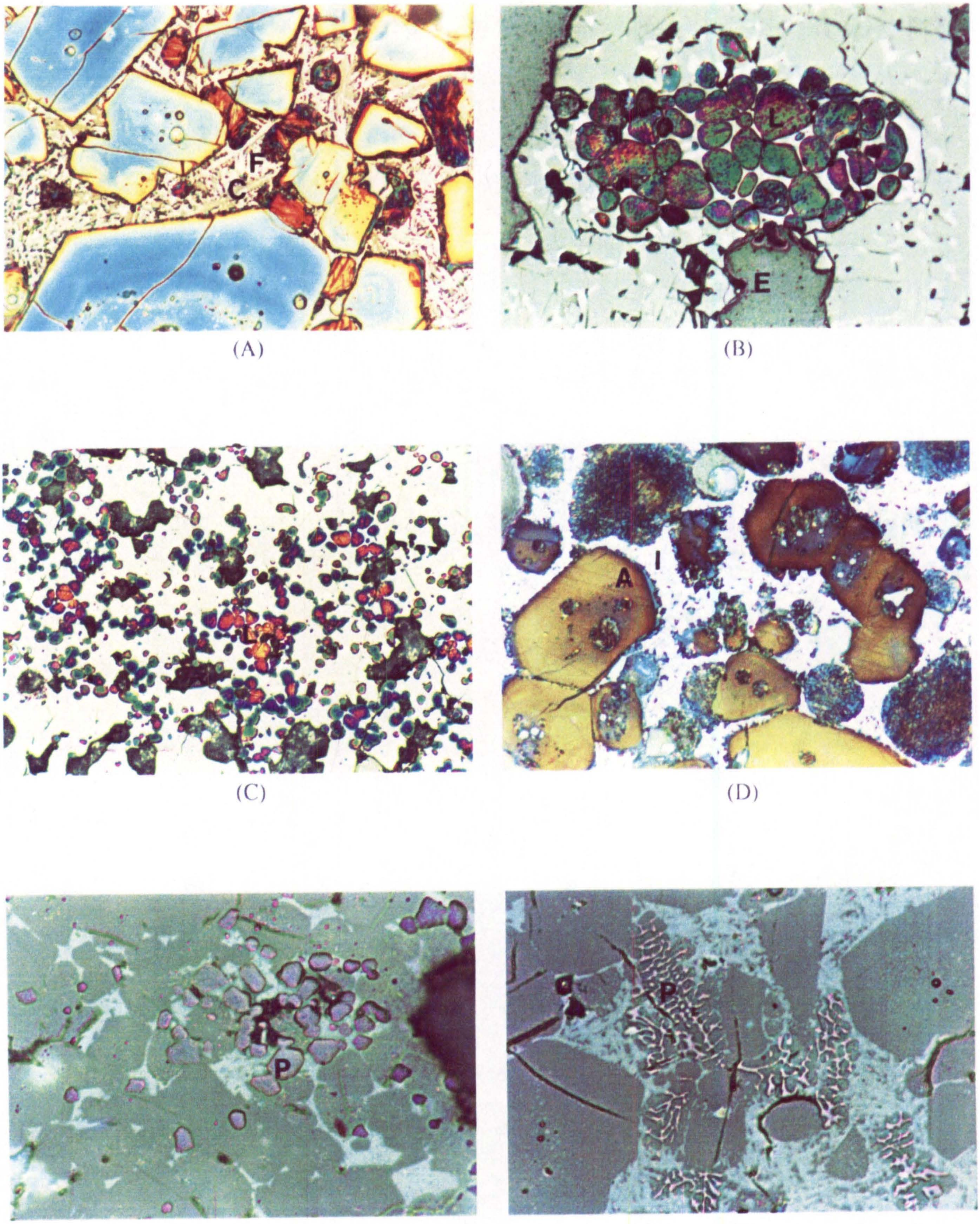
C. Multi-coloured free lime crystals (L) distributed throughout the clinker nodule.
Clinker from BCC - Lichtenburg
Polished specimen with 10 second distilled water etch
Field of view = 600 μm x 435 μm

D. Free lime and belite occurring as a fringe around euhedral brown/tan alite crystals (A). The aluminate and ferrite form the cryptocrystalline matrix.
Clinker from PPC - Jupiter
Polished specimen with 10 second Nital etch
Field of view = 150 μm x 110 μm

E. Euhedral pink periclase crystals (P) - sample has been "relief" polished - form a small cluster in unetched grey/brown alite and belite. The creme matrix consists of cryptocrystalline C_3A and C_4AF. A dark pore is visible on the extreme right of the photograph.
Clinker from PPC - Jupiter
Relief-polished specimen with no etch
Field of view = 150 μm x 110 μm

F. Pink periclase occurring as dendritic crystals (P) in between unetched grey/brown alite and belite crystals. The matrix consists of creme, cryptocrystalline C_3A and C_4AF. (The sample has been relief-polished.)
Clinker from Coplay Cement Company, Indiana, USA
Polished specimen with no etch
Field of view = 150 μm x 110 μm

PLATE 3



(A) (B)

(C) (D)

(E) (F)

6.3 INTERPRETATION OF MICROSTRUCTURES

The identification and interpretation of microstructural features in Portland cement clinker can indicate the extent to which manufacturing parameters are met in producing a Portland cement clinker of good quality.

The parameters which can have an effect on the quality of the Portland cement clinker can be divided into the following categories;

Raw materials - mineralogical variations
Raw mix preparation - particle size distribution and homogeneity
Burning conditions of kiln
Cooling conditions in kiln and cooler

6.3.1 RAW MATERIALS - MINERALOGICAL VARIATIONS

The mineralogy of the raw materials required to produce a Portland cement clinker can vary considerably. For example, the SiO_2 could be supplied as a sand (pure quartz) or in the form of a clay mineral or feldspar (combined silica), and the Al_2O_3 could be derived from clays and shales, or from industrial by-products such as fly ash. Fe_2O_3 could also be derived from a number of sources (clays, shales, industrial by-products or pure compounds). Although the chemical compositions may be identical, the different mineralogical mixtures will have different hardness (affecting the particle size distribution) and different combinabilities during burning (affecting the formation of the Portland cement clinker phases). The clinker resulting from kiln feeds of identical chemistry but different mineralogy will show variations, particularly in the size and distribution of the Portland cement clinker phases.

Microstructures depicting a change in the source of one or several of the components in the raw mix are shown in Plates 4 (C) and 4 (D). Plate 4 (C) shows a clinker from the Blue Circle Cement Lichtenburg plant which has been produced from a mix which is traditionally difficult to burn (a large proportion of the SiO_2 occurs as free quartz). The alite crystals are large (an average size of 80 μm) and fused together, and there is an abundance of belite clusters. These are both characteristic signs of hard burning. In contrast, Plate 4 (D) shows a clinker which, although produced from a raw mix with **the same chemistry as above**, shows much smaller alite crystals (an average size of 40μm) with less fusion. The belite is distributed throughout the clinker and clusters are rare. The mineralogy of the latter kiln feed resulted in an easier burnability and a clinker of better quality because of a reduction in the proportion of SiO_2 as free quartz.

6.3.2 RAW MIX PREPARATION

The preparation of the raw mix is one of the most critical parts of the Portland cement clinker manufacturing process and the effects of poor preparation can easily be seen in the clinker.

6.3.2.1 PARTICLE SIZE DISTRIBUTION

The particle size distribution and the maximum size of the limestone and quartz particles has a great effect on the rate of reaction in the kiln (Hawkins 1979), Dorn (1987).

Increased particle sizes will require a longer heating time and a higher temperature to combine them to form the Portland cement clinker phases.

The microstructures seen in a Portland cement clinker which has over-size particles (particularly limestone and quartz) in the kiln feed are shown in Plates 4 (E), 4 (F) and 5 (A).

The inability to convert a coarse particle of quartz into belite and alite results in the formation of a belite cluster with a void at its centre (Plate 4 (E)).

A coarse particle of dolomite in the kiln feed results in a cluster of periclase and free lime in the resulting Portland cement clinker (Plate 4 (F)). Similarly, Plate 5 (A) shows the remnants of a coarse limestone particle, which has resulted in the formation of a cluster of free lime in the Portland cement clinker.

6.3.2.2 HOMOGENEITY OF KILN FEED

If the kiln feed is not properly homogenised before entering the kiln, the evidence will again be present as particular microstructures in the Portland cement clinker. Typically, poor homogenisation will manifest itself as streaks of clinker minerals through the nodules.

Szabo, (1994) differentiates between clusters of belite (the result of coarse quartz grains in the kiln feed), discussed in 6.3.2.1 above, and nests/streaks of belite, which he interprets as the result of a heterogeneous kiln feed.

Plate 5 (B) shows streaks of belite in a Portland cement clinker, probably the result of a poorly homogenised kiln feed.

PLATE 4 CAPTIONS

A. Large areas of K_2SO_4 (K) - dark speckled material - in voids between light brown alite and rounded tan belite crystals. The Na_2O of the clinker was approximately 1,2 per cent, resulting in the crystallisation of the alkali sulphate in the voids.

Clinker from Blue Circle (UK) - Plymstock
Polished specimen with HF vapour etch
Field of view = 150 μm x 110 μm

B. Small areas of dark alkali sulphate (K) which show a characteristic "halo" of light grey in the normally brown surrounding alite. Ill-formed, speckled blue belite and white ferrite are also visible.

Clinker from Blue Circle (UK) - Aberthaw
Polished specimen with HF vapour etch
Field of view = 150 μm x 110 μm

C. Large alite crystals (A) which are fused together. The belite (B) occurs predominantly as clusters in the clinker.

Clinker from BCC - Lichtenburg
Polished specimen with 20-second Nital etch
Field of view = 600 μm x 435 μm

D. A clinker microstructure showing the alite and belite crystals well distributed through the clinker.

Clinker from BCC - Lichtenburg
Polished specimen with 20-second Nital etch
Field of view = 300 μm x 215 μm

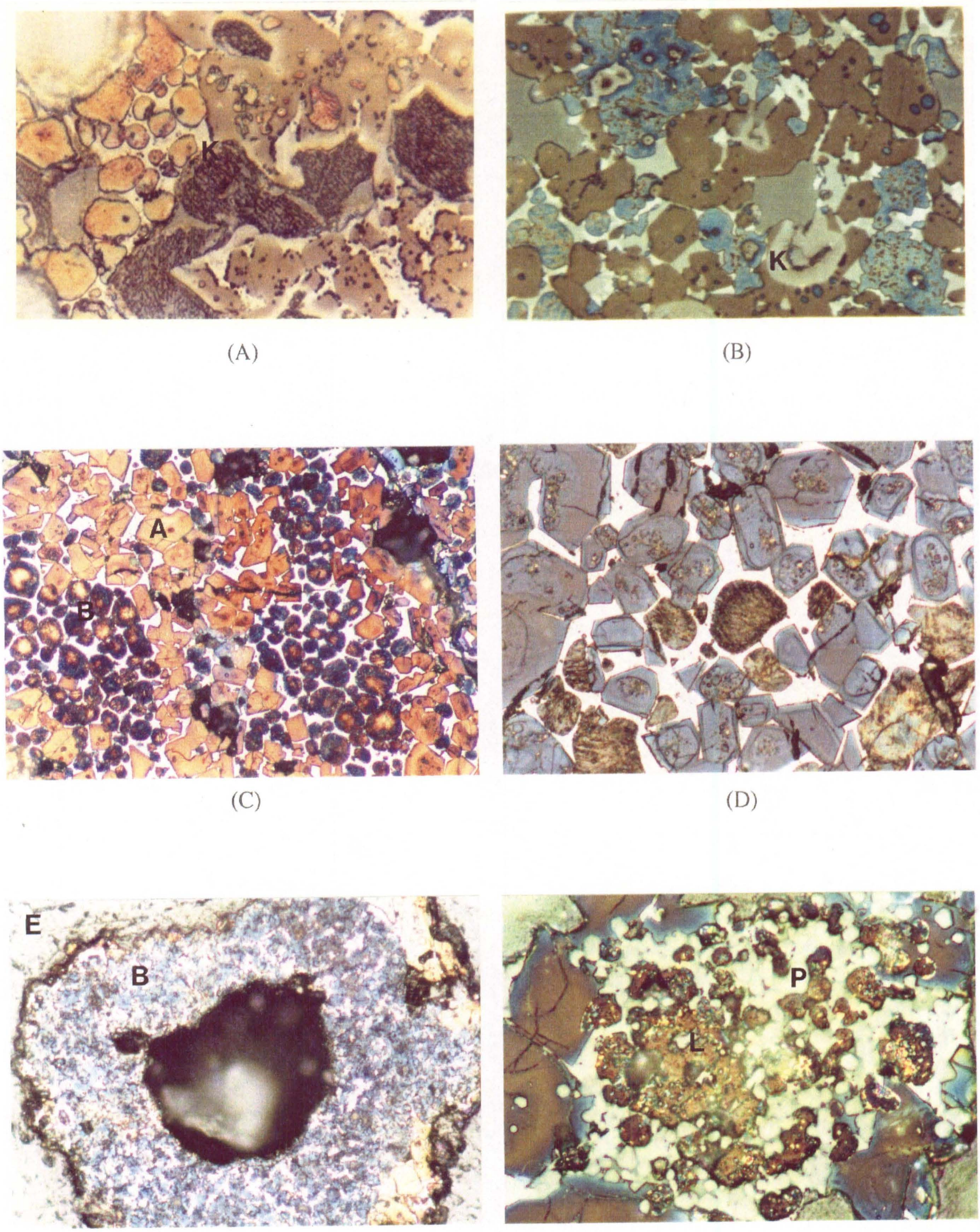
E. A large, pore-centered, grey/blue belite cluster (B) resulting from a large quartz particle in the kiln feed. The green/brown epoxy impregnation media (E) is visible surrounding the clinker.

Clinker from PPC - Riebeeck Wes
Polished specimen with 20-second Nital etch
Field of view = 300 μm x 215 μm

F. A large particle of dolomite in the kiln feed which has not combined totally, resulting in a cluster of free lime (L) and periclase (P), surrounded by blue/green alite crystals.

Clinker from PPC - Hercules
Polished specimen with 10-second distilled water + 20-second Nital etch
Field of view = 150 μm x 110 μm

PLATE 4



(A) (B)

(C) (D)

(E) (F)

6.3.3 BURNING CONDITIONS IN THE KILN

The burning conditions in the kiln are usually interpreted by using the Ono Method as described in Chapter 7, but microstructures are also seen in polished specimens which indicate either good or poor burning conditions in the kiln. In both powder and polished specimens however, the alite crystal size is used to infer the rate of temperature increase into the burning zone (from 1 100 to 1 450 °C), while the belite crystal size is used to gauge the length of time spent at the maximum clinkering temperature (ca. 1 450 °C).

The length and temperature of the burning zone in the kiln can vary greatly, depending on the amount of fuel, induced draft (ID) fan speed and level of feed in the kiln to name only three variables (Hawkins, 1979). In general, the slower the heat rise, the larger the alite crystals. Similarly, the longer time spent at maximum temperature, the larger the belite crystals. Ono (1981) states that an average alite size of 15 to 20 μm indicates a quick heating rate, while an average belite size of 5 to 10 μm indicates a short burning time.

Plate 5 (C) shows a polished specimen of a good clinker microstructure in which the average alite size is 30 μm and average belite size is 25 μm. This implies that the heat rate was moderately fast and the burning time long. The crystal sizes for both alite and belite could be decreased by altering the length and temperature of the burning zone.

6.3.4 COOLING CONDITIONS

The most important period of Portland cement clinker cooling is that which occurs from a position behind the flame to the nose of the kiln. In this area, the temperature drops from 1 450 to below 1 280 °C, at which point the liquid phase freezes. If the clinker is allowed to cool slowly in this zone, the crystallisation of all the Portland cement clinker phases are affected. Further cooling which takes place in the cooler itself does not affect the formation of the Portland cement clinker phases (Hawkins, 1979).

The alite may show transformation along its edges (to belite and free lime) and the belite edges become ragged if the cooling behind the flame is slow. The interstitial matrix of C_3A and C_4AF shows an increase in crystal size on slow cooling. Plate 5 (D) shows alite crystals which exhibit transformation boundaries of belite and free lime. The edges of the belite crystals are not sharp and show slight decomposition. Plate 5 (E) shows coarse crystallisation of the C_3A and C_4AF phases in the interstitial space between the alite and belite crystals.

6.3.5 REDUCING CONDITIONS

As mentioned in section 3.3.6 the effects of reducing conditions on the Portland cement clinker include the decomposition of C_3S and the formation of C_3A at the expense of C_4AF. Plate 5 (F) shows the extensive development of C_3A and the decomposition of alite typical of reducing conditions.

PLATE 5 CAPTIONS

A. A coarse limestone particle in the kiln feed which has not combined totally has resulted in a cluster of multi-coloured free lime (L). Original banding in the particle is still evident.

Clinker from PPC - Hercules
Polished specimen with 20-second Nital etch
Field of view = 150 μm x 110 μm

B. A coarse band of multi-coloured, rounded belite (B) in the clinker. Blue crystals of alite (A) are also visible. This is the result of poor homogenisation of the kiln feed.

Clinker from PPC - Hercules
Polished specimen with 20-second Nital etch
Field of view = 300 μm x 215 μm

C. Moderately large brown alite (A) and multi-coloured belite crystals, indicating a moderate heating rate and long burn time of the kiln feed.

Clinker from PPC - Jupiter
Polished specimen with 20-second Nital etch
Field of view = 300 μm x 215 μm

D. Brown alite crystals (A) showing transformation boundaries and multi-coloured belite crystals with ragged edges.

Clinker from BCC - Lichtenburg
Polished specimen with 15-second Nital etch
Field of view = 150 μm x 110 μm

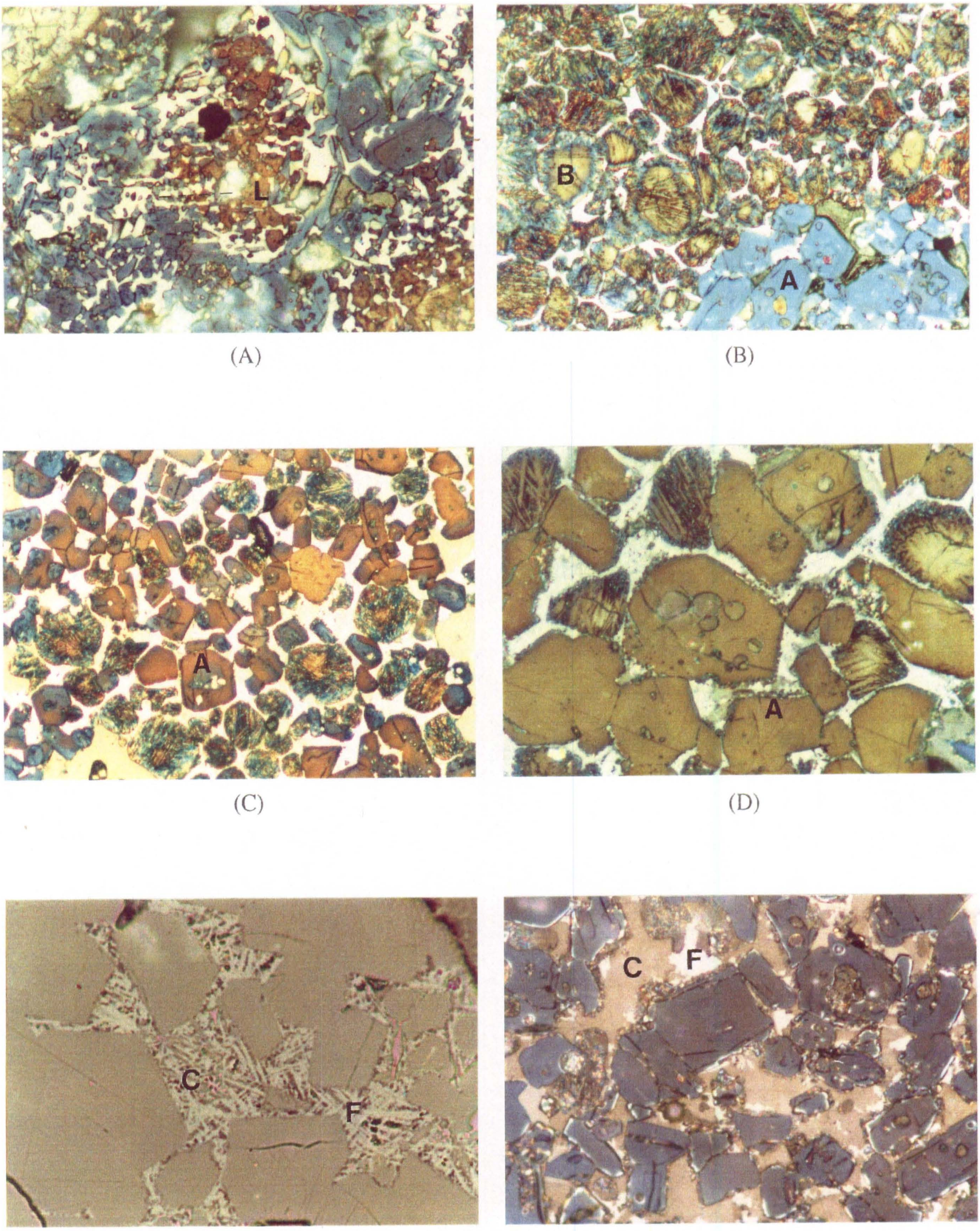
E. Coarse crystallisation of brown C_3A (C) and creme C_4AF (F) phases due to slow cooling. Unetched alite and belite crystals appear grey/brown.

Clinker from ICMA #32 sample
Polished specimen with 10-second KOH etch
Field of view = 300 μm x 215 μm

F. Dull blue alite crystals showing decomposition to belite and free lime. Large, light brown C_3A crystals (C) are easily distinguished from the creme C_4AF (F) in the reduced clinker.

Clinker from Simuma, Natal
Polished specimen with 10-second KOH + 20-second Nital etch
Field of view = 150 μm x 110 μm

PLATE 5



(A) (B)

(C) (D)

(E) (F)

Table 13. Composition of Portland cement clinker phases (after Taylor, 1990).

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	Mn_2O_3	K_2O	Na_2O	SO_3	P_2O_5
Pure C_3S	73,7	26,3	-	-	-	-	-	-	-	-	-
Alite	71,6	25,2	1,0	0,7	1,1	0,0	0,0	0,1	0,1	0,0	0,2
Pure C_2S	65,1	34,9	-	-	-	-	-	-	-	-	-
Belite	63,5	31,5	2,1	0,9	0,5	0,2	0,0	0,9	0,1	0,1	0,2
Pure C_3A	62,3	-	37,7	-	-	-	-	-	-	-	-
C_3A (cubic)	56,6	3,7	31,3	5,1	1,4	0,2	0,0	0,7	1,0	0,0	0,0
C_3A (ortho)	53,9	4,3	28,9	6,6	1,2	0,5	0,0	4,0	0,6	0,0	0,0
Pure C_4AF	46,1	-	21,0	32,9	-	-	-	-	-	-	-
C_4AF	47,5	3,6	21,9	21,4	3,0	1,6	0,7	0,2	0,1	0,0	0,0

Table 14. Optical characteristics of Portland cement clinker phases (modified from Bogue, 1955).

Mineral	Refractive Indices			Optical Characteristics			Reference
	α	β	γ	Character	Birefringence	2V	
C_3S (T_1)	1,713		1,717	Biaxial (-)		20-60°	Taylor, 1992
C_3S	1,718		1,723	Uniaxial (-)	0,005	small	Weyer, 1931 *
Alite	1,716-1,720		1,722-1,724	Uniaxial (-)			Burke, 1952 *
α-C_2S	1,652		1,661		0,009	0-20°	Nagelschmidt, 1937 *
α'-C_2S	1,712	1,716	1,725		0,013	30°	Tilley and Vincent, 1948 *
β-C_2S	1,717		1,735	Biaxial (+)	0,018	large	Rankin and Wright, 1915 *
γ-C_2S	1,642	1,645	1,654	Biaxial (-)	0,012	60°	Rankin and Wright, 1915 *
C_3A		1,710		Isotropic			Rankin and Wright, 1915 *
C_4AF	1,98	2,05	2,08	Biaxial (-)	0,10	medium	Hansen et al, 1928 *
CaO		1,83		Isotropic			Sosman et al, 1915 *
MgO		1,736		Isotropic			Knibbs, 1924 *
K_2SO_4	1,493	1,494	1,497	Biaxial (+)			Newkirk, 1952
(Na,K)$_2$(SO$_4$	1,480-1,500			Uniaxial (-)			Newkirk, 1952
Na_2SO_4	1,471	1,477	1,484	Biaxial (+)		84°	Newkirk, 1952

* all cited by Bogue, 1955

7. THE ONO METHOD

7.1 HISTORY

The Ono method is the result of over 30 years of research by Ono and co-workers (Ono, 1957; Yamaguchi and Ono, 1962; Ono, Kawamura and Fujimura, 1964; Ono and Shimoto, 1967; Ono and Shimoto, 1968) in Japan to perfect the technique of estimating the burning and cooling conditions in the kiln by transmitted light examination of powdered samples of cement clinker. Perhaps the most important publication is that by Ono, Kawamura and Soda (1968), presented at the Fifth International Symposium on Chemistry of Cement, which discusses the relationship between the optical properties of alite and belite and the hydraulic strength of cement.

A very important milestone in the history of the Ono method was the introduction of the technique to American cement manufacturers by Mau (1975). Ono (1975) also presented his work to representatives of cement companies at a seminar in Hawaii in 1975.

Since the introduction of his technique, there have been many views expressed as to advantages and disadvantages of the method. Its limitations are that the structure, particle size, and particle interaction of cement clinker phases cannot be studied in depth. These needs may be satisfied by the use of polished sections.

Fundal (1982) and Pennell (1987) expressed reservations about the method of measuring the crystal width and its influence on the value of the alite birefringence as set out in the formula. These and other misconceptions of the Ono method have been largely clarified in recent publications (Campbell, 1986).

Ono himself states that variations in the powder-mount parameters reflect **relative** changes in the kiln conditions. This is probably the most important element of the Ono method, because if the technique can be used to determine the relative changes in kiln conditions, then changes can be made to improve the conditions for formation of the clinker.

7.2 EXPLANATION

The Ono method is based on the measurement of optical parameters of clinker particles mounted in a liquid medium on a glass microscope slide.

The values obtained are used to imply the heating and cooling rates of formation of the clinker minerals, and the technique can be carried out in approximately 30 minutes. It is recommended however, to supplement the data from transmitted light observations with those obtained from incident light observations of polished specimens.

The sample for examination for Ono parameters is prepared by wet-sieving the ground clinker (using iso-propyl alcohol) through 75-μm and 45-μm sieves. A small representative sample of the -75 μm, +45 μm fraction of the clinker is mounted on a glass slide with a few drops of oil of refractive index (RI) 1,715 to 1,720 (Campbell, 1986).

A standard polarised-light microscope with a Sénarmont compensator (a thin mica plate which is oriented parallel to the analyser and produces a path difference of one quarter wavelength), and rotatable analyser is used, and the following properties recorded:

Alite size
Alite birefringence
Belite size and
Belite colour

A brief description of each of these parameters and their significance are stated below.

7.2.1 ALITE SIZE

Alite size in the Ono method refers to the average length of the alite crystals. The measurements of at least ten of the most commonly occurring size of alite crystals are recorded. Alite crystal length can also be measured using incident light examination of polished surfaces which have been suitably etched or stained. Plate 6 (A) shows alite crystals in a polished specimen which can be measured for length.

Alite size according to Ono depends on the heating (burning) rate and the crystallisation rate. Quick burning in a short flame produces small alite crystals while slow burning in the long flame produces large alite crystals.

7.2.2 ALITE BIREFRINGENCE

To determine the birefringence, the retardation and thickness of the crystal must be measured.

The formula relating these parameters is:

$$\mathit{Retardation}(\delta) = \mathit{Birefringence}(B) \times \mathit{Thickness}(t)$$

thus

$$\mathit{Birefringence}(B) = \frac{\mathit{Retardation}(\delta)}{\mathit{Thickness}(t)}$$

The term n_s-n_f is called birefringence and is the difference between the indices of the fast and slow light rays as they pass through optical material which divides the light into two refracted rays travelling in slightly different directions at different velocities. Its numerical value depends on the path followed by the light through the mineral. The maximum birefringence is a characteristic of each mineral (Nesse, 1986).

Retardation (δ) is the distance that the slow ray lags behind the fast ray and is related to the birefringence of the material and its thickness (Kerr, 1959).

The measurement of the retardation and crystal thickness may be sources of error and must be measured carefully. The retardation can be measured with the use of the Sénarmont compensator. The phase difference can thus be reduced to zero by rotating the analyser by a measurable amount (θ). Monochromatic light with a wavelength (λ) of 546 nanometre is required and a green filter is used to obtain this wavelength.

The retardation is a direct function of theta and the wavelength of the light passing through the filter. These are related by the formula:

$$\textit{Retardation} = \frac{\lambda \ x \ \theta}{180}$$

Combining the two formulae for retardation and birefringence, the result is:

$$\textit{Birefringence} = \frac{\lambda \ x \ \theta}{180 \ x \ 0{,}75 \ x \ W \ x \ 1000}$$

where θ = angle of analyser rotation
λ = wavelength of green filter in nanometre (546) which is divided by 1000 to convert to micrometre
W = crystal width in micrometre

This equation, therefore reduces to:

$$\textit{Birefringence} = \frac{\theta}{W} \ x \ (0{,}004044)$$

To measure the alite birefringence using a Sénarmont compensator, the following simplified procedure may be followed:

1. Select a relatively bright alite crystal (in the 45° position using plane-polarised light with crossed nicols), having approximately 2:1 length:width measurements. This will ensure that the crystal chosen has the correct orientation to measure the birefringence.

2. Measure and record the crystal width using a graduated eye-piece scale, calibrated by a micrometer scale.
3. Rotate the crystal 45° from the extinction position, using plane-polarized light with crossed nicols. Plate 6 (B) shows an alite crystal which is correctly oriented and of the correct dimensions to measure the birefringence.
4. Insert a green filter in the light path below the stage and the Senarmont compensator above the analyser.
5. Rotate the analyser until the crystal appears dark. Read the angle (theta) off the analyser scale. The crystal should darken from the edges inwards (compensating position). If the crystal darkens from the centre to the edges the angle of analyser rotation is subtracted from 180 to obtain theta.
6. The values are substituted into the equation above to obtain the alite birefringence.

7.2.3 BELITE SIZE

Belite size in the Ono method is the average of the longest diameters of approximately ten belite crystals. Belite size may also be determined in polished section. Plate 6 (C) shows belite crystals in a cluster (polished specimen) which can be used for size measurement.

The crystal size of belite is dependent on the time maintained above 1 400 °C, in other words, the burning time. Between 1 100 °C and 1 400 °C, small crystals of α'-belite form from the mix constituents, and this is converted to larger α-belite above 1 400 °C.

7.2.4 BELITE COLOUR

Belite colour is estimated using an arbitrary numerical scale:

Amber	1
Yellow	2
Pale yellow	3
Clear	4

At least ten belite crystals, which are not coated with ferrite interstitial phases, should be examined. Belite can contain up to 5 per cent impurities. If the belite cools slowly, the impurities exsolve out from the belite crystal lattice structure and this causes the colour to change from clear to faint yellow to yellow to amber. The slower the cooling rate, the darker the belite colour. Plates 6 (D), (E) and (F) show belite crystals of different colour according to the criteria of Ono. Plate 6 (D) shows a clear belite, Plate 6 (E) a pale yellow belite and Plate 6 (F) a belite which is yellow to amber in colour.

7.3 USE OF ONO PARAMETERS

The values obtained for the Ono parameters can be used to evaluate the kiln conditions as set out in the Table 15 (after Ono 1981).

In addition to being able to interpret the kiln burning conditions from the table, Ono (1981) also developed a multi-regressional equation to predict the 28-day mortar-cube strength from the microscopical data. This is discussed in detail by Campbell (1986).

PLATE 6 CAPTIONS

A. The length of the euhedral brown alite crystals (A) can easily be measured in a polished specimen to record the Ono parameter "alite length".

Clinker from PPC - Jupiter
Polished specimen with 15-second Nital etch
Field of view = 150 μm x 110 μm

B. An alite crystal (A) of the correct dimensions and oriented at 45° from the extinction position. The birefringence can be measured according to the Ono Method.

Clinker from ICMA #28 sample
Powder mount in refractive index liquid 1,715
Field of view = 150 μm x 110 μm

C. The size of individual belite crystals (B) in the belite cluster can be measured in polished specimen.

Clinker from ICMA #31 sample
Polished specimen with 20-second Nital etch
Field of view = 150 μm x 110 μm

D. A round, clear belite crystal which can be measured in powder mount to record the Ono parameter "belite colour".

Clinker from PPC - Hercules
Powder mount in refractive index liquid 1,715
Field of view = 150 μm x 110 μm

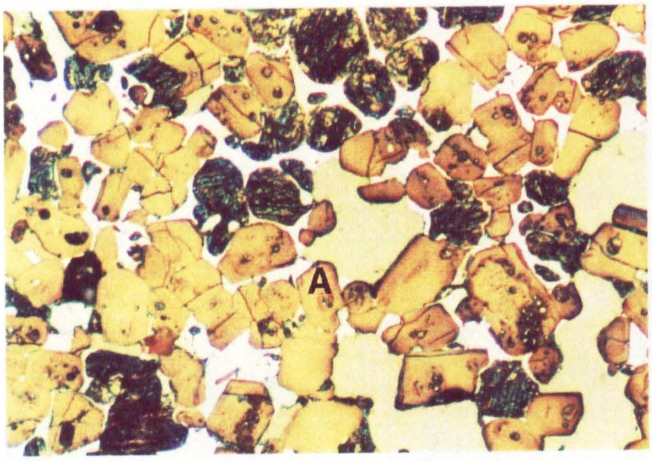
E. Two round, pale yellow belite crystals which can be measured in powder mount to record the Ono parameter "belite colour".

Clinker from PPC - Jupiter
Powder mount in refractive index liquid 1,715
Field of view = 150 μm x 110 μm

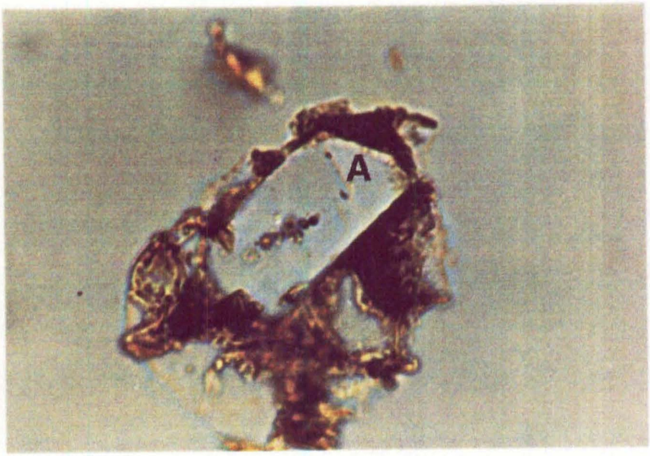
F. A round, greenish brown belite crystal which can be measured in powder mount to record the Ono parameter "belite colour" as amber.

Clinker from PPC - Jupiter
Powder mount in refractive index liquid 1,715
Field of view = 150 μm x 110 μm

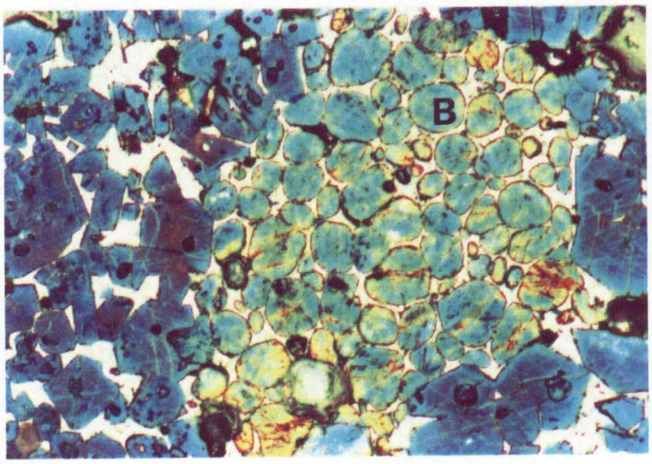
PLATE 6



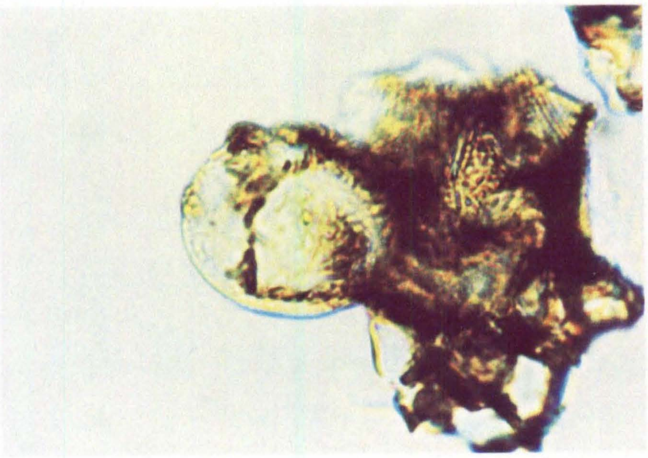
(A)



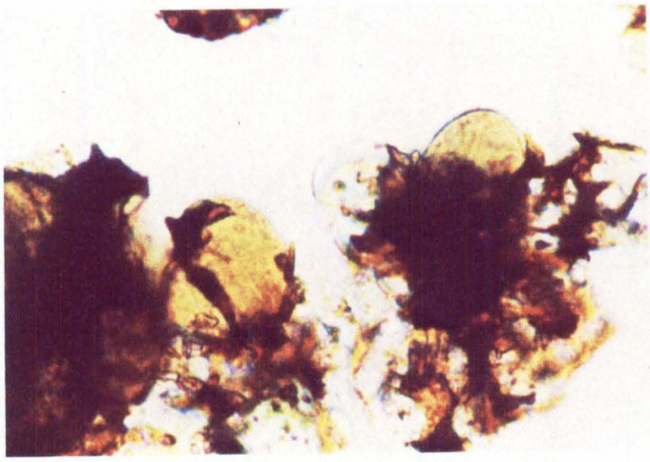
(B)



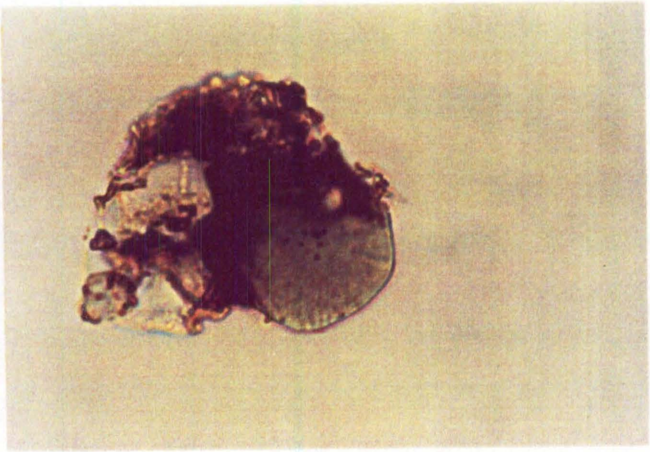
(C)



(D)



(E)



(F)

Table 15. Burning and cooling conditions related to microscopical characteristics of alite and belite (after Ono, 1981).

BURNING/		Hydraulic	Activity	
COOLING CONDITION	Excellent	Good	Average	Poor
HEATING RATE	Quick			Slow
Size of alite (μm)	15 - 20	20 - 30	30 - 40	40 - 60
(AS)	4	3	2	1
MAX TEMPERATURE	High			Low
Biref of alite	0,01-0,008	0,007-0,006	0,006-0,005	0,005-0,002
(AB)	4	3	2	1
BURN TIME	Long			Short
Size of belite (μm)	25 - 40	20 - 25	15 - 20	5 - 10
(BS)	4	3	2	1
COOLING	Quick			Slow
Colour of belite	Clear	Faint yellow	Yellow	Amber
(BC)	4	3	2	1

The parameters AS (alite size), AB (alite birefringence), BS (belite size) and BC (belite colour) are assigned numerical values 4, 3, 2, and 1. The relationship between these parameters and the burning and cooling conditions in the kiln is then obtained from the table. The hydraulic activity is also obtained.

For best results of interpretation of burning and cooling conditions, the Ono method should be used in conjunction with other methods such as reflected light microscopy. By itself, the Ono method will indicate **relative** changes in burning conditions.

A number of workers (Jany and Warmkessel, 1987; Campbell and Weiss, 1987) have used the Ono method to good effect at cement plants in the United States of America to improve the quality of the clinker.

A number of workers however, feel that the Ono size limits for alite crystals should be increased to reflect changes in kiln technology in recent years (DeHayes, 1990 and Jany, 1990).

8. CASE STUDY I - THE USE OF MICROSCOPY TO IMPROVE THE QUALITY OF CLINKER FROM THE PPC JUPITER PLANT

8.1 GENERAL

Kiln feed and cement clinker samples were studied over five months to establish base line data and trends in the production of cement clinker at the PPC Jupiter plant. The results of the microscopic study of the raw materials and cement clinker were used to recommend raw material preparation and clinkering processes to produce a clinker of consistent quality. The results given below were presented at the International Cement Microscopy Association Conference in Vancouver, Canada (du Toit, 1990).

8.2 KILN CHARACTERISTICS

The Jupiter plant has one FL Schmidt coal-fired, single stage pre-heater dry kiln, measuring 110 m x 4,75 m ∅ (the back end has a slightly larger diameter to accommodate a chain section and a cross). Approximately 5 m of steel chain and 10 m of steel cross are positioned in this widened section. A planetary cooler is used.

The raw materials are dried using hot gases drawn from the stack before being ground in the raw mill. Standard FL Schmidt equipment (ball mills, weigh feeders etc.) are used to process the raw materials, coal and clinker.

8.3 SAMPLING AND SAMPLE PREPARATION

Kiln feed and cement clinker were collected over five months during periods when the kiln was running in a stable condition. A kiln feed sample was not collected with the first cement clinker sample, but subsequent samples consisted of both kiln feed and cement clinker. Approximately 5 kg of kiln feed and cement clinker were collected each time. Sample preparation was done as described in Sections 5.3 and 5.4.

In order to assess the coarseness of the kiln feed samples, sub-samples were wet-sieved through a 125-μm and a 45-μm sieve. To calculate the amount of carbonate material coarser than 125 μm and quartz coarser than 45 μm, the kiln feed was analysed using classical wet chemistry techniques (described in Section 4.4) to determined the oxide analysis. The amount of carbonate and quartz was then calculated according to the criteria of Fundal (1979).

Representative samples of the cement clinker were prepared for both transmitted light (see Chapter 7 for the Ono Method) and incident light microscopic examination.

For transmitted light examination, the cement clinkers were crushed and wet-sieved and the fraction passing a 75-μm sieve and retained on a 45-μm sieve examined. The powder was mounted on a glass slide in liquid with a refractive index (RI) of 1,715 and covered with a cover-glass.

For incident light examination, both crushed nodules and whole nodules were impregnated with epoxy resin under vacuum. Rough grinding of the resin mounts was done on metal-bonded diamond discs with grit sizes of

68 μm and 30 μm. Polishing was done on a metal-bonded diamond disc (6-μm grit size) and then on a synthetic cloth using successively 1-μm and 0,3-μm alumina powder. The lubricant used throughout was a mixture of iso-propyl alcohol and propylene glycol. The samples were cleaned in an ultrasonic bath between grinding and polishing stages.

Polished specimens were then etched with either 0,1 M KOH (aqueous) for 15 seconds, or Nital for 20 seconds to facilitate the identification of the cement clinker phases and microstructures.

8.4 RESULTS OF EXAMINATION

8.4.1 KILN FEED SAMPLES

The coarseness of the kiln feed samples was determined to get an idea of the burnability of the raw materials.

According to Fundal (1979) and Christensen (1979), the critical upper limits for calcite and quartz for good burnability of the kiln feed, are 125 μm and 45 μm respectively. Any particles of calcite (or dolomite) larger than 125 μm will result in an increase in CaO and this will manifest itself as clusters of free lime in the clinker. Similarly, quartz particles larger than 45 μm will not be able to react totally and will result in belite clusters in the clinker.

The amount of material retained on the 125-μm and 45-μm sieves are given in Table 16.

Table 16. Kiln feed material retained on 125-μm and 45-μm sieves

Sieve size	Per cent retained for sample				
	A *	B	C	D	E
125 μm	-	4,7	3,5	4,2	4,0
45 μm	-	32,0	32,0	32,0	30,6

* Kiln feed sample not collected

Table 17 presents the data of the wet chemical analysis of the amount of carbonate and SiO_2 in the kiln feed.

Table 17. Percentage of carbonate and SiO_2 in the kiln feed

Mineral	Per cent mineral for sample				
	A *	B	C	D	E
Calcite +125 μm	-	5,2	5,3	5,3	5,3
Dolomite +125 μm	-	1,0	0,9	1,0	0,9
SiO_2 +45 μm	-	2,3	2,1	2,2	2,1

* Kiln feed sample not collected

In terms of the criteria of Centurione (1993), the amount of limestone (calcite and dolomite) greater than 125 μm should not exceed 6 per cent and the amount of quartz greater than 45 μm not more than 2 per cent. The results given in Table 17 indicate that both these values have been marginally exceeded and that the burnability of the raw materials will be adversely affected.

8.4.2 THE ONO METHOD

The values for the Ono parameters were determined as described in Chapter 7, section 7.2 and are used to infer the kiln burning and cooling conditions. The relationship between the alite and belite microscopic characteristics and the kiln burning and cooling conditions are set out in Table 15, Chapter 7. The Ono parameters and interpretation for the clinker samples are listed in Table 18.

Table 18. Ono parameters and interpretation for the clinker samples examined

Sample	Alite size (μm) Heating rate	Alite birefringence Max temperature	Belite size (μm) Burn time	Belite colour Cooling
A	25 Quick 3	0,0089 High 4	20 Fairly long 3	FY-Y Fairly slow 3
B	55 Slow 1	0,0086 High 4	35 Long 4	FY Fairly quick 3
C	35 Moderately slow 2	0,0087 High 4	20 Fairly long 3	FY-Y Fairly slow 3
D	55 Slow 1	0,0081 High 4	30 Long 4	FY Fairly quick 3
E	35 Moderately slow 2	0,0088 High 4	20 Fairly long 3	Y Slow 2

8.4.3 POLISHED SECTION EXAMINATION

8.4.3.1 SAMPLE A

The alite crystals are subhedral and small (10 to 30 μm). In many instances the crystals have fused. The edges of the alite crystals are sharp and show no signs of conversion to belite and free lime. The alite crystals occur to a large extent as a circumferential feature of the belite clusters.

The belite crystals are well rounded and occur predominantly in the form of clusters. The individual crystals are fairly large (up to 35 μm) while the diameter of the clusters may be up to 200 μm. Plate 7 (A) shows a belite cluster surrounded by alite crystals, while Plate 7 (B) shows small fused alite crystals in association with free lime.

The interstitial matrix is micro-crystalline and the C_3A and C_4AF are indistinguishable from each other.

Free lime occurs as rounded blebs in the matrix mainly as clusters. These clusters may be up to 150 μm in diameter with the individual free lime crystals up to 30 μm in diameter.

Periclase occurs in the clinker as individual euhedral grains or as clusters. The clusters may be up to 100 μm in diameter with the individual crystals ranging in size from 5 to 12 μm.

8.4.3.2 SAMPLE B

The alite crystals are euhedral to subhedral and range in size from 30 to 75 μm with an average size of approximately 55 μm. In many instances the crystals are fused. In general the edges of the alite crystals are clean but conversion to belite is present in places. Plate 7 (C) shows the edge corrosion which occurs on the alite crystals and badly-formed belite crystals. Belite inclusions are present in the alite.

The belite crystals are not well rounded and occur predominantly in the matrix The individual crystals average about 35 μm in diameter. Belite also occurs as small crystals in the matrix.

Free lime occurs only occasionally in the matrix.

The interstitial matrix phases C_3A and C_4AF are finely crystallised.

Periclase occurs in the clinker as individual euhedral grains or as clusters. The clusters may be up to 75 μm in diameter, with individual crystals ranging in size from 5 to 12 μm.

8.4.3.3 SAMPLE C

The alite crystals are subhedral to anhedral in shape and small in size. The average size is 35 μm.

The belite crystals are also badly formed and occur mainly as clusters. In places the belite crystals appear to be partially converted to alite. The average size of the belite crystals is 20 μm. Plate 7 (D) shows a large belite cluster surrounded by small, fused, alite crystals.

The interstitial matrix phases are finely crystallised.

Periclase occurs in the matrix as small crystals (15 μm) or in the form of clusters (up to 75 μm in diameter).

8.4.3.4 SAMPLE D

The alite crystals are subhedral to anhedral and range in size from 30 to 80 μm, with an average size of 55 μm. Fusion between the crystals is common. The edges of the alite crystals are generally clean (no signs of corrosion). Small belite inclusions are present in the alite.

The belite crystals are not well rounded and occur predominantly as amoeba-shaped crystals in the matrix, closely associated with dendritic periclase. Where they occur as semi-rounded crystals the average size is 25 μm. Plate 7 (E) shows amoeboid belite crystals with periclase crystals in the "fingers" of the belite.

The interstitial matrix phases C_3A and C_4AF are coarsely crystallised.

Periclase occurs mainly as dendritic crystals in the matrix closely associated with the amoeboid belite. Single, euhedral crystals do occur in some instances.

8.4.3.5 SAMPLE E

The alite crystals are subhedral to anhedral and small (average size is 30 μm), although there are some very large alite crystals present (up to 65 μm). In many instances the alite crystals are fused.

The belite crystals are rounded in most cases but do not occur as interstitial crystals in the ground-mass between the alite crystals. Rather, the belite occurs as clusters with surrounding alite crystals. The average size of the belite crystals is 25 μm. Plate 7 (F) shows subhedral, fused alite crystals surrounding a small cluster of multi-coloured belite.

The interstitial matrix phases are finely crystallised.

Free lime is present in some of the clinker grains and occurs predominantly as individual grains up to 30 μm in diameter.

Periclase occurs in the matrix phases as euhedral grains, up to 15 μm in size.

8.5 INTERPRETATION OF DATA

8.5.1 SAMPLE A

The Ono parameters indicate that the burning conditions of the kiln were close to optimum. The small alite size indicates a rapid heating rate and the birefringence of the alite is very high, indicating a high maximum temperature in the burning zone of the kiln. The colour of the belite crystals indicates an average cooling rate of the clinker while the size of the

PLATE 7 CAPTIONS

A. A large multi-coloured belite cluster (B) surrounded by small blue alite crystals (A). Note the fusion of the alite crystals. The white matrix consists of C_3A and C_4AF, while the epoxy is green/brown.

Clinker from PPC - Jupiter
Polished specimen with 20-second Nital etch
Field of view = 150 μm x 110 μm

B. Small blue alite crystals (A) occurring together with large brown/tan free lime crystals (L).

Clinker from PPC - Jupiter
Polished specimen with 20-second Nital etch
Field of view = 150 μm x 110 μm

C. Subhedral, brown alite crystals (A) which exhibit edge corrosion. The multi-coloured belite crystals are badly formed.

Clinker from PPC - Jupiter
Polished specimen with 20-second Nital etch
Field of view = 150 μm x 110 μm

D. A large multi-coloured belite cluster (B) surrounded by small, blue, fused alite crystals (A).

Clinker from PPC - Jupiter
Polished specimen with 20-second Nital etch
Field of view = 150 μm x 110 μm

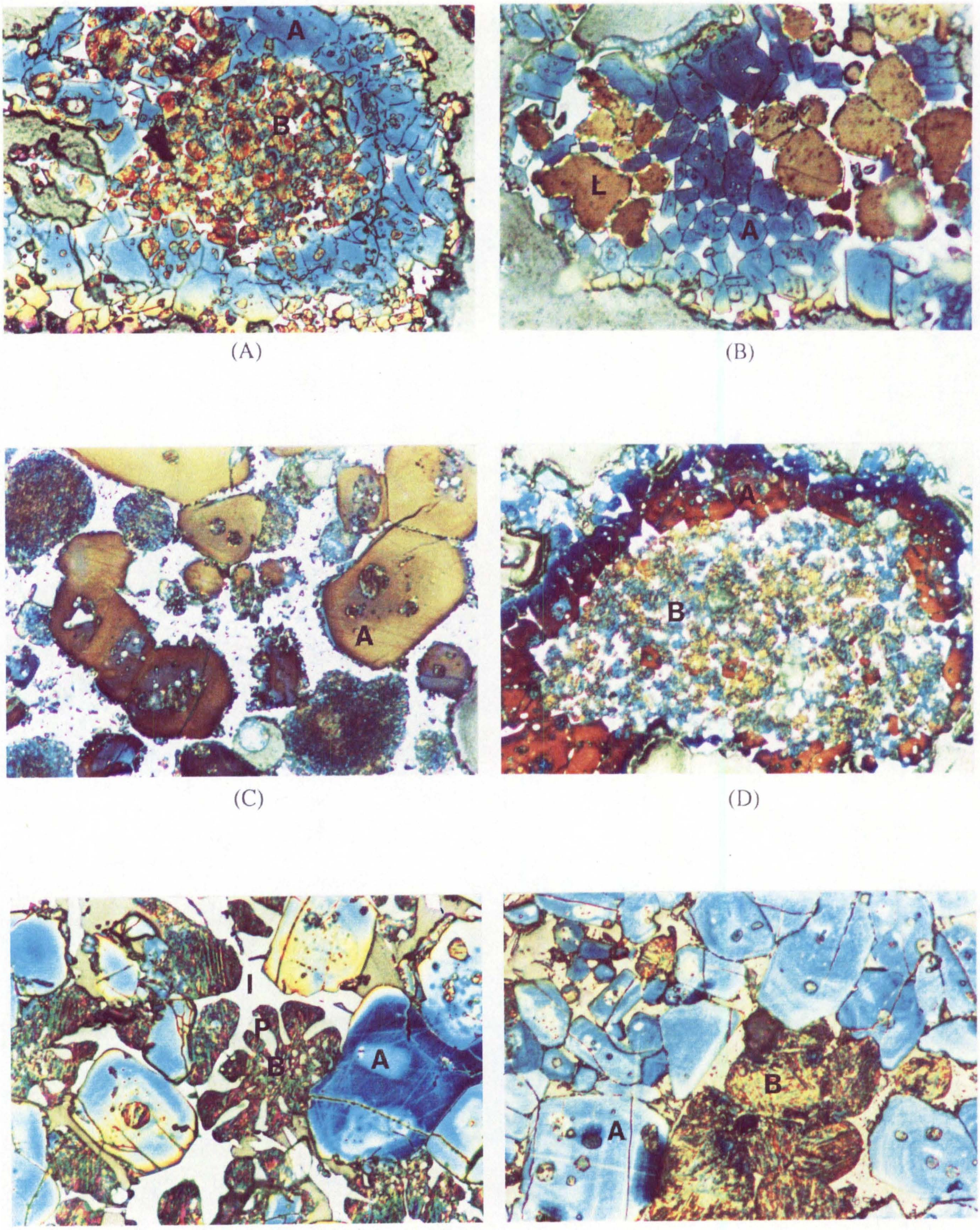
E. Amoeboid shaped, multi-coloured belite crystals (B) between large, blue alite crystals (A). Greenish periclase (P) occurs in the belite as dendrites. The matrix consists of grey-brown C_3A and white C_4AF (I).

Clinker from PPC - Jupiter
Polished specimen with 20-second Nital etch
Field of view = 150 μm x 110 μm

F. Subhedral, blue alite crystals (A) fused together which surround a small multi-coloured belite cluster (B).

Clinker from PPC - Jupiter
Polished specimen with 20-second Nital etch
Field of view = 150 μm x 110 μm

PLATE 7



(A) (B)

(C) (D)

(E) (F)

belite indicates a fairly long burn time (see interpretation of Ono parameters in Table 15). Although the burning and cooling conditions in the kiln were good, the microstructures seen in polished specimen indicate that the kiln feed was not of the correct size and/or homogeneity for good clinker formation (burnability). The presence of large free lime clusters is an indication of coarse calcite grains in the raw feed, while the large belite clusters indicate the presence of coarse quartz grains. Periclase clusters, together with free lime are an indication of coarse dolomite grains in the raw feed. The clean edges of the alite crystals and rounded belite shape seen in polished specimen confirm the adequate cooling rate of the clinker.

8.5.2 SAMPLE B

The Ono parameters indicate a slow heating rate of the raw material (large alite size) and a high maximum temperature in the burning zone of the kiln. The burn time was long and the cooling rate quick.

In general, the microstructures recorded for this sample confirm the Ono findings. The maximum temperature was high, as indicated by the belite occurring as a secondary phase in the matrix. The edge degradation of the alite crystals is an indication that the clinker may have cooled slowly behind the flame in the kiln before being discharged into the cooler. The slightly large size of the alite and belite may indicate a slightly over-sized raw feed (Table 16 shows that this kiln feed had a high percentage of material coarser than 125 μm).

8.5.3 SAMPLE C

The Ono parameters indicate that the heating rate of the kiln feed was average and the maximum temperature high. The burn time was fairly long and the cooling rate fairly slow.

Although the Ono parameters indicate adequate burning and cooling conditions in the kiln, the microstructural features seen in polished specimen indicate that the homogeneity and size of the kiln feed was not optimum. The presence of large amounts of free lime in association with alite may indicate a clinker with a high LSF (an over-limed mix). Alternatively, the clusters of free lime could indicate that excess lime is present because it has not been able to combine with the silica which is is the form of belite clusters.

8.5.4 SAMPLE D

The evaluation of the Ono parameters indicates that the burning temperature in the kiln was high (birefringence of the alite is high). The large alite size is an indication of a slow heating rate of the feed to maximum temperature in the kiln. The size of the belite crystals is difficult to measure because of the nature in which it occurs, but the dendritic character itself is an indication of re-melting at high temperatures and re-crystallisation on the periclase crystals. The colour of the belite crystals indicates a fairly quick cooling rate of the clinker.

Observations made in polished specimen confirm the findings of the Ono parameters. The maximum temperature was high as indicated by the belite occurring as a dendritic (secondary) phase in the matrix. Belite is very likely to occur in this form when the MgO content of the clinker is high. The burn time may also have been too long (large belite crystals). The large fused alite crystals are an indication of a coarse raw feed, possibly in conjunction with a slow heating rate.

The overall large size of the alite and belite crystals also indicate a slightly over-sized raw feed.

8.5.5 SAMPLE E

The Ono parameters indicate a high maximum temperature, as displayed by the high alite birefringence. The rise to this burning temperature was moderately slow (average alite size) and the residence time long (large belite). The cooling rate was slow as shown by the yellow belite colour.

The microstructural features seen in the polished specimen of cement clinker are consistent with the evaluation of the Ono parameters. The rise to maximum temperature is fast, as seen by the small alite crystals and the retention time adequate. The amount of free lime present may, however, be a cause for concern. This may be due to the silica being "locked-up" in belite nests and therefore unable to combine with the lime to form alite.

8.6 CONCLUSIONS AND RECOMMENDATIONS

The microscopic examination of the kiln feed and cement clinker samples raises the following points as to the raw feed preparation and burning and cooling conditions in the kiln.

The presence of free lime clusters, belite clusters and periclase clusters indicates that neither the fineness of the raw feed (see Table 17) nor the homogeneity is adequate. The periclase is a result of the high MgO content of the raw material and the slow cooling of the clinker. In order to improve the quality of the clinker from this kiln, the finer grinding of the raw material should be carefully controlled. This, together with better mixing of the raw feed will improve the burnability of the feed. As pointed out in Section 3.2.5, if the kiln feed is not ground fine enough, a higher temperature is required for combination.

The Ono parameters indicate that the heating rate in the kiln varied between slow and quick and the burn time was fairly long, an indication that the flame profile was "long and lazy" (Peray, 1986). The cooling conditions in the kiln were generally adequate because a quick cooling rate is difficult to achieve with planetary coolers. The amoeboid-like belite crystals in which the periclase occurs as dendrites in the "fingers" is typical of very high temperatures in the burning zone. The burning and cooling conditions in the kiln can be improved by adjusting the flame profile. The length of the burning zone can be decreased and the cooling improved by using a shorter "snappy" flame which is closer to the outlet of the kiln.

The relationship between raw material preparation and pyroprocessing is illustrated in this case study. The inadequate grinding and homogenisation of the raw materials has resulted in a kiln feed which is difficult to burn, thus the long flame and high maximum temperature that must be used to combine the raw materials.

According to Klemm and Skalny (1977), of the three major steps in cement manufacture, raw materials processing utilises only 10 per cent of the total energy, while pyroprocessing and finish grinding account for 83 and 7 per cent respectively. Thus, in this case, if more time (energy) is spent on raw materials preparation (grinding and blending), the result would be an easier burning material and a clinker requiring less energy to grind.

As a result of the findings of this study, certain changes were made to the operating conditions of the kiln, and recommendations made with regard to the raw material preparation. The flame profile was altered to obtain a short "snappy" flame. In order to improve the cooling rate of the clinker, the flame was situated as close to the outlet ports of the planetary coolers as possible. To decrease the burning zone temperature, the thickness of the clinker bed in the burning zone was increased. This was achieved by reducing the kiln speed slightly whilst maintaining the same kiln feed rate. To improve the burnability of the raw materials, a recommendation was made to reduce the size of the kiln feed from the maximum limit of 12,0 per cent retained on a 90-μm sieve to a maximum of 11,5 per cent (Murnan, 1995). Constraints of the milling system made it difficult to achieve this last recommendation.

Currently, the PPC Jupiter plant are using their Technical Services Department (where a microscope facility is available) to evaluate clinker for them. Those parameters identified in this study which are critical for good clinker production (kiln feed size, feed rate and kiln speed) are closely monitored. At the moment, the production and quality departments at the plant try to maintain the kiln feed at 12,0 per cent retained on the 90-μm sieve, a feed rate of 76,5 tons per hour and a kiln speed of 70,75 revolutions per hour (Limbada and Crouss, 1995).

9. CASE STUDY II - THE USE OF MICROSCOPY TO AID THE PROCESS CONTROL OF THE TSWANA-ONLY LIMESTONE TRIAL AT BLUE CIRCLE CEMENT LICHTENBURG PLANT

9.1 GENERAL

This trial is referred to as the Tswana-only trial and the aim was to evaluate the potential of using low-grade limestone from the Tswana Quarry to replace the low-grade limestone from Lovedale Quarry. The limestone used for the kiln feed under normal operation is a blend consisting of approximately 78 per cent Tswana high-grade limestone and 14 per cent Lovedale low-grade limestone. For the Tswana-only trial, the blend of limestone was 80 per cent Tswana high-grade and 10 per cent Tswana low-grade limestone. The other raw materials, common to both raw mix designs, are magnetite and bottom ash.

The chemistry of these two mixes (normal operation versus Tswana-only) is almost identical and provides no indication of differences (if any) in the burnability. Given the similarity in the chemistry of the kiln feeds, it was felt that the Tswana-only material could be used, but only by burning the Tswana-only material would an actual clinker analysis be obtained.

Two previous trials were conducted using the Tswana low-grade limestone. The first trial was aborted soon after its start because the Tswana-only material was introduced into the kiln suddenly (once the silo containing the normal kiln feed was empty). This resulted in refractory loss in the kiln to such an extent that the trial was aborted.

The second trial was aborted after approximately 4 days. At this stage, the raw-mill LSF target had increased to such an extent that no low-grade Tswana limestone was being used, which defeated the object of the trial. Two reasons were given for the unsuccessful trial: firstly, the LSF of the high-grade Tswana limestone was too close to the raw mill target, and secondly, not all the Si (expressed as SiO_2) could be detected in the pressed pellets which were used for the XRF analysis. This also affected the calculation of the LSF value.

The Portland cement clinker from this second trial was thought to be of such inferior quality that it was not considered possible to mill it together with other Portland cement clinker. The decision to dump the approximately 10 000 tons produced from this second trial on a stockpile in the open air was based more on visual appearance of the Portland cement clinker than on clinker chemistry. Visually, the Portland cement clinker appeared totally over-burnt and fused. At stages during the second trial however, the clinker chemistry also deteriorated and the C_3S content (Bogue calculation) was very low (see analysis in Table 19).

A microscopic examination of polished specimens showed that the "fused" appearance to the naked eye was mainly due to the extremely fine crystal size of the Portland cement clinker phases. The fine crystal size of the Portland cement clinker phases was essentially due to the Tswana-only kiln feed being much easier to burn (under the same burning conditions as the normal kiln feed). This easier burning of the kiln feed led to some over-burning (long burning time at a high temperature), (Long, 1982).

Table 19. Portland cement clinker chemistry for the second Tswana-only trial

Parameter	Per cent
LSF	89,51
SR	2,58
AR	1,33
C_3S	48,72
C_2S	28,79
C_3A	6,94
C_4AF	11,65
Free CaO	0,60

However, the result of the microscopic examination showed that the bulk of the approximately 10 000 tons of Portland cement clinker produced during the second trial could be milled together with normal Portland cement clinker. This was in actual fact done and a cement of consistent quality was produced, leading to cost savings in not having to dump the clinker from the second trial.

A third trial was carried out, aiming to avoid the previous mistakes by using a fixed amount of Tswana low-grade limestone in the kiln feed, carrying out XRF analyses using fused beads (to detect all the Si), and taking due cognisance of the microscopic findings from the second trial. Davies and Smith (1994) have compiled an in-house technical report which gives more details on the raw mix designs, quality control log sheets and performance of the ordinary Portland cement and rapid-hardening Portland cement made from this Portland cement clinker for the period October 1993 to January 1994.

9.2 KILN CHARACTERISTICS

All the trials were carried out on the Number 6 kiln at the Blue Circle Cement Lichtenburg works. The kiln is a Krupp-Polysius 4 stage pre-heater pre-calciner kiln with a Claudius Peters grate cooler. The coal used to fire the kiln is typically split between the firing pipe and the pre-calciner in the ratio 40:60.

Exhaust gases drawn through the kiln by the induced draft fan are passed through pre-conditioning towers before being cleaned in electrostatic precipitators and discharged into the atmosphere.

The raw materials are milled in a double-rotator, central-discharge ball mill in closed circuit with a dynamic separator. From there the kiln feed is transported to the blending/homogenising silos from where it is introduced into the upper stage of the pre-heater via two ducts.

Portland cement clinker leaving the kiln falls into the grate cooler and then onto a metal conveyor belt for transport to the Portland cement clinker silos.

9.3 RAW MATERIAL CHARACTERISTICS

The chemical analyses for the raw materials used in normal burning operation (using Lovedale low-grade limestone) as well as the Tswana-only trial are given in Table 20.

Table 20. Base chemistry of raw materials for third trial

Oxide (%)	Raw material				
	Tswana HG	Tswana LG	Lovedale LG	Magnetite	Bottom ash
CaO	46,21	40,88	40,73	0,66	6,33
SiO_2	11,84	21,38	20,62	2,40	34,53
Al_2O_3	1,21	1,75	2,94	2,98	20,88
Fe_2O_3	0,95	1,42	1,83	76,55	6,19
MgO	1,41	1,51	1,43	0,60	0,75
K_2O	0,05	0,07	0,21	0,00	0,33
Na_2O	ND	ND	ND	2,96	0,74
SO_3	ND	ND	ND	0,00	1,14
LOI	36,5	33,0	32,3	1,3	10,6
Total	98,17	100,01	100,06	87,45	81,49

HG = high-grade
LG = low-grade
ND = not determined

To achieve the desired Portland cement clinker chemistry and phase composition, the analyses of the raw materials are entered into a mix design programme which proportions the raw materials accordingly. The programme requires inputs of LSF, SR and four raw materials and also takes into account variables such as retention of SO_3, fuel consumption, per cent ash in the coal and the per cent ash retained in the Portland cement clinker. Table 21 shows the mix proportions for the Lovedale low-grade mix (normal operation) and Tswana-only mix for an LSF of 93 and an SR of 3,0.

Table 21. Normal mix and Tswana-only mix proportions and Portland cement clinker chemistry for third trial

Materials	Normal operation	Tswana-only mix
Tswana high-grade, %	78,33	81,16
Lovedale low-grade, %	13,96	-
Tswana low-grade, %	-	10,21
Bottom ash, %	6,93	7,83
Magnetite, %	0,78	0,80
Moduli	Normal operation	Tswana-only mix
LSF, %	93	93
SR	3,0	3,0
AR	1,4	1,4
Bogue composition	Normal operation	Tswana-only mix
C_3S, %	59,9	59,6
C_2S, %	18,1	18,0
C_3A, %	6,2	6,2
C_4AF, %	9,3	9,3
Flux, %	19,4	19,3

The proportions of high to low-grade are very similar, with only a slight increase in the consumption of Tswana high-grade limestone in the Tswana-only mix. The ash consumption also increases slightly (by about 1 per cent) because there is less Al_2O_3 in the Tswana low-grade when compared with the Lovedale low-grade material.

The chemistry of these two mixes for both the kiln feed and Portland cement clinker is given in Table 22.

Table 22. Chemistry of Lovedale low-grade and Tswana-only for third trial

Oxide (%)	Normal operation		Tswana-only trial	
	LSF = 93		LSF = 93	
	SR = 3,0		SR = 3,0	
	Raw mix	Clinker	Raw mix	Clinker
CaO	42,33	63,97	42,18	63,74
SiO_2	14,57	22,02	14,51	21,94
Al_2O_3	2,83	4,28	2,82	4,27
Fe_2O_3	2,02	3,06	2,02	3,05
MgO	1,36	2,06	1,36	2,06
K_2O	0,09	0,14	0,07	0,11
Na_2O	0,07	0,11	0,08	0,12
SO_3	0,08	0,12	0,09	0,14
LOI	33,85	0,0	33,83	0,0
Total	97,20	95,76	96,96	95,43

A comparison of the chemistry for the normal operation versus the Tswana-only mix shows very little difference with respect to the major oxides. For example, the CaO changes from 42,33 per cent in the normal operation to 42,18 per cent in the Tswana-only mix and the SiO_2 shows a change from 14,57 to 14,51 per cent.

As previously mentioned, the chemistry of the two mix designs (whilst similar) does not indicate whether the kiln feed will produce a good quality Portland cement clinker. Only a microscopic examination of the kiln feed will provide an insight to its burnability and the examination of the resulting Portland cement clinker will confirm such findings.

9.4 BURNABILITY OF TSWANA-ONLY KILN FEED

The burnability of the Tswana-only material for the third trial was determined using the method of Miller (1981) as described in Centurione (1993). This uses a combination of selective chemical dissolution and microscopy of the kiln feed to determine the potential free lime content.

Miller (ibid.) gives a formula which calculates the potential content of free lime with respect to various parameters (chemical and optical) of the kiln feed and this enables a comparison to be made of different kiln feeds with respect to their burnability.

The chemical moduli (LSF and SM), and three groups of minerals are important. Miller does not differentiate between the carbonate minerals calcite, dolomite or siderite, but refers to them all as limestone grains.

Limestone grains larger than 125 μm
Quartz grains larger than 45 μm
Acid-insoluble grains larger than 45 μm

The parameters determined are used in the following burnability formula:

$$\%\,Free\,CaO = 0{,}31\,(LSF-100) + 2{,}18\,(SM-1{,}8) + 0{,}73\,Q_{45} + 0{,}33\,C_{125} + 0{,}34\,Aq$$

Where LSF = lime saturation factor
SM = silica modulus
C_{125} = per cent limestone >125 μm
Q_{45} = per cent quartz >45 μm
Aq_{45} = per cent acid-insoluble residue >45 μm

For the determination of the parameters described above, the following procedure was carried out according to the method described in Centurione (1993) and a worked example of a calculations is given in Appendix II:

9.4.1 DETERMINATION OF COARSE LIMESTONE PARTICLES:

Sixty grammes of kiln feed (*R0*) were sieved through a 125-μm sieve and the amount of material retained (*R1*) was calculated.

This fraction (*R1*) was dissolved in 20 per cent HCl solution at 80 °C for 30 minutes. The percentage material dissolved (*R2*) after the acid treatment (acid-soluble) was calculated.

The limestone grains $>$ 125 μm $=$ percentage material dissolved (*R2*) expressed as a percentage of the material retained on the 125 μm sieve (*R2*).

9.4.2 DETERMINATION OF COARSE QUARTZ PARTICLES:

Fifteen grammes of kiln feed were sieved through a 45-μm sieve and the amount of material retained (R1) was calculated.

This fraction (*R1*) was dissolved in 20 per cent HCl at 80 °C for 30 minutes and the percentage material remaining (*R2*) (the acid-insoluble minerals and minerals released from limestone particles) was calculated.
This fraction (*R2*) was re-sieved through a 45-μm sieve and the residue (*R3*) calculated.
The quartz $>$ 45 μm $=$ per cent quartz by microscopic counting of *R3*.

To determine the percentage of quartz in this last residue (R3), a representative portion of the residue was immersed in a refractive index liquid on a glass slide and examined using transmitted polarised light at magnifications between 100x and 200x. Approximately 500 particles were counted and the percentage quartz calculated.

9.4.3 DETERMINATION OF THE ACID-INSOLUBLE PARTICLES:

The $Aq > 45\ \mu m = 100$ - percentage quartz determined by microscopy.

The values obtained from the above analytical technique (for two Tswana-only kiln feeds) were inserted into the Miller formula for burnability and the potential free CaO obtained. The chemical moduli and values for $CaCO_{3\ +125\mu m}$, $SiO_{2\ +45\mu m}$, and $Aq_{\ +45\mu m}$ are given in Table 23.

Table 23. Tswana-only kiln feed analysis

Component of Miller formula	Tswana-only Kiln feed No. 1	Tswana-only Kiln feed No. 2
LSF, %	93	93
SM	3,0	3,0
% $CaCO_{3\ +125\mu m}$	4,99	3,14
% $SiO_{2\ +45\mu m}$	3,55	5,02
% $Aq_{\ +45\mu m}$	6,10	4,48

Table 24 gives the values of each variable in the Miller formula so that the contribution to the free CaO from each component in the Miller formula is identified. Once the parameter which has the largest influence on the amount of free CaO is established, this parameter can be changed in the raw material stage of clinker manufacture to improve the burnability of the kiln feed.

Table 24. Potential free CaO from Tswana-only kiln feed according to the Miller formula (Centurione, 1993)

Parameter	Miller Formula	Tswana-only Kiln feed No. 1	Tswana-only Kiln feed No. 2
LSF	0,31 (LSF-100)	-2,17	-2,17
SM	2,18 (SM-1,8)	2,62	2,62
SiO_2 $_{+45\mu m}$	0,73 (Q_{45})	2,59	3,66
$CaCO_3$ $_{+125\mu m}$	0,33 (C_{125})	1,65	1,04
Aq $_{+45\mu m}$	0,34 (Aq_{45})	2,07	1,52
Potential Free CaO		6,76	6,67

The potential free CaO from the two Tswana-only kiln feed samples taken during the trial are 6,76 per cent and 6,67 per cent respectively, of which the contribution from the LSF is negligible, and the contribution from SM and coarse quartz particles the highest. The potential free CaO calculated in the Miller formula is not the amount of actual free CaO occurring in the Portland cement clinker but is used in this evaluation only as a relative value. It is used to compare different kiln feed samples and gives an indication of which component contributes to the poor burnability of the raw materials.

Results obtained by Centurione (1993), who studied kiln feed samples from 14 cement plants in Brazil, showed that the potential free CaO in these samples ranged between 3,0 per cent and 6,6 per cent. The result of the Tswana-only kiln feed indicates that the high SM and large amount of coarse quartz in the kiln feed could lead to difficult burning of the material to produce Portland cement clinker.

9.5 MICROSCOPY OF TSWANA-ONLY PORTLAND CEMENT CLINKER

Both transmitted and incident light microscopic examination of the Tswana-only clinker was carried out. The preparation of the samples was done as described in Chapter 5.

The Ono parameters (listed in Table 25) indicate that the kiln feed was heated fairly rapidly to a high maximum temperature and then cooled relatively slowly behind the burning zone, before being discharged into the cooler. The retention time in the burning zone was moderately long, indicating a long hot flame profile. Details of the interpretation of the Ono parameters to indicate burning and cooling conditions in the kiln are given in Chapter 7, section 7.3.

Table 25. Ono parameters for Tswana-only Portland cement clinker

Ono parameter	Tswana-only clinker	Interpretation of burning and cooling conditions
Alite size (μm)	30 - 35	Moderately quick heating rate to maximum temperature
Alite birefringence	0,0071	High maximum temperature
Belite size (μm)	20 - 25	Moderately long burn (retention) time
Belite colour	FY to Y	Moderately slow cooling rate

Polished specimens of the Tswana-only Portland cement clinker were examined to determine the characteristics of the phases and the relationships between phases.

Plates 8 (A) to (F) show features seen in the polished specimens of the Tswana-only Portland cement clinker.

The presence of large quartz particles in the kiln feed usually manifests itself as belite clusters in the Portland cement clinker as shown in Plate 8 (A). Streaks of belite crystals usually indicate a kiln feed which has not been thoroughly homogenised. This feature is shown in Plate 8 (B).

The moderately slow cooling of the Portland cement clinker behind the flame is deduced from the ragged edges of the belite crystals as seen in Plate 8 (C).

During the Tswana-only trial, Portland cement clinker of good quality was produced (although showing fused crystals typical of being slightly over-burnt). Plate 8 (D) shows a good microstructure of small, euhedral alite crystals and belite crystals which are evenly dispersed through the Portland cement clinker. The fusion of the alite crystals is evident (indicating high temperature), as are the ragged edges of the belite crystals (slow cooling).

Plates 8 (E) and (F) show the small alite crystal size, rounded belite crystals and micro-crystalline interstitial matrix of C_3A and C_4AF, indicating optimised manufacturing conditions.

PLATE 8 CAPTIONS

A. A large blue belite cluster surrounded by small brown alite crystals (A). Note also the large belite cluster on the right of the photo which is approximately 450 μm across. The white matrix consists of C_3A and C_4AF, while the voids in the cement clinker are dark.
Clinker from BCC - Lichtenburg
Polished specimen with 5-second HF vapour etch
Field of view = 630 μm x 450 μm

B. Small light blue/yellow belite crystals (B) occurring as streaks in alite crystals (A). Voids appear dark.
Clinker from BCC - Lichtenburg
Polished specimen with 10-second HF vapour etch
Field of view = 1250 μm x 850 μm

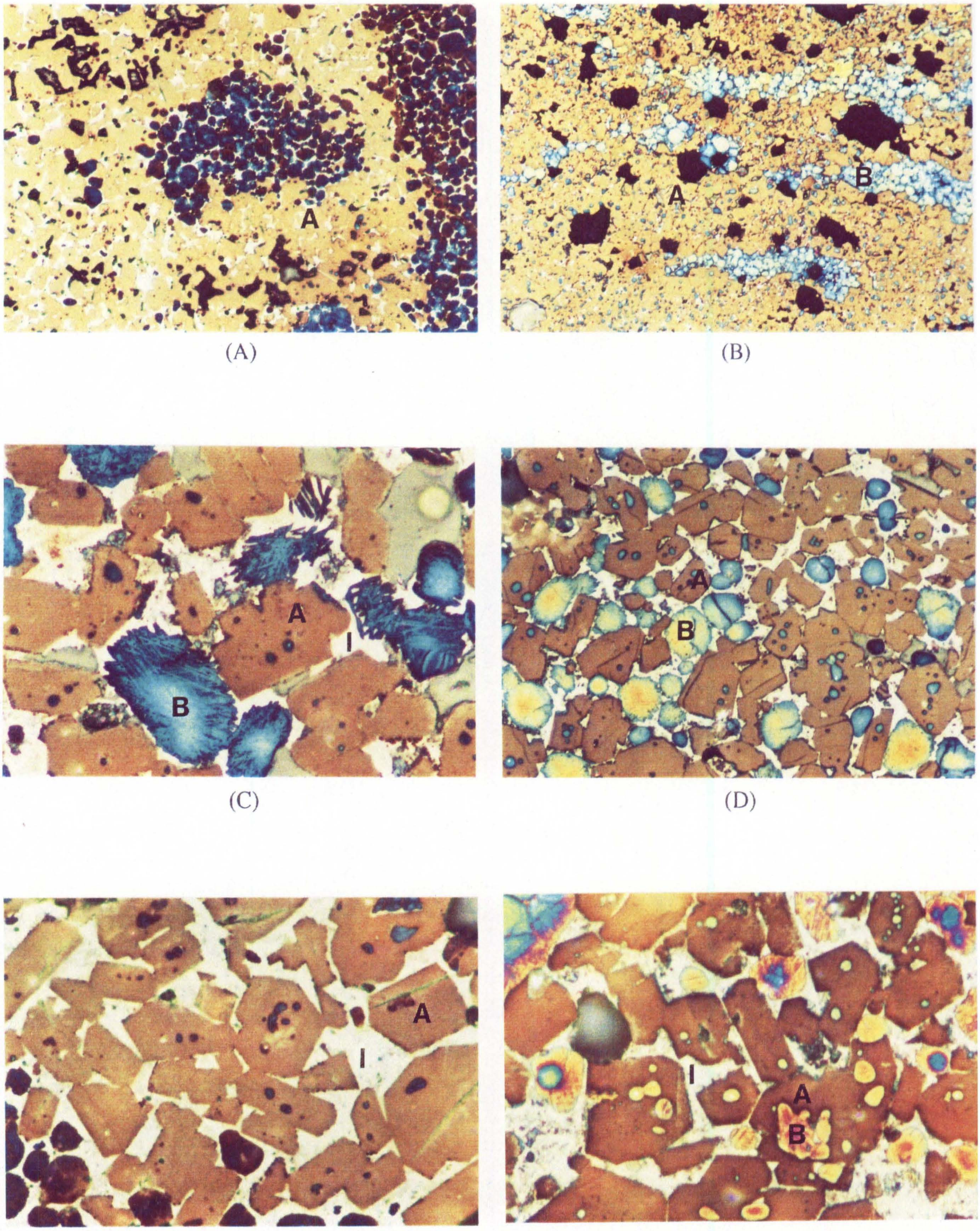
C. Blue belite crystals (B) which exhibit ragged edges due to slow cooling. Alite crystals (A) are brown and the interstitial materials consists of C_3A and C_4AF (I).
Clinker from BCC - Lichtenburg
Polished specimen with 10-second HF vapour etch
Field of view = 150 μm x 110 μm

D. Small, euhedral, brown alite crystals (A) in which the rounded, light blue and yellow belite crystals (B) are evenly distributed.
Clinker from BCC - Lichtenburg
Polished specimen with 10-second HF vapour etch
Field of view = 315 μm x 220 μm

E. Small brown alite crystals (A) set in the interstitial matrix of C_3A and C_4AF (I).
Clinker from BCC - Lichtenburg.
Polished specimen with 10-second HF vapour etch
Field of view = 150 μm x 110 μm

F. Brown alite crystals (A) with yellowish belite inclusions (B). The interstitial matrix consists of micro-crystalline C_3A and C_4AF (I).
Clinker from BCC - Lichtenburg
Polished specimen with 10-second HF vapour etch
Field of view = 150 μm x 110 μm

PLATE 8



(A) (B)

(C) (D)

(E) (F)

9.6 DISCUSSION AND CONCLUSIONS

The burning of the Tswana-only kiln feed in the third trial resulted in the production of a Portland cement clinker of acceptable quality. Excessive amounts of belite in the form of clusters and streaks indicate that there is a problem with the milling of the raw materials to the correct fineness. This aspect of the process needs to be addressed. Under similar burning conditions to those used for the normal raw material mix design (Lovedale low-grade mix) it was concluded that the Tswana-only mix was slightly easier to burn. A comparison of the microstructures is shown in Plate 3 (C), the Lovedale low-grade mix, and Plate 3 (D), the Tswana-only mix. The alite and belite crystal sizes are smaller in the Tswana-only Portland cement clinker, indicating the easier combinability of the raw materials. Therefore the third trial produced a slightly over-burnt Portland cement clinker, but less so than in the second trial. It should therefore be possible to reduce the burning temperature which will result in cost savings due to improved energy efficiency. The microscopy of the Tswana-only raw materials and Portland cement clinker has shown that if necessary, the Tswana-only material can be used to produce a good quality Portland cement clinker for cement production.

Subsequent to the use of microscopy in these trials, it has been recognised as providing an important tool in determining quality and consistency of Portland cement clinker. Microscopy is now used regularly as a diagnostic and monitoring tool.

With the planned expansion of the Blue Circle Cement operation, the location of the plant will determine the raw material source i.e. Tswana-only or Tswana and Lovedale.

If the location of the location of the plant is at the Tswana quarry, then the Tswana-only option will come into play.

Microscopy will then be a valuable tool is assessing:

grade control (day to day as well as projected) from the quarry

the granulometry of the kiln feed and

The burning and cooling conditions of the kiln by examining clinker produced.

10. SUMMARY AND CONCLUSIONS

The nomenclature of cement clinker established at the turn of the century has not changed significantly from the pioneering work of Törnebohm, Tavasci and Insley. The terms alite, belite, aluminate and ferrite are still the most commonly used names for the cement clinker phases. The abbreviations C_3S, C_2S, C_3A and C_4AF are also used extensively and commonly referred to as the cement chemist notation.

Cement clinker manufacture has undergone a major change from the wet process, through semi-wet to semi-dry, and finally to the dry process. A major step forward in processing technology was the development of the pre-calciner where most of the energy requirements of de-carbonation and material preparation is carried out outside the kiln. This has led to major cost savings in terms of refractory life in the kiln.

X-ray fluorescence (XRF) is undoubtedly the most popular method for analysing the raw materials, kiln feed and cement clinker to obtain an accurate oxide analysis. From the oxide analysis of the raw materials, the proportions of the various components are calculated to give a kiln feed capable of producing a cement clinker of good quality. The XRF analysis (of the cement clinker) is also used to calculate the potential phase composition using the Bogue formulation. The use of other techniques (X-ray diffraction and microscopy) to establish the phase composition of the cement clinker have become popular recently because these methods give a truer reflection of the phase composition. In addition, microscopy shows the relationships between the phases, which can be used to interpret the actual burning and cooling conditions in the kiln.

Many sampling and sample preparation techniques exist for examining raw material, kiln feed and cement clinker. The preferred method of examining polished specimens used by this author is to vacuum impregnate the cement clinker in epoxy resin before grinding and polishing, using metal-bonded diamond discs and then polishing on synthetic cloths using alumina powder.

For the examination of powder samples (kiln feed and cement clinker), a small portion of the powder mounted in an appropriate Refractive Index liquid is the preferred means.

While the Ono Method is used to interpret data obtained from powder mounts of cement clinker, concern has been expressed by some authors (DeHayes, 1990 and Jany, 1990) as to the relationship of some of the parameters, (particularly the alite size) to the interpretation of conditions in the kiln. Ono suggested to DeHayes that the alite size parameter needs investigation because the technique was developed on long wet kilns and in the light of present kiln technology, the heating rates had changed significantly. This author has found in the examination of many cement clinker samples, that the alite sizes in particular tend to be on the large side according to the Ono criteria. See for example the large alite crystal size in the clinker samples shown in Plates 1 (B), 1 (E) and 2 (F) and the data presented for samples B and D in Table 18. This aspect of the Ono method needs further investigation.

The preparation of raw materials and cement clinker for microscopical examination needs careful attention because conclusions are usually drawn from the study of small samples. Therefore, the sampling and preparation techniques must ensure that the results obtained are representative and conclusions are therefore meaningful. Spot samples of kiln feed and cement clinker are preferred because they reflect the condition of the clinker quality at a particular stage of the manufacturing process.

The relationship between microstructures and the manufacturing process gives an insight of how each stage in the process can be analysed by various microscopical techniques and improvements made by adjusting or rectifying the process linked to that particular stage.

The case studies have shown that theoretical knowledge gained in the study of Portland cement clinkers from South African and overseas plants has been used in a practical environment to improve the quality and consistency of cement clinker. In this study, the results of the examination of Portland cement clinkers from 5 South African and 4 overseas plants have been presented. The samples are identified in the Plates. In addition, information from samples from 6 South African and 6 overseas plants was also gathered.

In the PPC Jupiter case study, the problems in manufacture lie in raw material preparation and pyroprocessing. Microscopical examination of the kiln feed showed that the raw materials were not ground fine enough. The criteria of Centurione (1993) have been exceeded for both minerals (see results in Table 17). The burning zone temperature was therefore high in order to combine the over-sized kiln feed as shown by the Ono parameters presented in Table 18. An improvement of the cement clinker from this plant was achieved by lowering the burning zone temperature, improving the cooling rate, and carefully controlling the grinding of the kiln feed.

In the BCC, Lichtenburg case study, the manufacture of cement clinker from the Tswana-only mix (as opposed to two sources of limestone) is possible, provided that the clinkering process is carefully controlled to prevent over-burning. Microstructures indicative of over-burning, such as fused or canabilistic alite crystals and large belites crystals are seen in the polished specimens. The high temperatures which are necessary to combine the materials is a result of the high percentage of +45 μm quartz (see results presented in Table 23). Producing a cement clinker at lower energy requirements will increase the life of the refractory lining in the kiln. Raw material reserves can be extended and costs in quarrying operations reduced. The production of Tswana-only Portland cement clinker means that only one and not two quarries have to be operated.

In conclusion, the microscope can be used as a tool for routine quality control, diagnostic purposes or trouble shooting and for scientific research into the cement manufacturing process. This requires experience and knowledge of the appropriate preparation and analytical techniques, optical mineralogy and cement chemistry on the part of the microscopist.

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12. APPENDIX I

This appendix gives a number suppliers of equipment and lists the equipment and consumables necessary to prepare polished specimens of Portland cement clinker. The method used by the author to prepare a polished specimen of Portland cement clinker is given. The problems which may occur during polishing and the reasons for these are also listed.

12.1 SUPPLIERS OF EQUIPMENT

CARL ZEISS (Pty) Ltd P O Box 3003 2125 Randburg	Microscopes (Zeiss) Preparation equipment Consumables
IMP Scientific and Precision Equipment cc. P O Box 1110 1460 Boksburg	Microscopes (Nikon) Preparation equipment Consumables
LECO Africa (Pty) Ltd P O Box 1439 1620 Kempton Park	Preparation equipment Consumables
MICRO Met Scientific Company P O Box 84386 2034 Greenside	Microscopes Preparation equipment (Buehler) Consumables
OPTOLABOR (Pty) Ltd P O Box 426 2125 Randburg	Microscopes
PREMIER Technologies (Pty) Ltd P O Box 173 2162 North Riding Consumables	Microscopes (Leica) Preparation equipment (Struers)
TBW Industries Inc. P O Box 336 Furlong Pensylvania USA 18925-0336	Preparation equipment

UNITED Scientific cc. P O Box 37010 7442 Chempet	Preparation equipment
WIRSAM Scientific & Precision Equipment (Pty) Ltd P O Box 91058 2006 Aukland Park	Preparation eqiuipment Consumables

12.2 EQUIPMENT REQUIRED FOR PREPARATION AND EXAMINATION OF PORTLAND CEMENT CLINKER

EQUIPMENT FOR PREPARATION

Small diamond cut-off saw

Grinding wheels

Spray bottles

Vacuum impregnation equipment

Engraver

Polishing equipment

Hair dryer

Polarising microscope with camera

Point count equipment (or stage micrometer)

Storage cabinet

CONSUMABLES

Diamond saw blade for cut-off saw.

SiC grit or abrasive paper for grinding. A range from 400 grit to 1 200 grit is preferable.

Metal bonded diamond discs for grinding.

Grid Abrade (TBW Industries). 68 μm, 30 μm, 12 μm and 6 μm

Alcohol. Industrial grade for general cleaning and iso-propyl alcohol for etching.

Nitric acid, potassium hydroxide, hydrofluoric acid and distilled water for etching and staining.

Epoxy for vacuum impregnation. A low viscosity epoxy is essential.

Araldite LY 5502 and HY 5502 from Ciba Geigy
Epo-Quick from Buehler
Epofix from Struers
Impset 20 from IMP

Moulds for making epoxy mounts

Polishing cloths. A range of different types of polishing cloths is required.

Metcloth (Buehler) is a cotton cloth with practically no nap which is used for rough polishing to prevent relief
Textmet (Buehler) or Pan-W (IMP) is a chemotextile material with a low nap which is preferred for hard metals, ceramics and petrographic samples
Microcloth (Buehler) or Impcloth (IMP) is a synthetic rayon cloth with a medium nap which is used if relief is not a problem

Polishing powders. Alumina or diamond may be used.

Alumina. 5 μm, 3 μm, 1 μm, 0,3 μm and 0,05 μm
Diamond. 9 μm, 3 μm, and 1 μm and 0,05 μm

Glass slides and sample press for mounting specimens for examination

Print and slide film

Self-indicating silica gel for storage of samples

12.3 METHOD FOR PREPARING POLISHED SPECIMEN

The author uses the following equipment and method to prepare polished specimens for examination.

Vacuum impregnation of clinker samples is carried out using a Buehler Vacuum Impregnation unit (Cat No. 20-1382) and Araldite LY 5502-HY 5502 epoxy. The sample is put into a sample cup and filled three-quarters full with epoxy. The vacuum pump is switched on and the air extracted from the vessel. Air is then introduced slowly into the vessel and this action forces the epoxy into the voids. This is repeated three times. The epoxy is allowed to harden for a period of approximately 12 hours.

The hardened epoxy mould is trimmed using an Isomet low speed saw (Buehler Cat No. 11-1180) or ground until the sample is exposed using the Grid Abrade (TBW Industries) metal bonded diamond disc (68 μm). The sample is moved by hand in an opposite direction to the wheel rotation for forty revolutions. On subsequent discs (30 μm, 12 μm and 6 μm), twenty revolutions is sufficient. The sample is cleaned with alcohol sprayed from a spray bottle between discs.

A hole (4,75 mm) is drilled into the back of the epoxy mount to a distance of about 5 mm from the front side of the specimen.

A Minimet from Buehler (Cat No. 69-1000) is used for the polishing.

The sample is polished on Texmet (Buehler) or Pan-W (IMP) cloth using successively finer diamond paste (9 μm, 3 μm and 1 μm) or alumina powder (5 μm, 3 μm, 1 μm, 0,3 μm and 0,05 μm). Between each step, the sample is thoroughly cleaned using alcohol from a spray bottle or in an ultra-sonic bath. For each stage of polishing approximately 6 minutes, 1 kg pressure and a speed setting of 6 is used (using the Buehler Minimet). After each stage, the sample is examined using the microscope. If the surface shows scratches from the previous stage, further polishing is required before moving on to the next stage.

Generally, once a preparation method has been developed and adjusted, it should produce the same result for the same material each time it is carried out. Rotational speed, force on the specimen, amount and type of polishing compound and lubricant and time for each stage must be recorded.

The finished polished specimen is cleaned with alcohol from a spray bottle and dried using warm air from a hair dryer.

The polished specimen can be examined under the microscope with or without etching or staining.

The polished specimen must be stored in a storage cabinet where silica gel is present to prevent any moisture from getting to the polished specimen.

12.4 PROBLEM SOLVING

During the polishing of a sample, the most common artifacts which may occur are scratches, edge rounding, relief, pull-outs and contamination. The features and reasons and remedies are discussed.

Scratches are grooves in the surface of the sample produced by the points of abrasive particles. Samples must be cleaned carefully after each step. If there are still scratches left over from the previous step after finishing the current step, increase the preparation time by 25 to 50 per cent as a first measure.

Using a polishing surface with high resilience (nap) will result in material removal from both the sample surface and around the sides. The effect of this is edge rounding. An alternative epoxy must be used to correct for this. Alternatively, initial polishing was carried out using short polishing times and low forces.

If material from different phases is removed at different rates due to varying hardness, relief is found. The most important parameters to avoid relief are preparation time and polishing cloth used. The preparation time should be as short as possible and the polishing cloth should have a low resilience (nap).

Pull-outs are cavities left after grains or particles are torn out of the sample during abrasion. They are found in hard and brittle materials. High forces and cloths with high resilience (nap) can be the cause of pull-outs.

Contamination occurs when material from another source other than the sample itself is deposited on the surface during grinding or polishing. Samples must be carefully cleaned between polishing steps and kept in a dust-free cabinet once polished. After etching and/or staining, the surface must be carefully washed using alcohol from a spray bottle and dried under a hair dryer. Etching and staining chemicals left on the surface of the samples (e.g. HF acid vapour) can damage microscope lenses.

13. APPENDIX II

This Appendix shows how the calculations are made to express the percentage of material retained on various sieves, according to the method described by Centurione (1993).

13.1 CALCULATION OF CARBONATE MATERIAL RETAINED ON A 125 μm SIEVE

Parameter	*R0*	*R1*	*R2*	$C_{+125\ \mu m}$
Mass, (g)	60	3,44	2,99	
Percentage, (%)	100	5,73	86,92	4,98

Start with a 60 g sample (*R0*) which is representative of the kiln feed to be examined and proceed as follows:

Using iso-propyl alcohol, wet sieve the sample through a 125 μm sieve. Calculate the residue on the 125 μm sieve (*R1*) and express as a percentage of the original mass of kiln feed

$$R1 = 3{,}44/60 \times 100 = 5{,}73\%$$

Dry the residue (*R1*) under an ultra-violet light or in an oven at 105 °C. Put the dried residue (*R1*) into a beaker containing 20% HCl and heat to 80 °C for 30 minutes while stirring. Filter the liquid through a Watman No. 41 filter paper, dry the filtrate and obtain the mass of the filtrate.

Calculate (by difference) the amount of the material dissolved in the HCl and express this amount as a percentage of *R1*. Call this *R2*.

$$R2 = 2{,}99/3{,}44 \times 100 = 86{,}92\%$$

The carbonate material larger than 125 μm ($C_{+125\ \mu m}$) is therefore the percentage of material retained on the 125 μm sieve (*R1*) multiplied by the amount dissolved (*R2*), expressed as a percentage.

$$C_{+125\ \mu m} = R1 \times R2 \times 10^{-2} = 4{,}98\%$$

13.2 CALCULATION OF QUARTZ AND OTHER ACID-INSOLUBLE MATERIAL RETAINED ON A 45 μm SIEVE

Parameter	*R 0*	*R 1*	*R2*	*R3*	*R4*	$Q_{+45\,\mu m}$	$Aq_{+45\,\mu m}$
Mass, (g)	15	5,63	1,52	1,45	0,53		0,92
Percentage, (%)	100	37,53	27,00	95,39	36,5	3,53	6,13

Start with a 15 g sample (*R 0*) which is representative of the kiln feed to be examined and proceed as follows:

Using iso-propyl alcohol, wet sieve the sample through a 45 μm sieve. Calculate the material retained on the 45 μm sieve and express as a percentage of the original mass of kiln feed

$$R1 = 5{,}63/15 \times 100 = 37{,}53\%$$

Dry *R 1* under an ultra-violet light or in an oven at 105 °C. Put the dried *R 1* material into a beaker containing 20% HCl and heat to 80 °C for 30 minutes while stirring. Filter the liquid through a Watman No. 41 filter paper, dry the filtrate and obtain the mass of this acid-insoluble residue. Express the amount of acid-insoluble material (*R2*) as a percentage of the *R1* fraction

$$R2 = 1{,}52/5{,}63 \times 100 = 27{,}00\%$$

Re-sieve the acid-insoluble material (*R2*) through a 45 μm sieve. This second sieving sieve is necessary to get rid of the -45 μm particles which may have been incorporated into the +45 μm fraction. Re-calculate the +45 μm acid-insoluble fraction (*R3*) and express this as a fraction of the first acid-insoluble residue

$$R3 = 1{,}45/1{,}52 \times 100 = 95{,}39\%$$

By microscopy, determine the percentage of quartz (*R4)* in the acid-insoluble fraction (*R3*).

$$R4 = \text{percentage of quartz in } R3 = 36{,}5\%$$

The amount of quartz greater than 45 μm is therefore:

$$Q_{+45\ \mu m} = R1 \text{ x } R2 \text{ x } R3 \text{ x } R4 \text{ x } 10^{-6} = 3{,}53\%$$

The amount of other acid-insoluble material (A_q) is calulated as the difference between the percentage quartz and the total acid-insoluble material and expressed as a percentage

$$A_{q\ +45\ \mu m} = (R3 - R4)/15 \text{ x } 100 = 6{,}13\%$$

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