
Microstructure and Chemistry of Unhydrated Cements [and Discussion]

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Microstructure and chemistry of unhydrated cements

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Cement clinker microstructure is a major factor in determining resultant cement properties and may be modified by changes in clinker chemistry, burning régime and manufacturing processes.

1. INTRODUCTION

Optical microscopy is a very powerful technique when applied to the study of Portland cement clinker. The technique employed is essentially the polished section method developed by Tavasci (1934) although thin sections and powder mounts are used to measure optical properties.

In contrast to other techniques such as X-ray diffraction or infrared spectroscopy, which can only present average qualitative and quantitative phase analysis, the polished section technique yields specific information on crystal size, distribution of the phases and heterogeneity as well as thermal history. The information obtained has been successfully applied in recent years to assessing, modifying and improving the quality of Portland cement.

The technique can also be usefully applied to high-alumina cement clinker, although this appears to have been restricted solely to identifying and quantifying the minerals present with little information published relating microstructure to quality and hydraulic activity.

This paper discusses the interrelations between Portland cement clinker chemistry and microstructure that are known to affect cement quality in terms of strength growth pattern, workability, flowability and volume stability. The understanding gained has enabled cements with specific properties to be developed and these are briefly described.

Phase identification in high-alumina cement clinker is also briefly discussed.

2. PORTLAND CEMENT CLINKER

Portland cements are based on the C–A–F–S system; the four main phases present are C_3S , C_2S , C_3A and a ferrite phase approximating to C_4AF . C_3S (or alite) has been shown to be the main contributor to strength development, with C_2S (or belite) contributing more to late strength. The C_3A and ferrite compose the bulk of the liquid at burning temperature and although they do not contribute significantly to cement strength they play an essential fluxing role in the sintering reactions that take place in the rotary kiln.

Comparison of the quality of cements of similar chemical composition manufactured under controlled laboratory conditions indicate that although the silicate content is the main factor governing cement strength, other factors related to the clinker microstructure influence cement quality (see table 1).

To define the microstructure, polished sections of whole clinker nodules are etched with hydrofluoric acid vapour. This etch produces a straw brown colour on the angular alite crystals, while the rounded belite displays a variety of colours from deep blue to dark red. The aluminate

is etched grey leaving the brightly reflecting ferrite phase apparently unattacked. Other minor constituents such as free lime, periclase, alkali modified aluminate, alkali sulphate, calcium langbeinite, anhydrite, oldhamite, spurrite, calcium sulphosilicate, $C_{12}A_7$ and $KFeS_2$ can also be identified with this etching technique.

(a) *Chemical composition*

The microstructure of the clinker, particularly the relative proportions of the phases present, depends largely, of course, on its chemical composition. In the U.K. the chemical composition is defined by three ratios: the lime saturation factor (l.s.f.), silica ratio (s.r.) and alumina ratio (a.r.). These ratios can be related to the degree of burning required for adequate combination and are effective guides to the potential quantities of alite, belite, aluminate, and ferrite in the clinker. An increase in the l.s.f., which increases the alite content at the expense of the belite, and other factors remaining constant, will require harder burning to reduce the level of uncombined lime to a satisfactory level.

The s.r. governs the ratio of silicates to aluminate and ferrite; the higher the s.r. the more alite and belite but the lower the clinker liquid content at a given temperature, and consequently the higher the burning temperature required to attain combination.

The a.r., which governs the ratio of aluminate to ferrite, also indicates both the quantity of the initial liquid phase formed during firing and the relative viscosity of the liquid phase at the sintering temperature.

Increases in l.s.f., s.r. and a.r. make combination more difficult to achieve, therefore these chemical factors dictate the degree of burning the clinker requires to obtain adequate combination. Another important factor, however, is the distribution of the phases, which can be influenced by the nature of the raw materials and the manufacturing process. In particular, the preparation of the raw feed (how well it is blended and how finely it is ground), the burning process (the heating régime and atmosphere), the fuel employed and the cooling rate have all been found to influence the distribution of the clinker phases.

(b) *Alite size*

Experimental work relating alite size to the degree of burning and cement quality showed a direct relation between alite size and firing temperature and an inverse relation between alite size and cement strength.

This is shown in table 1, where it can be seen that at very small alite size the alite content is also a limiting factor. The latter relation has been used by Ono (1973) as part of a rapid microscopic method of predicting the 28 day concrete strength. Unfortunately there is no absolute firing temperature to obtain the optimum alite size and content since changes in l.s.f., s.r. and a.r. will alter the required firing temperature and affect crystal size development.

(c) *Blending of materials*

The heterogeneity arising from coarse raw materials can affect alite crystal size in two ways. First, the coarser particles will require a higher firing temperature to attain combination, which will promote alite crystal growth, and second, the presence of coarse silica will also induce large alite crystals to form.

By examining the reactions that occur as a raw material is clinkered it can be seen that small particles of silica and clay produce small belite, while large silica particles initially form a

silica rich melt at low temperature. This is sucked into the adjacent porous material formed by decarbonation and as the temperature increases reacts to form a pore centered cluster of densely packed belite crystals. Belite formed in this way does not usually contain the ions needed to stabilize it in the β form and it readily inverts to the γ form on cooling, the associated volume increase breaks up the clinker. With time or temperature or both, lime is transported to belite, converting it to alite, the size of the alite formed being related to the size of the belite from which it forms. Thus coarse silica will promote the formation of large densely packed alite crystals, and usually these contain small belite inclusions.

TABLE 1. RELATION BETWEEN ALITE CRYSTAL SIZE AND QUALITY

(Experimental clinkers of identical composition burnt at different temperatures.)

burning temperature/°C	burn 1 1350	burn 2 1400	burn 3 1450	burn 4 1500
	clinker composition measured microscopically (percentage by mass)			
alite	63	70	73	77
belite	22	15	8	5
celite (flux)	10	12	17	17
free CaO	5	3	2	1
average alite crystal size/ μm	13	15	19	24
	compressive strengths† of 100 mm concrete cubes/(N mm ⁻²)			
3 days	16.5	18.5	17.5	16.5
7 days	24.0	29.5	27.0	25.5
28 days	33.0	44.5	42.5	40.5

† Cement specific surface area 330 m² kg⁻¹.

There are no low temperature melts formed at the high lime end of the phase system and clusters of free lime are formed from coarse limestone particles. However, these particles lose a considerable part of their mass during decarbonation and the porous structure that results absorbs the clinker liquid phase thereby aiding assimilation of the lime. Localized concentrations of periclase, possibly associated with free lime, may occur from coarse particles of dolomite. Coarse shale particles also form belite clusters but in this instance the presence of alumina and iron results in the belite having associated aluminates and ferrite phases within the cluster.

Where the kiln is fired with coal, poor distribution of the coal ash may form similar clusters of belite dispersed in aluminates and ferrite phases. However, the size of the belite clusters formed can be several orders larger and, depending on the cause of the poor ash distribution, may occur either as peripheral layers or veins in clinker nodules, or even as cores to clinker nodules. The presence of residual carbon in the coal ash can induce an associated localized reducing environment in the clinker, which, as described later, adversely modifies the cement properties.

Poor blending of raw materials (rare in modern cement plants where sophisticated measures of control are employed) produces intranodular heterogeneity, such that the overlimed and underlimed clinker nodules that are formed have to be fired at excessively high temperatures to obtain the required combination. In fact all of the above heterogeneity effects require higher temperatures to achieve combination, with the result that alite size increases and cement quality decreases.

(d) Cooling rate

Since the aluminate and ferrite phases are liquid at firing temperature, their crystal size development can be related to the rate of cooling that the clinker experiences. Very rapid cooling, achieved by water quenching for example, may retain the liquid as a glassy phase, whereas slow cooling produces large aluminate and ferrite crystals.

A typical clinker contains about 25% liquid at the burning temperature, the crystalline phases being principally C_3S and C_2S . Under moderately fast cooling conditions the liquid phase solidifies without any significant interaction with the silicate minerals, i.e. non-equilibrium conditions prevail. But under slow cooling conditions, equilibrium is more nearly established, and at high a.r.'s results in a reduction of C_3S content. This is observed as erosion of the alite crystals leaving a layer of belite on the surface. Simultaneously, silica crystallizes out of the liquid phase as small 'pinhead' crystals of incipient belite. At a.r.'s above 2.5 slow cooling can result in a reduction of the 28 day concrete strength by up to 10%.

If during slow cooling the temperature of the clinker is maintained at about 1200 °C for any appreciable time, the alite tends to degrade, producing intimately mixed belite and free lime pseudomorphic after alite. This instability is accentuated when the clinker has been fired in a reducing environment, as discussed in §2(g).

(e) Magnesia

It is known that the presence of periclase may cause long term concrete durability problems. In this respect both size and quantity of periclase crystals have been reported to be important, and are governed by the firing temperature and cooling rate that the clinker experiences. With high temperature firing (over 1500 °C) the MgO goes into solution in the clinker liquid phase, and upon rapid cooling or water quenching, much of the MgO remains in solid solution and only a small quantity of small periclase crystals form. Upon slow cooling from high temperatures, around 1.5% (by mass) MgO is retained in solid solution while any quantity over this will form large periclase crystals. At lower firing temperatures (under 1450 °C) MgO is not so readily taken into solution and small periclase crystals usually form, regardless of clinker cooling rate.

Our work indicates that both free lime and magnesia have to be considered for concrete stability, particularly as determined by the ASTM C151 autoclave expansion test.

(f) Alkalis and sulphates

Alkali sulphates are among the last compounds to crystallize and occur in the clinker pore structure. Alkali sulphates are etched black with hydrofluoric acid vapour and characteristically inhibit the etching of the adjacent crystals, producing an unetched halo.

Both sodium sulphate and potassium sulphate are known to modify the concrete strength growth pattern; potassium sulphate can also promote air setting of the cement by reacting with gypsum to form syngenite.

When there is an excess of sulphate over the equivalent alkalis, the double salt of potassium and calcium, known as calcium langbeinite, is found in the interstitial phase. This compound also crystallizes into available pore space but causes less problems with air setting than potassium sulphate. Both alkali sulphate and calcium langbeinite form low temperature melts and

can play a useful role in the modern dry process of manufacturing clinker by promoting agglomeration and nodulization of the feed.

When the clinker contains an excess of alkali over the equivalent sulphate, the prismatic alkali-modified aluminate phase and the alkali-modified belite form may be found. If sufficient excess alkalis are present they may stabilize belite to the extent that it will no longer react with lime to form alite, the result being an intimate mixture of belite and free lime.

(g) *Reducing environment*

When a normal Portland cement clinker is fired in a reducing environment the iron- and sulphur-containing phases are affected. Fe^{III} is initially reduced to Fe^{II} , and upon severe reduction to metallic Fe, with the loss of ferrite phase and an increase in aluminate content, while the clinker colour changes from grey to brown. FeO that forms goes into solid solution with lime, or substitutes for CaO in compounds, thereby increasing the overall basicity of the mix. The effective l.s.f., s.r. and a.r. of the clinker are raised, making combination more difficult; the higher firing temperature required for combination increases alite crystal size and cement quality is depressed. Alite that forms in a reducing environment and contains FeO as a lime replacement is more susceptible to degrading to belite and free lime when slowly cooled. Reoxidation of the Fe^{II} in alite at low temperature (below 1300 °C) causes the Fe^{III} formed to be thrown out of the alite crystal structure. The Fe_2O_3 reacts with the CaO in the alite and an intimate mixture of dicalcium ferrite and belite forms along the alite crystal lattice planes.

The effect of a reducing environment upon the sulphate-containing phases depends on the level of reduction. At a moderate level SO_2 is evolved from sulphates and is swept away by the kiln gases. What happens to the alkalis at this stage is not yet clear, but if quickly cooled the clinker becomes deliquescent when exposed to moisture. When such clinker is ground to a cement, the water pick-up causes surface hydration of particles and the cement will have poor flow properties. The cement will also have an increased water demand to produce a workable concrete, which will depress concrete strength. With slow cooling, alkali modified aluminate forms, which depresses the late concrete strength development.

Sulphides form with more severe reduction of the sulphates with the formation of oldhamite and KFeS_2 . The effect of these compounds on cement quality is uncertain because of the overlying effect of all the other changes resulting from reduction.

3. SPECIAL TYPES OF PORTLAND CEMENT

(a) *White Portland cements*

White cements are produced by carefully selecting raw materials low in iron and other transition elements, and firing in a controlled reducing environment such that the small quantities of iron oxide present are converted to Fe^{II} , thus avoiding the formation of the strongly coloured ferrite phase. The clinker is water quenched from burning temperature to prevent reoxidation.

(b) *Sulphate-resisting Portland cement*

Sulphate-resisting clinker requires a minimal C_3A content and is produced from high iron materials to ensure that ferrite is formed in preference to the aluminate phase. The highly mobile iron rich flux promotes alite crystal growth and, at the same fineness, strength develop-

ment is less than with ordinary Portland cement. The purpose of sulphate-resisting Portland cement is to produce concrete that will resist chemical attack; this requires an impermeable concrete made according to BRE Digest 250 and hence strength development is not so important.

(c) *Expansive cements*

Various types of expansive cement have been developed and are generally based upon the expansive formation of ettringite, brucite, or portlandite.

Cements of high free lime content that are used to produce expansion through portlandite formation unfortunately suffer from premature aeration of the free lime, thereby changing the expansive properties. To overcome the effects of aeration several processes involving the encapsulation of free lime in a melt have been developed, the product being blended with Portland cement.

Pollitt & Brown (1975) patented a novel method of encapsulating free lime within individual alite crystals, obtained by the use of calcium sulphate as the predominant clinker liquid phase. It was found that the presence of calcium sulphate stabilized belite, preventing it reacting with free lime. On firing at temperatures in excess of 1500 °C desulphation occurred, the belite was destabilized and reacted readily with adjacent free lime crystals to form alite, which contained free lime inclusions. The hydration of the free lime is delayed until the surrounding alite hydrates, and hence the expansion occurs without loss of concrete strength, unlike other expansive systems.

(d) *Mineralized cements*

In an endeavour to lower the firing temperature of the expansive clinker described above, calcium fluoride was added to the raw materials. The calcium fluoride inhibited the belite stabilization and the alite formed no longer contained free lime inclusions. Thus by firing relatively pure limestone and silica with gypsum and calcium fluoride at moderate temperatures (*ca.* 1400 °C), a clinker rich in alite and anhydrite was produced. This was shown to produce a high late strength cement.

Potassium sulphate was also incorporated into the raw materials with the fluoride and gypsum to change the slowly soluble anhydrite in the clinker into the more readily soluble calcium langbeinite, which provides sufficient calcium and sulphate ions for control of the initial hydration reactions. The calcium langbeinite modified the cement strength growth pattern to give both high early and high late strength. Microprobe analysis of the trigonal alite formed showed it to contain more potassium, sulphur and aluminium than the trigonal or monoclinic types of alite found in normal production cement. This cement is discussed by Dr Moir in this symposium.

4. ALUMINATE CEMENTS

(a) *Cements based on $C_{12}A_7$*

Phase equilibria precludes the formation of $C_{12}A_7$ and C_3S in the same composition. Therefore, to utilize the quick setting and early strength development of $C_{12}A_7$ in Portland cement compositions, it is necessary to make two separate clinkers and intergrind them.

A cement based on $C_{12}A_7$ was developed by Murray & Brown (1975) as a quick setting cement for binding coal contaminated aggregates at high w/c ratios, in connexion with the construction of 'Gateside Packs' in the Longwall coal mining technique used in the U.K.

A special clinker containing mainly C_2S and $C_{12}A_7$ is made in a rotary kiln from a mixture of limestone bauxite and clay. Low iron materials are selected to minimize the quantity of C_4AF and thus prevent the depletion of $C_{12}A_7$. Careful control of the raw mix is required to avoid the formation of C_3A or CA . To obtain the required strength growth characteristics, the special clinker is ground with Portland cement, the $C_{12}A_7$ producing early strength, the C_3S and C_2S ensuring a continued strength growth.

Investigations into the effect of fluorides on the C–A–S system showed that fluorine substituted for oxygen in $C_{12}A_7$ to form a modified version $C_{11}A_7 \cdot CaF_2$. It was also found that, in the presence of sufficient quantities of fluorine, the equilibrium composition could be changed from the C_3S – C_2S – C_3A compatibility triangle to the C_3S – C_2S – $C_{11}A_7 \cdot CaF_2$ – CaF_2 compatibility volume.

By using fluorine rich compositions, quick setting cements of high early strength composed mainly of C_3S and $C_{11}A_7 \cdot CaF_2$ were produced by Greening (1971). Setting times as low as 10 min and significant strength development after 1 h were obtained, while final strengths were comparable to those of normal Portland cements. This cement required careful control of firing temperature. The temperature had to be sufficient to ensure adequate combination but not so high as to cause loss of fluorine such that C_2S and C_3A would form instead of the required $C_{11}A_7 \cdot CaF_2$ and C_3S .

(b) *High alumina cement*

High alumina cement is based around the CA region in the C–A–F–S system. As the main component of the clinker, CA produces normal setting but rapid strength development. CA occurs as short prismatic crystals and in polished sections it can be etched a blue–brown colour when immersed in boiling 10% (by mass) $NaOH$ solution for 20 s. $C_{12}A_7$, which is usually restricted in quantity since it imparts undesirably rapid setting properties to the cement, can be identified by etching with boiling 1% (by mass) borax solution for 30 s.

Pleochroite is formed in the reduced regions of the clinker. It consumes alumina that would otherwise form CA , and if present in any quantity would cause a marked reduction in strength development. The composition of pleochroite is still in dispute, but it approximates to $C_{22}A_{13}F_3S_4$. Pleochroite is also etched by boiling 1% borax solution but can be readily identified in polished section by its fibrous or needle habit. C_2AS (or more correctly melilite) can be coloured with hydrofluoric acid vapour etch or an alcoholic nitric acid etch. It has poor hydraulicity and, as it consumes alumina that would otherwise form CA , its presence lowers the early strength development. Therefore the silica content of the cement is usually controlled to limit the C_2AS quantity.

Both HF vapour and alcoholic nitric acid etch C_2S although a more specific etch is 10% (by mass) $MgSO_4$ solution at 50 °C. The quantity of C_2S is usually low and it makes little contribution to strength development. The ferrite phase approximating to C_4AF also makes little contribution to strength and can be identified by its high reflectivity.

CA_2 is more usually formed in white high alumina cement, its high alumina content making it more applicable for refractory purposes than CA , although its strength development is more moderate. Glass can be etched with HF vapour and alcoholic nitric acid, but does not significantly contribute to strength development.

A small amount of perovskite may be formed from the TiO_2 present. In the fusion process of manufacturing high alumina clinker, the raw materials are fired in a reducing environment to aid melting. When the molten material is cast, the sudden cooling as the melt strikes the mould

produces a layer of glass at the base of the cast. The rest of the cast undergoes variable cooling with the top layer quickly cooled and the centre slowly cooled. Variable reoxidation can occur as the melt is run into the mould and as it cools. These effects produce both a variation in crystal size, and a heterogeneous distribution of compounds throughout the cast.

The clinker cooling rate is reported to modify the strength growth properties. Very quick cooling markedly reduces the rate of strength development whereas very slow cooling leads to a growth in size of the CA crystals, and promotes both quicker setting and a higher initial strength.

5. CONCLUSIONS

The application of the polished section technique to cement clinkers enables an insight to be gained both into their potential properties when ground to cement and also into the process variables that affect cement quality. The technique is particularly useful in defining problems, thereby enabling remedial action to be taken. This particularly applies to phenomena such as heterogeneity, reducing conditions etc.

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Discussion

S. SPRUNG (*Research Institute of the German Cement Industry, Düsseldorf F.R.G.*). Does the different velocity of cooling of clinker influence the properties of cement?

G. R. LONG. The cooling that affects microstructure and cement properties is largely that occurring in the time that the clinker takes to pass between the burning zone and nose ring in the kiln, i.e. above 1200 °C. Modern coolers of all types cool very rapidly from that point on with minimal effect upon microstructure. Although the design of planetary coolers usually requires the burning zone to be away from the kiln exit, a moderately fast cooling rate can still be obtained in the kiln and resultant cement strengths will be comparable to those obtained with other types of coolers.

R. W. DAVIDGE (*A.E.R.E. Harwell, U.K.*). Could Mr Long please define the mechanism whereby fine magnesia causes long term degradation of cement? A fine dispersion of MgO particles (few micrometres) could give highly localized microcracking and hence a toughening effect as described in my paper on ceramics (this symposium).

G. R. LONG. Periclase present in Portland cement is very tardy in hydrating and tends to remain as anhydrous grains after concrete made from the cement has set and hardened.

Subsequent ingress of water can expansively hydrate the periclase, thereby inducing disruptive cracking in the concrete. The occurrence of such cracking will depend upon both the size and quantity of the periclase crystals present.

D. PEARSON (*A.E.R.E. Harwell, U.K.*). Are polymorphic modifications of the cement clinker constituents an important factor in the development of strength of cements?

G. R. LONG. Reflected light microscopy does not lend itself to the ready identification of individual polymorphs unless considerable structural differences exist, such as between the β and γ polymorphs of C_2S . We would normally use X-ray diffraction techniques to detect the polymorphism of any constituent.

The increase in cement strengths mentioned by Dr Pomeroy was not related to changes in polymorphism of the clinker minerals. Alite forms a number of polymorphs, which are stabilized by various minor elements. As reported in Dr Moir's paper to this symposium, superior strength development properties are associated with rhombohedral alite. However, the levels and nature of the minor elements responsible for stabilization of a particular polymorph may have a much greater influence on hydraulic activity and strength properties than the actual polymorphic form itself.