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Cement in its Conventional Uses: Problems and Possibilities [and Discussion]

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Cement in its conventional uses: problems and possibilities

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Although Portland cement is used almost exclusively in the construction industry it can nevertheless form the basis of certain special products that perform similarly to cast iron, timber or aluminium. In this paper, some of the parameters that characterize Portland cement are discussed in relation to the requirements of the user. It is acknowledged that as a consequence of improved manufacturing processes modern Portland cements are not identical with those produced several decades ago, but there are misconceptions about these changes, which are discussed.

Introduction

In the John Player lecture 'Concrete, an alternative material' (Pomeroy 1978), it was shown that Portland cement is potentially a versatile raw material that can be used in combination with other, usually more expensive, materials to manufacture products that have in the past been fabricated from plastics, timber or metals. Portland cement-based products are generally of low energy, particularly when assessed on the basis of performance, such as load bearing capacity (Pomeroy 1978). Table 1 provides some comparative figures that emphasize this point.

During the period when oil prices were low, materials research throughout the world was dominated by the organic chemist and metallurgist who had little interest in inorganic materials, particularly those having a direct relevance to the ceramic, building product and construction industries. More recently it has been widely realized that inorganic materials are more useful than was believed and in particular that hydraulic Portland cements have considerable potential for development and use in novel ways. The necessary materials are in abundant supply and available worldwide.

The principal reason why cement-based products have been confined to construction is that concrete is weak in tension and steel reinforcement must be provided to carry the tensile loads. Because steel rusts it must be protected and the high alkalinity of hydrated cement will provide this protection when it is sufficiently thick and impermeable. Thus traditionally, the use of concrete is largely confined to fairly massive elements that have adequate (20–75 mm) cover to the reinforcement, dependent upon the exposure environment and use of the element. Plain, unreinforced concrete is used in compression, building blocks for example.

In this introductory paper some of the factors that control the performance of Portland cements are discussed. Subsequent papers in this Seminar elaborate on some of the associated topics including ways in which cement-based materials can be tailored by the selective inclusion of fillers or polymers.

Portland cement manufacture

Portland cement clinker is made from a carefully proportioned and finely ground mixture of calcareous and argillaceous materials blended together either in the dry state or slurried

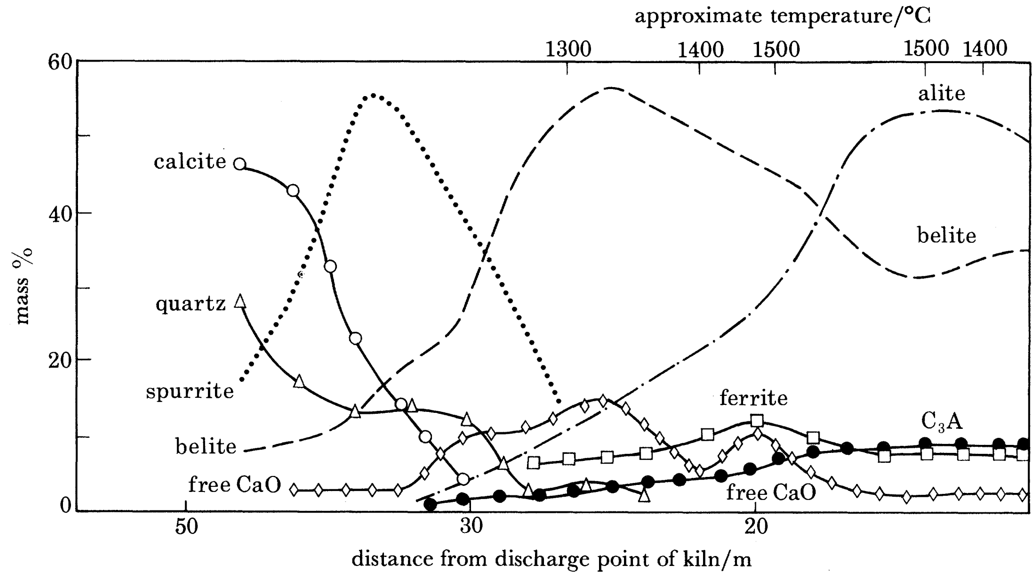

FIGURE 1. An example of the formation of the cement minerals within a kiln.

TABLE 1. TYPICAL MATERIAL PROPERTIES, COMPARED ON A PRODUCTION ENERGY BASIS

material	density t/m	elastic modulus GPa	tensile strength MPa	energy per metre GJ	$\left(\frac{\text{energy per metre}}{\text{unit tensile strength}}\right)/\text{kJ}$
aluminium	2.8	70	100	360	3.6
copper	8.9	130	200	530	2.6
mild steel	7.8	210	300	300	1.0
cast iron	7.9	150	150	360	2.4
glass	2.5	65	60	50	0.8
concrete	2.4	30	6	3.4	0.6
reinforced concrete	2.5	35	30	3.9	0.13

in water to produce a homogeneous raw feed of a specified composition (defined conventionally in terms of the oxides of calcium, aluminium, silicon and iron). This raw meal is burnt in a large rotary kiln (fired either by pulverized coal, oil or natural gas) and is fed gradually along the temperature gradient within the kiln to reach a maximum temperature of approximately 1500 °C. The raw mix is transformed by a series of reactions that take place between 400 and 1500 °C; this reaction sequence is illustrated in figure 1. Sintering and partial fusion occur and hard granular nodules of cement clinker form, which emerge from the lower end of the kiln into a cooling unit. In the cooling unit, heat exchange takes place between the clinker and combustion air, and the clinker exits at a temperature at which it can be conveyed and stored.

Experience has shown that reducting conditions during the burning and cooling processes should be avoided. Clinker that has experienced reduction will, in general, yield a cement with inferior strength properties to those prepared from oxidized clinker. Cement properties can also be influenced by the clinker cooling rate in the temperature interval 1500–1200 °C. Cooling through this interval is normally achieved in the kiln, and rapid cooling generally has a beneficial effect on cement strength properties. The clinker is ground in ball mills together with a small quantity of gypsum or other form of calcium sulphate to act as a retarder. Cement fineness, which is one of the important variables that will ultimately influence the compressive strength properties of the cement, is normally expressed in the form of surface area determined by an air permeability method. A typical fineness is 350 $m^2\ kg^{-1}$, at which fineness approximately 90 % of the particles will be finer than 45 μm.

Within the framework of raw feed composition, firing temperature, rate of cooling and grinding, it is possible to produce Portland cements with different properties. Two common examples are ordinary Portland cement and sulphate resisting Portland cement.

PORTLAND CEMENT CONSTITUENTS

There has been a considerable amount of research performed on cement. In the late nineteenth century Le Chatelier (1882*a*, *b*) and Tornebohm (1897) had published their findings as to the composition of cement. It is interesting to recall that by 1898 there were probably 1000 bottle kilns on the Thames and Medway alone, producing some 25000 tons of cement clinker a week (Francis 1977). By the early 1930s there was substantial agreement as to the description of the principal phases, which Tornebohm had named alite, belite, celite, felite and an isotropic residue. Alite was generally accepted to be essentially tricalcium silicate. Tavasci (1934) had shown that polished samples of cement clinker, suitably etched and viewed under an optical microscope in reflecting light, could be used to study the clinker phases. Bogue (1929) formulated a potential compound composition and during the post war years Jeffrey (1952), C. M. Midgley (1952), H. G. Midgley (1957), Yamaguchi & Uchikawa (1961), Regourd (1967), Maki (1974) and many others have extended our knowledge of the phase composition of the cement clinker. Mills (1968) Richartz (1968) and Chatterji (1969) were among the early workers who used the electron microscope to examine the morphological features produced during cement hydration. The electron probe microanalyser has been used to study the minor compounds, or so-called impurities, which enter in solid solution in the principal phases. These minor compounds originate principally from the accessory minerals of the rocks from which the raw feed is made, from the fuel, refractory linings, worn parts of equipment and from admixtures or mineralizers, which may have been added to the raw feed.

Alite is now recognized as a substituted tricalcium silicate having a total of seven polymorphic forms whose structures have either a rhombohedral, monoclinic or triclinic unit cell. It is rare to find the triclinic variety in commercial U.K. clinker. Maki (1979) has reported that the monoclinic alite found within clinkers produced by modern processes (and containing MgO) can occur in either the M_1 or M_3 form or as a combination of these, depending upon the amount of MgO that has gone into solid solution. Thus the composition of an alite in a cement is far from a unique parameter; although the different forms may be expected to have different hydraulic properties, lattice defects are also important.

The term 'belite' is now reserved to describe the monoclinic or β form of the substituted dicalcium silicate that occurs in cement clinker. Other forms can occur, namely α, α′ and γ, but the latter rarely occurs in commercial U.K. clinker.

The terms 'celite' and 'felite' are rarely used now. The ferrite and the tricalcium aluminate phases are described as 'interstitial'. In a Portland cement the ferrite phase extends from approximately C_6AF_2 to C_6A_2F and is often substituted with several minor impurities. The tricalcium aluminate phase usually occurs in a form that has either a cubic, an orthorhombic or a tetragonal unit cell. In clinkers with an excess of alkalis over sulphate, the alkalis Na_2O and K_2O may be present in the C_3A solid solution and their presence has a distinct influence upon the reactivity of this phase. Periclase (MgO), free lime (CaO) and Apthitalite ($K_3Na(SO_4)_2$)

are some of the minor phases often present in clinker. The identification and quantitative analysis of a clinker by techniques such as Bogue potential compound composition, optical point counting and X-ray diffraction have become routine procedure, each associated with a particular precision. There is no procedure available at present that will produce an absolute quantitative analysis for the phases present. Numerous authors have reported results relating to the quantitative analyses obtained by the various procedures. At the Cement and Concrete Association both Bogue analysis and quantitative X-ray powder diffraction are used to describe a Portland cement. Results obtained from an X.r.d. analysis of a typical U.K. Portland cement are presented in figure 2.

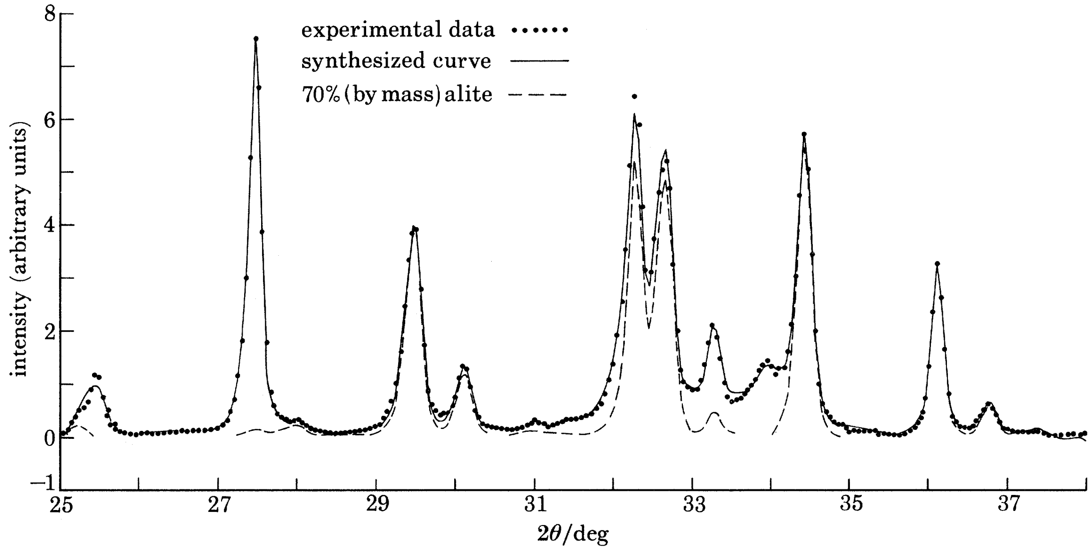

FIGURE 2. X.r.d. analysis of a typical ordinary Portland cement (2θ is the angle of deviation of the X-ray beam). The diffraction profiles for some components, used to obtain the analysis, are not shown: namely 11% belite, 6% $C_3A(0)$, 1% $C_3A(c)$, 6% ferrite, 4.5% $CaSO_4$, 0.5% CaO (all percentages by mass).

DEVELOPMENTS IN THE PERFORMANCE OF PORTLAND CEMENTS

Views have been expressed that modern Portland cements are very different from those that were manufactured several decades ago. Corish & Jackson (1982) have published tables that show that in the U.K. the amount of alite in a typical cement has risen from about 14% in 1848 to 40% in 1939 and is in the range 45–64% today. This increase has usually been accompanied by a reduction in the C_2S. Many people believe that the changes in behaviour, which have occurred over the years, such as the rates of hydration and strength gain, can be attributed exclusively to the change in alite:C_2S ratio and to the greater finenesses of modern cements. While these factors are important, they provide only part of the answer and other parameters can be equally important. In fact, for U.K. cements, the data published by Corish & Jackson (1982) show no general increase in the fineness of cement produced in the years between 1960 and 1980, although the particle sizes and gradings of a particular cement may have changed over that period. Results of the BS 4550 concrete cube-crushing tests showed an average increase for 3 day (20 °C wet-cured) strengths from 16 to 24 N/mm^2 and for 28 day strengths from 35 to 44 N/mm^2 during the 20 year period.

It can thus be seen that there have been changes in cement manufacture that have altered cement performance. On the single basis of potential early strength, or even maximum 28 day strength, it can be claimed that improvements have been made in the quality of the cement, but concurrent with these changes is an increase in the reactivity, leading to higher heats of hydration and also to changes in the morphology or pore structure of the hardened cement paste. The requirements of cement users vary widely: the precaster may demand very high early strengths so that his production rate is maximized; the foundations engineer will require a low-heat cement to keep the temperature rise and gradients in mass concrete within acceptable bounds; other engineers may seek a cement that will have a high resistance to chemical attack or to the permeation of gases or liquids. Some of these and other objectives place conflicting requirements on the formulation of a particular cement.

Table 2. Cement phases

cooling rate	
slow	MgO, more periclase
	C_4AF and C_3A, crystalline
approximately	alite and belite, more ordered, less reactive
4 °C/min	↗ more crystalline form
	liquid formation
fast	↘ glasses
approximately	alite and belite, disordered, more reactive
20 °C/min	C_4AF and C_3A, glassy
	MgO, remains glassy

Table 3. Cement properties

cooling rate	
	less hydraulically active
slow	larger particles (crystallites)
	higher early strength, lower 28 day strength
approximately	easier to grind
4 °C/min	less sound
	less sulphate resistant
	more sulphate resistant
fast	more sound
	harder to grind
approximately	lower early strength, higher 28 day strength
20 °C/min	smaller particles (crystallites)
	more hydraulically active

As mentioned before, the fineness to which the clinker has been ground is one of the factors influencing the compressive strength of a cement. Regourd *et al.* (1978) and Bernard (1978) have shown that hydration is more complete when a cement has been jet milled rather than ball milled. In general the reactivity and hence the strength at early age is increased by an increase in the content of C_3S, C_3A and soluble alkali in the clinker or by finer cement grinding.

The cooling rate of the clinker can affect the size and form of the cement phases (Chatterjee & Ghosh 1980), see table 2, these changes having an influence on the hydraulic activity of the cement (table 3).

The w/c ratio in a cement paste determines the amount of space in which hydration can occur and has an influence upon the final physical form of the hydration product. The degree of supersaturation within the paste fluid increases with decreasing w/c ratio and influences the rate at which nucleation can occur. Curing temperature has a pronounced effect upon hydration and not only affects the rate at which reaction occurs but also the hydration products (figure 3, Dalziel 1980). A higher curing temperature has a beneficial effect on strength at early ages but at later ages it may be detrimental. The pore sizes and pore volume within the cement paste are influenced by the amount of reaction induced by the temperature increase. It is convenient to divide the pore system into capillary pores and gel pores. Mercury porosimetry has shown that large capillary pores occur within the cement paste matrix between the unhydrated clinker particles and the hydration products. Total pore volume and the size of pores decrease as hydration proceeds and this reduces the permeability of the hardened cement paste. There are therefore several factors which affect the hydration and ultimately the strength attained by cement. Most hydraulic phases within the cement contribute to strength via reduction in porosity, which results from their hydration.

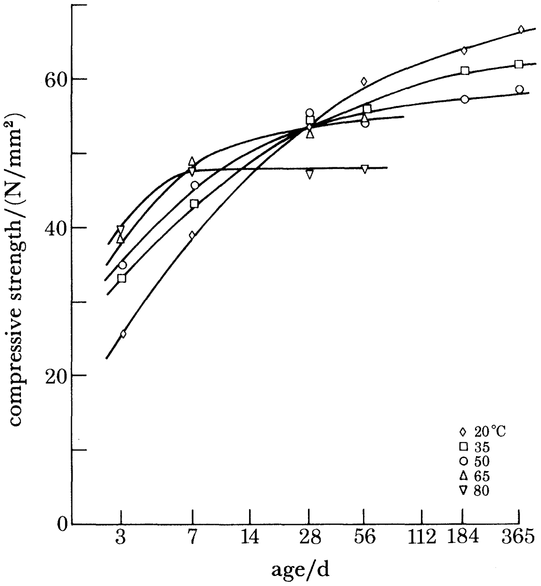

Figure 3. Effect of curing temperature upon the compressive strength of plain cement mortars.

Concluding remarks

An attempt has been made to illustrate some of the ways in which cements differ and how these differences affect their hydration. In the past, a dominant objective has been to achieve strength development and close relationships were obtained between the total porosity of hydrated cement and compressive strength (Lawrence 1969; Roy & Gouda 1973). Recently, it has been realized that the pore size distribution is sensitive to the cement characteristics, the duration of hydration and the curing régime. Parrott (this symposium) shows clearly that such changes in distribution have a significant effect on the potential ingress of chemicals into the paste. There is thus a growing interest in the way that cement constitution relates to the pore structure within the hydrate, since an open hydrate structure will permit liquids or gases to enter more freely, which can result in degradation of the concrete, such as sulphate or chemical attack and depassivation of steel reinforcement consequent upon carbonation.

More rapidly reacting cements, and those containing P.F.A., ground granulated slag or a pozzolana, are all more sensitive to curing temperature and duration of exposure to a moist environment, and there is evidence that it is the pore structure that is most affected (see, for example, Scislewski 1975). Such cements are *less tolerant* to variations in the hydration history than the ordinary Portland cements are, so that performance specifications for concretes are becoming less concerned with strength and more with durability and long-term behaviour.

If a customer is prepared to pay more for a cement that he intends to use for a special purpose, such as for use in oil wells or for stabilizing rock-fill in mining operations, the selection and blending of raw materials and the control of the manufacturing processes can provide a wide range of closely specified cements.

Further opportunities to manipulate the properties of cement-based materials are provided by admixtures that can be added to a concrete mix. These are frequently organic materials or fillers, such as pulverized fuel ash, ground granulated blast furnace slag or finely divided powders. Typically, these may affect the workability or mouldability of the mix, the early age strength development and the durability of the product. Glass, steel or polymer fibres can also be added to concrete and mortar mixes and these also have a major effect on the properties of the material both in the fresh and hardened states. However, the hydraulic cement is the basic ingredient in the concrete formulations and in this paper a few of the controlling parameters have been discussed in an attempt to dispel the often quoted view that modern cements differ solely because of changes in either their fineness or in the relative amount of alite and belite that they contain.

There are many factors that can be controlled to produce a cement to meet specific needs. It is the specification of these needs and the means of verification that the needs are satisfied in practice that are often missing. The cement makers and the concrete producers have the expertise to make cement-based materials with widely different mechanical properties, but the specifiers are not always able to define their needs; it is hoped that this will come.

Subsequent papers elaborate on the possibilities. It is from the optimization of cement chemistry, the use of suitable admixtures or fibres in the mix formulations and from the introduction of novel fabrication techniques that the new generations of cement-based products will come. The opportunities for inorganic materials seem unlimited.

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Discussion

D. D. DOUBLE (*Department of Metallurgy and Science of Materials, University of Oxford, U.K.*). Dr Pomeroy mentioned that there has been a progressive increase in alite (C_3S) contents in Portland cements over the years, presumably due to more efficient heat treatment methods during clinkering. Is the cement industry looking at the possibility of altering the phase composition of Portland cement? For example, it has been suggested that there may be energy-saving advantages in producing lower temperature belite (C_2S) rich cements.

C. D. POMEROY. The Cement and Concrete Association does not undertake research into the cement manufacturing processes, so that I am unable to answer this question. However, Dr Moir is presenting a paper at this symposium, which describes some of the changes in cement composition that are under investigation.

F. MASSAZZA (*Italcementi S.p.A. – Via Camozzi* 124, 24100 *Bergamo, Italy*). The compressive strength to tensile strength ratio of pozzolanic cements is different from that of Portland cements. Is there any reason for this behaviour?

C. D. POMEROY. I have not studied this problem, but if the use of finely divided pozzolan enables closer packing of the cementitious grains to be realized, it is possible that the elimination of larger interparticle voids could result in a higher tensile strength, whereas the total porosity governs the compressive strength. This subject is discussed by Birchall *et al.* in their paper in this symposium.

P. L. PRATT (*Imperial College, London, England, U.K.*). q.X.r.d. analysis suggests that there are 100% (by mass) crystalline components in O.P.C. What was the glassy phase content in this cement and how would it be detected?

C. D. POMEROY. The quantitative analysis referred to by Professor Pratt appears as figure 2 in our paper, where because of the limitations imposed on the reproduction of the figure it does not include the diffraction profiles of the components used to obtain the analysis. In this particular cement the diffraction profiles of the ferrite phase were not that of a well crystallized material and our analysis is given in terms of a ferrite, the diffraction profiles of which have been broadened accordingly. Satou *et al.* (1970) have suggested that the glassy to crystalline content of the ferrite phase, extracted from five Japanese cements, is about 3:7. Our limited experience with U.K. cement suggests a ratio of 1:4. On this basis the 'glassy' ferrite content of the O.P.C. would be just over 1 %.

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Satou, S., Tamura, T., Takahashi, Y. & Muto, H. 1970 Studies on the ferrite phase separated chemically from industrial cement clinkers. *Rev. 24th tech. Session, May* 1970, The Cement Association of Japan, pp. 8–13.

H. A. W. CORNELISSEN (*Delft University of Technology, Holland*). How can the tensile strength of Portland cement be increased (i.e. by the chemical composition)?

C. D. POMEROY. I have no answer to this question, though my reply to Professor Massazza may apply.