

Concrete petrography: a review

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Abstract

Concrete strength depends on the amount, composition and quality of the hydrated binder to the fine and coarse aggregate. This paper reviews the way in which concretes can be examined with the petrographic microscope using both thin sections and polished plates. It reports observations made on actual samples, noting the similarity between the densities obtained by petrographic assessment and those established in laboratory tests.

The paper highlights the value of carrying out a petrographic investigation to obtain quantitative information in support of and prior to the conventional chemical investigation, including aggregate/cement paste ratio and void content, assessment of the weight fractions of water, cement and aggregate; assessment of the composition of the binder including the slag to Portland cement ratio, assessment of the PFA to Portland cement ratio and possibly the assessment of the type of Portland cement employed in the mixture. Attention is also drawn to the implications of aggregate shape and grading.

Introduction

The term concrete petrography, although being semantically dubious, has become a useful shorthand way of describing the examination and description of hardened concrete using the techniques of the geological petrographer. The Geomaterials Group at QMW has been applying these procedures in a routine way since 1969 following and adapting the work of others in many parts of the world.

The use of the polarizing microscope in examining Portland cement began no later than 1887 when Le Chatelier reported on the examination of cements using the polarizing microscope. He identified the presence of abundant clear colourless tricalcium silicate (known as C3S for short), turbid yellowish crystals of dicalcium silicate (C2S), a dark brown interstitial calcium alumino-ferrite (now referred to as ferrite or C4AF) and another material which he inferred should be tricalcium aluminate (C3A). The shorthand names for these materials are used throughout this paper for brevity as follows: alite (C3S), belite (C2S), aluminate (C3A), and ferrite (C4AF).

The modern science of cement microscopy has been

covered in a number of texts including the remarkable book by Campbell (1986) of the Portland Cement Association of the USA in which the materials are illustrated in colour (see also Barnes & Ghose 1983). The illustrations generally show fields of view of about 0.2 mm and in some of the photographs there are more than seventy separate phases. The small size of the particles means that the advance of cement microscopy owes much to the scanning and transmission electron microscopes and the energy dispersive analytical systems which can be attached to them. Campbell provides an atlas of the various phases present in cement powders taken with the scanning electron microscope. He describes cement powder recovered from barrels sunk in the Thames in 1848 and believed to have been made by William Aspdin, son of Joseph Aspdin, who patented Portland cement in 1824. Although the retrieved material shows essentially the same mineralogy and texture as modern Portland cement, cements have changed in important ways over the decades and it is sometimes possible to estimate an approximate date for a structure from observations of the cement paste (e.g. see Nixon 1986).

The petrographic examination of concrete also has a long history, as is illustrated by the reviews published by Mielenz (1962) and Mather (1966). Also of importance are the ASTM Standards: C-823 deals with the examination of concrete and sampling and C-856 outlines the practical procedures for preparing samples, making petrographic observations and interpreting the observations made. The ASTM Specification C-457 covers the determination of composition by the method of point counting and C-294 and C-295 are relevant to the description and interpretation of aggregates.

Only very recently has attention been given to the creation of British Standards for the petrographic examination of aggregate and concrete and Standard Procedures are not yet available. This paper seeks to review the nature of hardened concrete as seen with the various microscopic techniques and to outline useful observations which should be included in a detailed but routine report. The important complementary relationship between the petrographic procedures and the standard chemical procedures is also discussed. A number of the procedures described are novel and based on work carried out at QMW while the

description of more general techniques and relationships that can be observed is strongly influenced by personal experience.

Samples

The most useful sample of concrete is generally a core of about 100 mm diameter. Reinforcement should be avoided, although its presence does not necessarily make for difficulties in the examination and could be beneficial in some types of investigation. The core length should normally be some 300 mm and the external surface should be present. In addition to a petrographic examination the core should be used for other types of measurement, such as the determination of compressive strength or possibly the modulus of elasticity and various chemical analyses. Care needs to be taken to ensure that the concrete of the structural unit is properly represented. It is common for two types of concrete to be present in a single structural unit and cores of inadequate length may not include both or may omit other important variations.

The number of cores required also needs careful consideration and the recommendations given in BS 1881: Part 124: 1988 may be helpful. Typically, small structures such as small footbridges will need three or four samples while large buildings, bridges, dams and similar structures may require fifty or more and some very large composite buildings have been studied using hundreds of samples.

If only one core is examined the data obtained can be highly misleading. Assessments of composition, magnitude of deterioration, depth of carbonation or penetration of other surface processes may not be representative and damage can be missed or exaggerated. Care is required in choosing sample locations in order to take account not only of variations in structural element and environmental conditions but also the types of concrete present as the aggregate and cement types may vary within even small structures.

It is also important that samples are labelled and stored in impermeable plastic containers within about half an hour of their removal from the structure. A convenient system is to wrap the core in cling film and to place it in a polythene tube or bag which can be sealed by heating at the ends and possibly evacuated.

For some purposes cores much larger than the standard 100 mm diameter may be necessary. If the aggregate exceeds 30 mm in nominal maximum size for example, the sample may need to exceed 150 mm in diameter. However, a good deal of useful data can be obtained from cores of smaller size where this is dictated by the structure and it is possible to work on cores of as little as 30 mm diameter or small lumps

some 30 to 40 mm across; indeed even small fragments may be valuable. However, small size may preclude the tests described below and it is often the case that concrete close to the surface is very different from that deeper in the structural element. Sometimes the petrographer is asked for a view based on examination of the core as received using the binocular microscope. The risks attached to such an approach are obvious and need to be appreciated by the user of the data obtained by this means.

Preliminary examination

While the sample remains intact it is photographed and its main features recorded using a high-quality stereoscopic microscope. The following types of observation may be made.

(i) Is the material coherent, strong, friable, absorbent, rich in air voids or honeycombed, cracked or microcracked, homogeneous or varied in aggregate distribution? Does it exhibit any unusual features calling for special investigation?

(ii) What is the nature of the external surface? Is it normal, weathered, eroded, vegetated, cracked, coated with surface deposits, spalled, friable? Has it exposed aggregate, is the aggregate damaged, is the paste damaged? Does the outer concrete differ from the inner? Commonly the outer 30 to 50 mm differs from the remainder of the concrete in a number of respects.

(iii) What is the coarse aggregate type? What is the size range and are there any special shapes present? Are cracks or hygroscopic patches associated with particular aggregate types on the sawn surfaces?

(iv) What is the fine aggregate type, and what is its shape and size range? Are cracks or hygroscopic patches associated with particular rock types in the fine aggregate?

(v) What are the characteristics of the binder? Is it light or dark, pigmented, dense or absorbent? Are there gaps on aggregate surfaces or is the paste/aggregate bond normal?

(vi) What is the size range, distribution and abundance of voids and do they have obvious infill materials?

(vii) What is the size and distribution of reinforcement? To what extent is it corroded? Has corrosion product entered the paste and are cracks associated with the metal?

(viii) What is the first impression of the distribution of carbonation? Has it penetrated along cracks and has it reached reinforcement? Phenolphthalein may be used as indicator.

(ix) Are macrocracks or fine cracks present and what is their distribution? Do they contain deposits such as portlandite, ettringite, or alkali-silicate gel?

How do they relate to the coarse and fine aggregate?

(x) Are any features present to indicate that special modes of deterioration may be present (e.g. abundant ettringite, alkali-silicate gel, obvious gypsum)?

Sample preparation

For routine examination three types of sample may be prepared:

- (i) large thin sections;
- (ii) polished plates and smaller polished pieces;
- (iii) freshly broken surfaces.

Thin sections

The thin sections need to be large in order to be reasonably representative of the concrete. The exact size will vary but for a 20 mm nominal coarse aggregate, for example, the section should be at least 65 mm × 45 mm. Larger sections are sometimes recommended, but generally it is better to make two sections of this size because the concrete is liable to vary with length along the core. Where alkali-aggregate reaction occurs, for example, there may be little or no indication of this in the outer 50 mm or so whereas clear evidence and fine cracking may be observed beyond 100 mm from the external surface. It may therefore be essential to make one section at the surface of the concrete and at right angles to the external face and a second at a depth of 150 mm or more. The cost of making very large sections is also a limiting factor.

The thin section of concrete must be prepared with care greater than required for most rocks. A plate of at least 10 mm thick should be cut from the concrete and impregnated with a cold setting resin *in vacuo*. It is helpful if the resin is coloured or contains a fluorescent dye. One surface of this plate is ground and polished to remove at least 1 mm and to ensure that no cracking or crazing from the cutting remains. The polishing must be carried out using an oil coolant to prevent solution and alteration of the cement paste phases. A second impregnation of the polished surface and second polishing may then be required, following which the plate is ground to the required thickness using an oil coolant after mounting on glass. The thickness chosen for the final section will depend on the problem being investigated. More evidence of alkali-aggregate reaction, for example, may be preserved if the section is some 40 μm thick while more detail of the cement paste can be obtained if the section is 20 μm thick or less.

Polished plates

Polished plates can be more useful than thin sections as they can not only cover a larger area of the concrete core more economically but also may be cut transverse to the core length, along the core length or in both directions and include the full length of the sample. The size required depends on the aggregate size and aspects of the distribution of the components; ASTM C-457 gives tables showing the area required for representative sections containing given aggregate sizes. The polished surface needs to be as flat as possible and at least as good as the thin section surface. It can be examined with the petrological microscope in reflected light or with a high-quality stereoscopic microscope. The finished plate must be stored in an airtight bag with a little water to reduce the potential for atmospheric alteration and to preserve hydrated phases such as alkali-silicate gel. It is often helpful to use chemical stains to aid identification of phases on the plate and to make distinctions between certain types of aggregate and cement phases. Phenolphthalein is useful for distinguishing between limestone dust and cement paste, zinc uranyl acetate and sodium cobaltinitrite for evaluating alkali distributions and alizarin red S for studying calcium distribution. Alkali-silicate gel can be coloured using cuprammonium compounds and other stains can be used for the detection of various carbonates and clay minerals.

The polished plate can be used for the assessment of the rock types present in the coarse and fine aggregate, the assessment of the distribution and magnitude of alkali reactive aggregates and reaction products, the identification of crack patterns including the structure and distribution of microcracks and the determination of volume proportions by point counting. As little as one part in ten thousand of alkali-silicate gel can be detected on suitable plates: an amount not likely to be significant unless the concrete is very young. The gel may be exuded under a slight pressure onto the polished surface but can usually be seen readily if the plate is mounted at an angle to the microscope axis. An important advantage is that whereas gel may not be found in cracks seen in thin section it is easily observed in the polished plate.

Small polished pieces are useful for examination with both the optical microscope in reflected light and the electron microscope. Typically up to about 30 mm in diameter, the pieces are embedded in resin, sometimes after impregnation for strengthening, and polished using diamond dust to give the best possible finish. These samples allow details of the binder to be studied and form the basis of the method for identification of the cement type (BS 1881: Part 124: 1988). As with the larger polished plates, etching and staining can be of great value in aiding identification

of phases with the optical microscope. Although in skilled hands the reflected light microscope gives useful results with respect to the determination of cement type and the interpretation of the structure of the paste, the higher magnifications available with the electron microscope coupled with the ability to obtain chemical data on spots in the cement paste make this a more generally useful and successful method. Indeed it may be argued that today the British Standard method for determination of cement type based on optical microscopy should be modified to provide a similar method based on electron microscopy.

Broken surfaces

The remnants of the core remaining after sample preparations are broken using a bolster and the freshly produced surfaces are examined with the stereoscopic microscope. Freshly broken surfaces are useful in revealing the nature of aggregate and crack surfaces and the contents of voids. Fresh gel may be seen to emerge onto the freshly broken surface where an alkali-aggregate reaction has taken place.

Small broken pieces can be examined with the electron microscope with considerable advantage as it can allow identification of crystallites on crack surfaces, in voids or on aggregate surfaces which would be missed on polished plates. Again materials difficult to find on transverse cut and polished surfaces may be seen more easily on the broken surfaces.

Observations on prepared samples

Aggregate

It is sometimes tempting for the petrographer to make exceptionally detailed observations on the rock types present in the aggregate, many of which may be of no significance for the engineering performance of the material. The information required is that relating to the influence of the aggregate on the quality of the concrete, i.e. its strength, workability, durability, density, elasticity and dimensional stability. The main features required in evaluation of the aggregate therefore are:

- rock types present and their abundances;
- size range and shape of particles;
- properties of rocks;
- mineralogy and texture, density, water absorption and strength;
- nature of the interface between aggregate and binder;
- internal cracking and associated cracks in binder.

Composition and texture

With respect to the rock types present in concretes, difficulties exist in the classifications employed in normal geological usage because the rocks seen in concrete are entirely removed from their field association; hence they must be named specifically with respect to their mineralogy and texture. However, ambiguities introduced by geological classifications are immense. For example, the ASTM specification C-294 defines the grain size limit of fine-grained igneous rocks as 1 mm with coarse-grained rocks being greater than 5 mm and some British texts have similar limits. However, BS 5930:1981 takes the limit of fine-grained rocks as 0.06 mm and coarse-grained rocks as 2 mm, applying these limits to all rocks including igneous, metamorphic and sedimentary types.

Ambiguities also arise in the use of rock names which may in practice convey little meaning for the engineer. Quartzite for example, can range from a sandstone made largely of quartz grains, through a thoroughly recrystallized rock dominated by quartz such as the Wrekin quartzite to hydrothermal vein material, or a plainly metamorphic metaquartzite. Similarly 'limestone' refers to chalk, weak oolitic limestones, recrystallized rocks such as the Carboniferous limestones or marbles like the Balluchulish limestones. Whether the rock is siliceous or dolomitic is also likely to be important but may not be clear in orthodox classifications. Full descriptions of the rocks are required, illustrated with photomicrographs, rather than the simple use of 'standard' terminology.

The difficulties of nomenclature also mean that it is generally unsatisfactory to make lists of rocks that are either suitable or not suitable for the manufacture of concrete; the exceptions to such lists are likely to be numerous and the resultant confusion may blight entirely satisfactory materials (see, e.g., Concrete Society Report 30, Highway Works Specification Part 5 and BRE Digest 330).

Unsatisfactory components of aggregates

With respect to the presence of possibly unsatisfactory materials in aggregate for use in concrete, guidance is given in some of the older versions of BS 882, ASTM C-294, in Concrete Society Report No. 30 (the report of the Hawkins Committee) and in the Specification for Highway Works (DOT1986). Materials which might prove unsatisfactory to a greater or lesser extent include:

- rocks making excessively elongate or flaky fragments or having much coarse mica;
- rocks with a high microporosity i.e. interconnected pores less than 3 μm in diameter (the smaller the worse);

rocks containing siliceous particles less than about 5 μm in grain size or including some glass;
 carbonate rocks containing dolomite and fine-grained siliceous phases;
 rocks containing bituminous residues;
 materials containing or liable to produce dust and those containing clay minerals, especially smectite;
 rocks containing sulphides and sulphates, especially pyrite, pyrrhotite, marcasite, and gypsum and anhydrite;
 materials containing organics, coals or lignites or possibly phosphates;
 certain zeolites, which can show volume changes or release alkalis into the cement paste;
 alkali-reactive minerals such as chalcedony, tridymite, cristobalite, opal and possibly finely divided sheet silicates such as chlorite and vermiculite;
 oxides which can be dispersive and staining.

Materials may be unsatisfactory for a variety of reasons and a careful assessment should be made for each specific structure and environment. It is important to consider whether the material may:

- affect the ultimate strength of the concrete, e.g. have poor shape, contain expanding or shrinking particles, weak particles, or flaky minerals such as mica;
- lead to surface damage or more penetrative cracking due to freeze/thaw processes;
- react adversely and expansively with the alkalis present in the pore fluid of the cementitious binder and cause cracking (e.g. zeolites, fine-grained siliceous materials, opal, tridymite, cristobalite, smectites, some dolomitic limestones, argillites, meta-argillites, greywackes and meta-greywackes).

Sulphides may also be significant as they may become oxidized and lead to staining of the concrete surface. In the alkali medium of the concrete and when oxygen and abundant water are available, sulphides may also react with aluminous phases in the paste and aggregate to produce needle-like crystals related to ettringite. Expansion and cracking may result.

Significant cracking and expansion of the concrete can also arise when gypsum is included in the aggregate. This is slowly replaced by portlandite, SO_4^{2-} ions being released which combine with the paste phases to produce ettringite. The process needs much water and can be exceptionally rapid if the concrete is wetted after some months of reaction have occurred.

Deleterious components of aggregates can become segregated onto the surface of the concrete, resulting in unsightly staining (e.g. bitumen in bituminous limestones).

Aggregate may influence the role of water in the binder or allow penetration of moisture and the atmosphere deeper into the concrete than is desirable

(e.g. porous limestones and argillites) while contaminants of aggregate can adversely affect the hydration of the cement paste (e.g. organics, sulphates, chlorides, phosphates).

Strained quartz

The presence of strain in quartz, indicated for example by the presence of undulose extinction, is often considered to be potentially deleterious in that it might cause alkali-aggregate reaction. However, the basis for this assessment is rather dubious and many aggregates containing strained quartz exhibit no significant reaction even when they occur alongside other reacting aggregates. In addition the criteria used in deciding that an aggregate is potentially reactive because it contains strained quartz are highly suspect.

A method for the measurement of strain in quartz is given by Dolar-Mantuani (1983) but an inter-laboratory test of this method gave wildly disparate results with some analysts finding the grains to have a very high potential for reaction while others indicated the same material to be much more benign (Anderson & Thaulow 1989). A study of extinction angles in various rock types shows that a number of factors influence the measurable extinction angles which are not all taken into account in the Dolar-Mantuani method. They include the size of the undulose domain which may be difficult to recognize, the optical orientation of the strain domain, the presence of strain lamellae in one or more directions and the commonly observed reversal of direction of undulose extinction which can occur in adjacent domains. Sometimes the impression is gained that the angle being measured represents all the strain domains in a given strained quartz. In most cases the angle through which the grain is rotated for extinction to pass from one side of a strain domain to the other is about 4° if the grain is orientated to give the maximum angle. Quartz grains may have many such domains, however, and sometimes the sense of rotation changes in going from one domain to the adjacent domain. What is meant by the undulatory or undulose extinction angle may then be obscure. Sometimes reference is made to strain angles of 40° or 50° but to obtain such angles in a single strain domain appears to be very unlikely because of the enormous distortion of the quartz lattice represented in the very small quartz volume.

In the author's experience where quartzite grains take part in reaction they usually have zones of extremely fine particle size and sometimes internal cracks. They may also have very thin strain domains and strain lamellae that are only a few micrometres thick (see also Grattan-Bellew 1987). The presence of undulose extinction presumably relates to lattice distortion brought about by the presence of crystal lattice dislocations. The potential for reactivity may therefore

be dependent on the abundance and distribution of these dislocations. If this is so, it would be useful to investigate the mineral with the transmission electron microscope. A prerequisite for such an investigation is the selection of grains which are unambiguously reactive because of the presence of strained quartz with no other potential cause of reaction. Until unambiguous petrographic tests are available it is necessary to treat quartz-rich rocks with caution. The petrographer should record the presence of strained quartz and indicate the style of strain observed. Appropriate mortar bar and concrete prism tests will also be required as well as observations of the service record of the material but it may not prove necessary to condemn all such rocks as potentially reactive simply because they contain some strained quartz.

Aggregate shape and grading

Shape factors. Although BS 812: 1975 provides details of methods for measuring both flakiness index and elongation index of aggregates before incorporation into concrete it is common in practice to use only the flakiness index. It may sometimes be necessary to assess the degree of flakiness of the aggregate in the hardened concrete. This may involve separation of the aggregate by solution of the cement paste or the shape factors of the aggregate can be assessed by measuring the aspect ratios (Figs 1-6) of a number of particles and calculating the proportion having aspect ratios greater than some pre-determined value. The aspect ratio can range from unity for simple highly spherical particles to about 1.7 for regular cubic grains. Experience suggests that if nearly all the particles have aspect ratios of 3:1 or less the shape factor has little influence on the quality of the concrete. However, the strength may be affected if more than 50% of the aggregate particles have aspect ratios in excess of 5:1, especially if these particles are orientated parallel to one another



FIG. 1. Extremely well-rounded highly spherical polymictic gravel aggregate of very good shape. Width of photograph = 80 mm.

as a result of the method of placement. Flaky particles make for a harsh mixture of low workability at a given water content. This leads to poor compaction and a high void content resulting in low strength and durability. In particular, the depth of penetration of carbonation is largely governed by the degree of compaction so that poor aggregate shape can influence

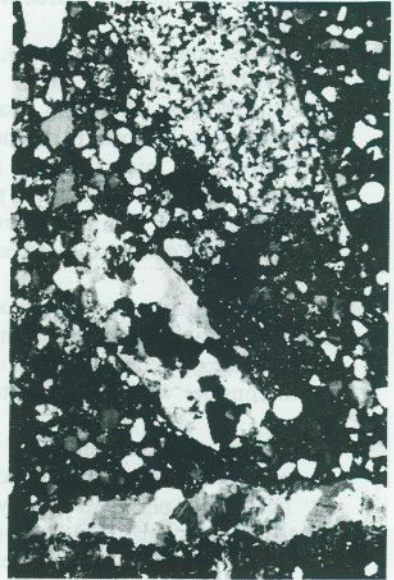


FIG. 2. The lower part of this photograph includes a flake of limestone which has an extremely rough surface. Other aggregate particles also have high aspect ratios and are angular. Width of photograph = 30 mm.

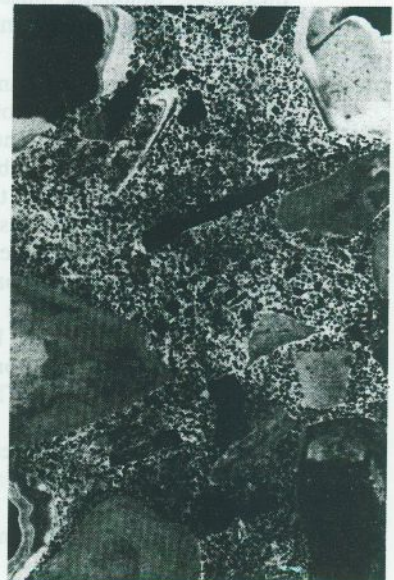


FIG. 3. A gravel consisting mainly of particles of good shape combined with material which is sharply angular and has very high aspect ratios. Width of photograph = 20 mm.

reinforcement corrosion. Observation of the aspect ratios may therefore be important when evaluating the quality of hardened concrete. Aggregate of good aspect ratio will have 90% of particles with a ratio of less than 3:1 and a moderate aggregate will have 50% or more of the grains having aspect ratios of less than 5:1.

5) or by the number of times the smooth surface intersects with the true rough surface.

The angularity of aggregate has a greater effect on strength and workability than the flakiness index. It is measured by the method given in BS 812: 1975 in which the aggregate is placed in a standard volume. In thin sections or polished surfaces two aspects of roundness are apparent: the degree of rounding at edges and corners and the angles defined by the surfaces making those angles and corners (Figs 4 & 5). It is the latter which has the greater influence on aggregate packing and the harshness of the aggregate, while the former is likely to affect the location of microcrack development. Both features need to be described and, if appropriate, measured on the thin section, polished plate or photographs of these. A simple measure of angularity is by the determination of the interfacial angle of the sharpest corner on the aggregate as seen in the thin section. The angle measured is that between the normals to the two facets so that a perfect sphere has an interfacial angle of zero and the most angular grain approaches 180° . Good crushed rock aggregate has an average interfacial angle of about 90° with a standard deviation of about 10° . Some crushed rock aggregates produced very high interfacial angles and in crushed flint aggregate, for example, the interfacial angles can commonly exceed 150° in many particles.

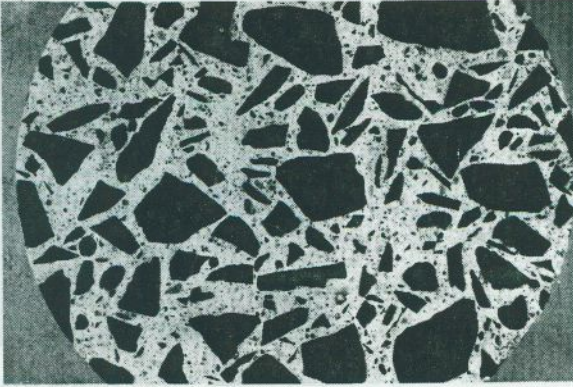


FIG. 4. A crushed limestone showing good shape for the larger particles with low aspect ratios and poor shape for the smaller particles which are sharply angular and have very high aspect ratios. Width of photograph = 100 mm.

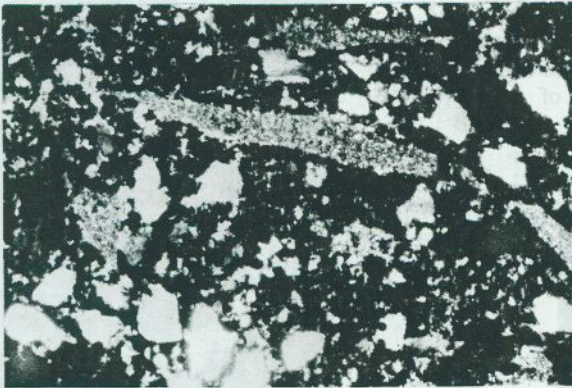


FIG. 5. Shards of very sharply angular flint. Width of photograph = 30 mm.

In addition to the sphericity or aspect ratio of the aggregate the roughness of the aggregate surface and its angularity are important. The roughness affects the potential bond between aggregate and paste, the potential for crack development on aggregate surfaces and the water demand created by the aggregate as a result of the increase in surface area. More collaborative work is required to standardize measurement procedures and further the work carried out by Wright (1955). However, an assessment of roughness can be made by comparing the length of the surface of an aggregate particle with the length of a best-fit smooth line drawn through the surface irregularities (Figs 2 &

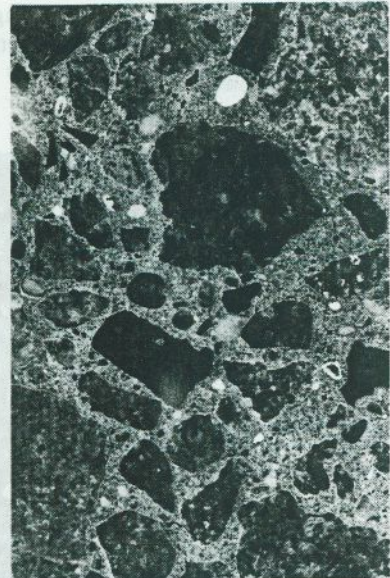


FIG. 6. A very well shaped crushed granite coarse aggregate with very small proportion of small angular particles. Width of photograph = 30 mm.

Grading. The grading of an aggregate is an important factor influencing the workability, strength and economy of concrete and should therefore be considered in the petrographic evaluation. It can be assessed directly

from the thin section or the polished surface. Calibration graphs can be drawn up relating the grading of aggregate as measured by sieving to that observed in the thin section. The measurement on the thin section or polished plate is conveniently carried out using the maximum apparent dimension of each particle or some function of the shape such as the square root of the product of minimum and maximum dimensions. The grading zone of the fine aggregate can be assessed by comparison with standard sections or where possible by measuring the mean apparent particle size of the aggregate. The 50 percentile for the aggregate is usually about 1.77 times the measured mean size unless the aggregate is of unusual shape. The method of determining the grading curve developed by sedimentologists for hardened sandstones is also directly applicable to concrete. By these means it is usually possible to indicate at least the BS zone of the sand which is a major factor influencing workability.

Aggregate surfaces. Aggregate surfaces require detailed examination. It is very common for cracks and microcracks to develop along the interface between the aggregate and the cement paste and there is often a difference in the coefficient of thermal expansion between the aggregate and the binder. Stresses are therefore commonly set up along these zones. In the case of siliceous aggregate, layers of calcium hydroxide frequently develop along the aggregate surfaces, with their form and abundance depending upon the composition of the binder and the conditions of curing (Fig. 9).

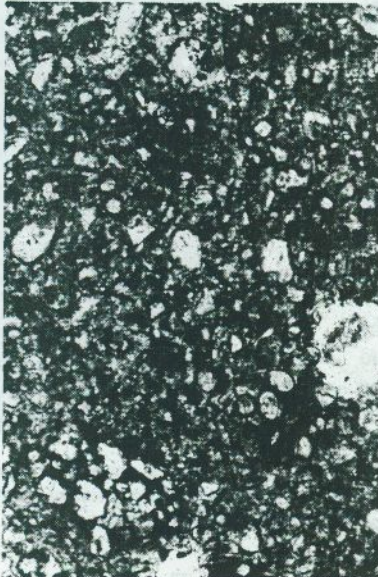


FIG. 7. Cement paste with a low water/cement ratio and with a large amount of residual unhydrated Portland cement clinker particles. Width of photograph = 0.2 mm.



FIG. 8. A zone of light crystals running along the length of the photograph. These are coarse crystals of calcium hydroxide developed within the hydrated gel. Width of photograph = 1 mm.

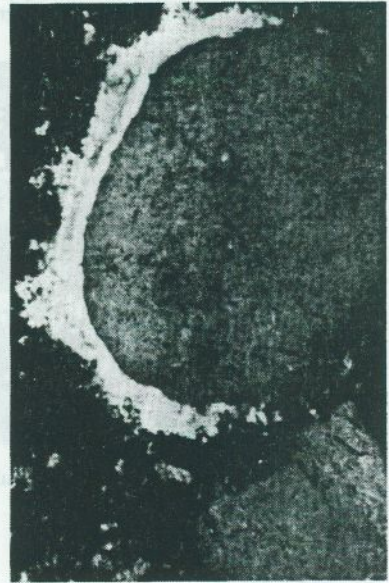


FIG. 9. A quartzite sand grain which is coated with a thick layer of calcium hydroxide. Width of photograph = 0.5 mm.

Re-mixing of partly set concrete may change the nature of the portlandite precipitation and its orientation, as growth of the hydroxide occurs through the critical setting phase. A great deal of work has been published over the years on the nature of this $\text{Ca}(\text{OH})_2$ layering (e.g. Grandet & Ollivier 1980). The amount of the portlandite precipitated usually increases as the particle size of the aggregate decreases,

so that much of the calcium hydroxide occurs on the surfaces of siliceous fine aggregate. Its local abundance and form may also be affected by water distribution and such processes as plastic settlement. It is also common to find portlandite forming a thin layer on the metal of reinforcement where there is little sign of corrosion, but where the metal becomes corroded this layer is generally absent. Some workers find that reactive aggregate particles have little or no portlandite on their surfaces, but this is not a general rule. Portlandite alongside cracks containing alkali-silicate gel may be reduced through ion exchange with the gel. Portlandite distribution and abundance is also changed by the presence of ground granulated slag, fly ash or rock dust.

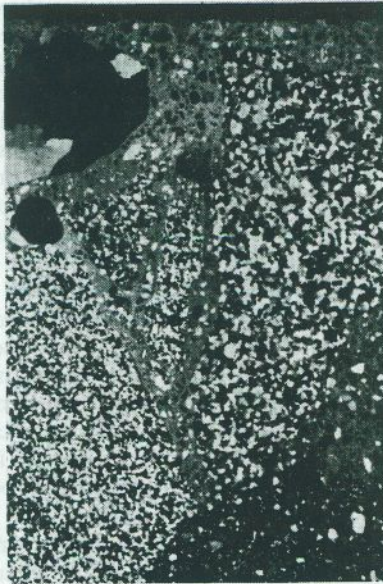


FIG. 10. This photograph shows carbonization of Portland cement paste with the carbonation forming a light zone at the top of the photograph and penetrating along fine cracks. Width of photograph = 3 mm.

Microcracks are commonly developed on the surfaces of coarse aggregate particles. These may also occur along the surfaces of fine aggregate grains if thermal stresses are high, as might occur when concreting in cold weather for example. The development of some cracks at this location is not unusual even in concrete that is well made and of considerable strength. It appears to represent early hydration shrinkage and is often the locus of the formation of chains of portlandite crystals. Cracks of this type are commonly encountered where the water/cement ratio of the mixture is as low as 0.40. Microcracking is discussed further in a later section.

It is not uncommon to find alkali-silicate gel along aggregate surfaces when the reaction occurs in concrete. However, such an occurrence rarely indicates

that the individual particle is itself reactive, as in most cases gel appears to migrate into fractures which could either pre-date the reaction or be generated from centres of reaction developed elsewhere in the concrete. In addition zones rich in ettringite frequently occur along aggregate surfaces particularly when the concrete has a high porosity and moisture can migrate through the concrete. The association of the ettringite with the aggregate surfaces probably relates to recrystallization of the sulpho-aluminates in the concrete as a result of movement of moisture in or through the concrete. In some cases it may be associated with sulphate attack of external origin. The development of the fine cracks along aggregate surfaces, especially if they contain alkali-silicate gel or ettringite, indicates deterioration of the concrete which may lead to some reduction in strength and perhaps more particularly reduction in elastic modulus.

Density, porosity and elasticity. The petrographer is able to estimate the properties of rocks (including strength, density, water absorption and compressibility and various elastic moduli) from his own experience or from compendia of data such as the US Geological Bulletins 1144-E (Manger 1963). This information aids in the assessment of mix proportions as well as the possible effects of the aggregate on the hydration of the paste and its workability. For the last one hundred cores examined by the author the estimated bulk density of the concrete based on the petrography has departed from the measured bulk density with a standard deviation of 8 kg/m^3 . A single set of six cores, for example, gave the results shown in Table 1.

TABLE 1. A comparison of measured bulk density with that estimated from petrography

	Density from petrography (kg/m^3)	Measured density (kg/m^3)
	2325	2285
	2295	2337
	2308	2310
	2299	2315
	2300	2315
	2331	2325
Mean	2310	2315

These observations were made in a routine way without making a full point count analysis. Nevertheless, a difference of 40 kg/m^3 between the two observations is the maximum usually encountered and the cause of such a difference should be investigated. If a full point count analysis is carried out, the agreement between the two methods is usually improved.

Changes within aggregate. One of the most obvious uses of the petrographic method is the evaluation of changes that occur within the aggregate in hardened concrete. Some of these changes may occur very rapidly while others may continue for several decades. The effects can vary from producing minor disfigurement to structural damage.

The large majority of rocks used as aggregate remain unaffected by the surrounding Portland cement paste but a few exhibit significant changes. Although some may be observed in thin section, they are better seen in polished plates or sometimes on sawn or broken surfaces. The most common types of change are:

- softening of the aggregate;
- development of internal cracks;
- shrinkage of the fragments;
- expansion.

Softening can take place where the aggregate includes weak or porous particles such as those containing clay minerals and it is common to see the ferruginous matrix of some fine-grained rocks dispersed into the surrounding paste with the remnant of the rock becoming extremely weak. Some types of aggregate also become softened through alkali-aggregate reaction, the generation of gel within the aggregate displacing substance and leading to a general weakening of the material. Pyrite may become converted to a weak mixture of hydrated iron oxide.

Shrinkage of clay-rich particles is extremely common, although these do not usually form a large proportion of the aggregate. Ferruginous argillites such as ironstones are generally more abundant and may show shrinkage cracks internally. A number of instances have been reported of shrinkage of materials which are robust initially, including greywacke, shale and mudstone (drying shrinkage $>0.085\%$) and slightly altered rocks containing some clay minerals including some dolerites and basalts (drying shrinkage 0.066% to 0.085%). Granites, limestone, quartzite, felsite, gabbroic rocks, flint and marble can show shrinkage of less than 0.045% (BRE Digest 35).

Bulk expansion of aggregate can sometimes take place in response to an alkaline environment particularly in the rock types exhibiting alkali-carbonate reaction, the rock prism test being useful in determining the alkali-carbonate reactivity. Concrete may also expand as a result of chemical reactions between various parts of the cement paste and the aggregate, such as alkali-silica or alkali-silicate reactions which induce cracks by the swelling of gel within the rock particles. Indeed even with glass, cracks may develop within the aggregate particles and pass out into the surrounding paste. Where reaction centres are in sufficiently close juxtaposition, the cracks tend to join and cause general

expansion of the concrete. For this to occur the gel produced must be sufficiently viscous not to leak into the abundant pore space available within most concrete, something analogous with crustal dilation through dyke injection.

Damaging chemical reactions also occur with rock types containing sulphides, often leading to the formation of iron oxides and sulphate ions which combine with the calcium-rich material of the Portland cement paste to generate gypsum. The process commonly leads to surface spalling and staining of concrete surfaces, particularly where the sulphide is disseminated as very fine particles in rocks such as argillites and meta-argillites. Any occurrence of certain types of pyrite, pyrrhotite or marcasite is likely to produce this surface damage.

If the concrete is extremely wet and sufficiently porous for the environment to be oxidizing the sulphides may liberate sulphate ions deeper in the material. These ions react with aluminous phases to produce the solid solution series that includes ettringite.

These acicular phases are also produced as a result of reaction between gypsum or anhydrite if these are present in the aggregate. Although any finely divided gypsum in the cement paste reacts out during the early hydration reactions, the larger crystals of gypsum will become progressively replaced by calcium hydroxide crystals. The concomitant liberation of sulphate ions into the surrounding paste leads to the formation of ettringite in the paste and in microcracks and can be extremely damaging. A wet environment is required; the most damaging circumstances being when concrete containing crystals of gypsum is maintained dry for a considerable period and then becomes wet. Expansion with abundant cracking can then occur extremely rapidly. Similar very rapid expansion would be expected from the presence of altered sulphides which become wetted.

Other chemical effects on aggregate include dedolomitization of dolomitic limestones. The release of magnesium into the Portland cement paste can lead to the formation of brucite or hydrated magnesium silicates. Both of these phases have little or no cementitious value. There may also be an overall expansion in this chemical exchange, but the dedolomitization is not always expansive. It is also theoretically possible that olivine in contact with an alkaline environment, such as that of cement paste, could be converted into serpentine minerals. Whether or not this alteration is expansive depends on the concomitant changes occurring in the surrounding paste. However, experiments have shown that this process is not significant at normal temperatures although in the event of such concrete coming into a damp environment at an elevated temperature of perhaps 200°C , some expansive reaction might occur (French & Crammond 1980).

Another chemical exchange reaction often encoun-

tered is the removal of bituminous material from limestones. It is normally extremely difficult to dissolve or remove the bituminous material that occurs in many limestones. However, the alkaline pore fluid of concrete appears to be able to extract much of the bituminous material from limestone so that the surrounding paste becomes stained. The presence of organics of this type, if abundant, could have effects on the setting rate of the paste. A more obvious and common effect is that bitumen is removed from the aggregate and deposited on the surface of the concrete resulting in staining. This may be a general mottling with brownish patches alternating with more normally coloured concrete or the development of streaks and tear drops of dark brown material arising from individual aggregate particles close to the concrete surface. This phenomenon has been observed in architectural blockwork as well as high-quality decorative concrete. Experiments have confirmed the release of bitumen from limestone by alkalis in the pore fluid of the cement paste. The process has been shown to cause alkalis to migrate through the porous bituminous limestones and to become concentrated on the surface of concrete where the aggregate is close to the concrete surface. In addition the experiments have shown that haloes of bituminous material develop around the bituminous aggregate throughout the concrete.

Description of binder

The investigation of the binder in concrete requires the use of magnifications which are close to the limit of the petrological microscope. Although the individual



FIG. 11. Hydrated gel containing large crystals of calcium hydroxide.

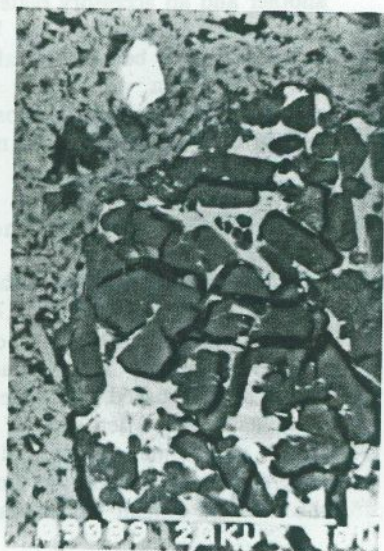


FIG. 12. A residual unhydrated clinker particle within carbonated paste. The clinker particle has become substantially recrystallized and pseudomorphed by carbonation product.

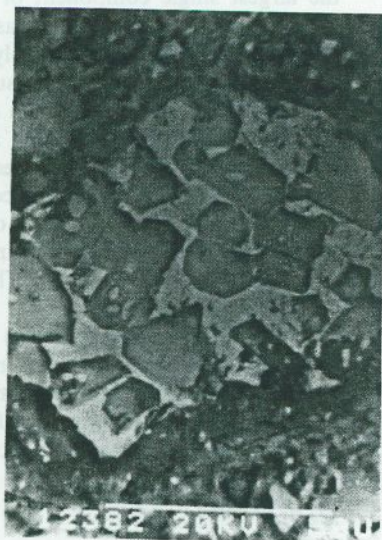


FIG. 13. A typical clinker particle with grains of alite dispersed in a matrix which is largely C3A.

particles may be greater than $30\mu\text{m}$ in diameter and seen clearly in thin section, they are usually very small and the polarizing microscopy of polished surfaces is more satisfactory. The reflected light optical system can be used on covered thin sections providing the magnification is not too high (i.e. less than 400 diameters) and the angle between the polars is capable of adjustment. It is important that the microscope can be switched directly from transmitted to reflected light without changing lenses or needing to move the specimen. It is also useful to be able to make observations

between polars which are at various angles to one another and an accessory plate will allow examination of apparently isotropic areas. Using special filters the paste can also be studied after impregnation with fluorescent resin with many observations becoming clearer. This procedure is most valuable in assessing the porosity of the paste and microcrack distribution.

Components of the binder

The principal components of the cement are granulated Portland cement clinker (Figs 7 & 13), and gypsum or anhydrite. In addition it is not uncommon to blend ground granulated blast furnace slag (Fig. 19), PFA (Fig. 18) or crushed limestone dust with the cement. The blending is often part of the cement production but is also sometimes carried out while mixing the concrete. Some of the more important constituents of the Portland cement binder material are as follows.

Alite

This is a solid solution series of tricalcium silicate. It is the largest single component of Portland cement and the amount of C3S has increased over the years. It may include up to approximately 4% of impurity with magnesium and aluminium substituting for silica. Other substitutions involve iron and sodium. The crystals are idiomorphic and often approach hexagons in outline. Alite crystallizes between about 1200°C and 1450°C and has refractive indices ranging from 1.716 to 1.724 and a birefringence of about 0.005. Ionic substitution causes variation in birefringence which can then be as high as 0.01. The crystals are usually colourless in transmitted light and the polarization colour in normal thin sections is usually low first-order grey; and if elongation is present, the phase is length slow. Crystal zonation is common and sometimes pseudo-polysynthetic twins are formed through inversion from monoclinic to triclinic forms.

Belite

Belite is a solid solution series of dicalcium silicate. As with alite, it exists in several polymorphs and contributes some 20% of many Portland cement clinkers. Minor ionic substitutions include magnesium, potassium and sodium, aluminium, iron and sulphur such that the total impurities may be as much as 6% by weight. Belite grains are normally rounded, glassy particles with marked multi-directional lamellae. The substance is often pale to deep yellow and may have shades of green. The birefringence is about 0.015. The substance generally gives polarization colours which are white to yellowish. Belite can be divided into four types according to the number of sets of inversion

lamellae and the presence of inclusions. The most common form of belite shows two or more sets of intersecting lamellae as well as polysynthetic twins within the lamellae. The refractive index is generally around 1.71 to 1.73 but is reduced by substitution of sodium.

Tricalcium aluminate

$\text{Ca}_3\text{Al}_2\text{O}_6$ usually appears as uniform anhedral to rectangular crystals making up to some 18% of clinker and forming between and in association with the C4AF crystals. It typically fills the interstices between crystals of ferrite and belite. The crystals are normally isotropic but vary from colourless to brown in transmitted light and have a refractive index of 1.71. Substitution of iron, magnesium, silicon, sodium and potassium is common and may reach 10% by weight.

Ferrite

This is a solid solution series ranging from $\text{Ca}_4\text{Fe}_4\text{O}_{10}$ to $\text{Ca}_4\text{FeAl}_3\text{O}_{10}$. Dark green to almost opaque, it has a refractive index close to 2.0 and a birefringence of about 0.01 and can be an interstitial material, prismatic, dendritic, or even fibrous. It makes a very large part of the matrix material in sulphate resisting cement clinker.

Periclase

Periclase (MgO) is often seen as small crystals in the interstitial phase of the clinker particles although it can range up to 6% or so in some clinkers.

Other components

Some clinkers may contain up to 1% free lime (CaO) and up to 2-3% alkali sulphate and alkali-aluminates including complex combinations of sodium potassium and calcium as sulphates. Some clinker types contain small amounts of glass of variable composition which may fill voids in rapidly cooled clinker. Carbon particles may also be present.

Gypsum or anhydrite typically forms 4% to 5% of the cement powder while fly ash and ground granulated blast furnace slag (GGBFS) are often blended with the Portland cement. Fly ash (PFA) consists of spherical and ellipsoidal beads and globules of glass usually containing cavities and often including other phases. The glass dominates but other constituents include carbon particles, iron oxides, tridymite, cristobalite, quartz, mullite and spinel. Generally very uniform in composition from a given source, the glass may vary slightly from source to source. The glass component is also dominant in the ground granulated blast furnace slag which also includes various calcium sili-

cate crystals such as polymorphs of larnite. There may also be opaque metallic particles and oxide particles in both the PFA and ground slag.

On hydration, Portland cement produces a wide range of very complex phases including the following.

Calcium hydroxide (Portlandite)

Portlandite (Figs 8, 9, 11) crystallizes as hexagonal plates or prisms with refractive indices of 1.574 and 1.545 and a high birefringence. Its solubility in water increases as the temperature decreases; at 0°C it is approximately 1.7 grams per litre expressed as CaO. The saturated solution gives a pH of approximately 12.5 at 25°C. Calcium hydroxide is precipitated from solution in the presence of alkali hydroxides and forms crystals of up to 100 µm. It develops mainly during the principal hydration reactions in the setting process and forms bright, clear, birefringent crystals often in clusters that are readily recognized in thin sections.

Calcium silicate hydrates

The typical calcium silicate hydrate has a calcium oxide to silica ratio of 1.5:1 although this will vary with water/cement ratio of the mixture. In addition, the calcium silicate hydrates in detail are complex with a range of compositions occurring as small crystallites. A review of these phases is given in Lee (1970). Electron microscopy is required to study these phases in detail and it is usual to refer to the mixture of calcium silicate hydrates, hydrated aluminates and sulphates as 'hydrated gel' in routine microscopy.

Calcium aluminium hydrates

The cubic hydrate C₃AH₆ is the main product of the hydration of the aluminates in portland cement. Various other aluminate hydrates are produced at various levels of hydration and carbonation ranging to gibbsite.

Calcium sulpho- and chloro-aluminates (Figs 14-16)

Needle-like phases are common in concrete paste which has been cured at very high temperatures, has been subject to sulphate attack, or moisture penetration. The most common of these phases is ettringite. They have a low to moderate birefringence and generally occur as needles with thicknesses of a few micrometres. Usually less than 1 mm in length they grow in cracks and voids or dispersed through the paste and require large amounts of water for their formation. The stoichiometric formula for ettringite is often represented as Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O but solid solutions containing iron and silica are common



FIG. 14. A cluster of radiating growths of ettringite needles within hydrated paste.



FIG. 15. Needles of thaumasite upon which calcium silicate hydrate crystals of low calcium to silicon ratio have developed.

and the sulphate content is frequently less than the full three molecules per formula unit. Thaumasite closely resembles ettringite but carbonate radicals replace the sulphate and silica the alumina. It is often found in the outer parts of concrete affected by sulphate attack and carbonation. There are probably also intermediate types between thaumasite and ettringite. Rarely, needles and plates of secondary calcium chloro-aluminate are produced where paste is affected by external chlorides.

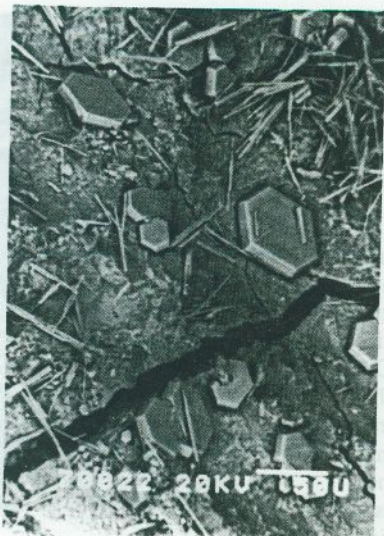


FIG. 16. Plates and needles of calcium chloro-aluminates developed in paste as a result of chloride ingress.

Setting history

In the early stages of the hydration process the alite and belite form calcium hydroxide and calcium silicate hydrate 'gel' with a calcium-to-silicon ratio of about 1.5. This early gel incorporates some of the alumina, the ferric oxide and sulphate. These phases react with sulphate so that the calcium aluminate combining with calcium sulphate produces ephemeral ettringite needles. These change to produce sulpho-aluminates of lower sulphate content as hydration proceeds. Iron may enter the sulpho-aluminates to produce solid solutions. Variation in the hydration products and timetable may occur with temperature and cement type and this brief summary over-simplifies the process. A general review is given in the Cement and Concrete Association (1976) publication *'Hydraulic Cement Pastes: their Structure and Properties'* (see also Jawal, Skalny & Young 1983).

Over the years secondary recrystallization may occur and it is extremely common to find not only the additional precipitation of calcium hydroxide but also substantial variation in the calcium silicate hydrates and the formation of abundant ettringite-like phases, often as crystals lining voids.

Portland cement paste

Most concretes contain Portland cement and water; ordinary Portland cement being much more common than the sulphate resisting or other special types such as rapid hardening Portland cement. It can be difficult

to distinguish between these various types of Portland cement in thin section; the use of reflected light on uncovered surfaces is helpful but, in general the diagnosis of cement type is best carried out with the electron microscope coupled with an energy dispersive analytical system.

Ordinary Portland cement is a carefully graded powder prepared to have a particular surface area. In modern cements the particles range up to about $100\ \mu\text{m}$ in maximum dimension but in older cements, although the surface area of the material was similar, the size range of the particles was much more varied with maximum dimensions commonly up to $0.5\ \text{mm}$ and sometimes almost twice that. Belite is generally more abundant in these older, coarser cements. The material from which the powder is prepared is generally referred to as cement clinker and some unhydrated cement particles remain visible in the concrete as 'clinker' grains.

Residual unhydrated clinker

The amount of unhydrated residual clinker is related to the original water/cement ratio of the mixture, and the conditions and duration of curing. In concretes made at normal ambient temperatures of around 20°C and where curing is limited to a few days, the amount of residual clinker is directly dependent on the original water/cement ratio. In practice it is found that if the water/cement ratio is approximately 0.61 or 0.62, the cement powder is virtually completely hydrated. At water/cement ratios of about 0.5, between 3% and 4% of the total cement paste typically consists of unhydrated material and if the water/cement ratio is as low as 0.4, 7% or 8% of the material may be unhydrated.



FIG. 17. Alkali-silicate gel which has become crystallized as a result of dehydration.

If the concrete is made at low temperatures (say, close to 0°C) the rate of hydration of the larger clinker particles is reduced and a much higher proportion of unhydrated grains can be found in the fully hardened concrete, possibly accompanied by pseudomorphed clinker. The long-term hydration of these unhydrated particles is generally very slow unless there are particularly hydrating curing regimes. If the ambient temperature is elevated to between 40° and 50°C, during curing the hydration of the cement particles is generally complete. At much higher temperatures, in addition to complete hydration, the composition of the hydrate mixture is changed substantially; for example the most obvious feature of steam cured concrete is that it develops large quantities of coarsely crystalline calcium hydroxide and often needles of ettringite.

The larger clinker particles in cement paste made with an ambient temperature of 20°C tend to become hydrated on their surface with complete recrystallization occurring in the surface zones for perhaps 10 µm or so. It is also common to find calcium hydroxide precipitated on the surfaces of these larger clinker grains and sometimes the original outlines of the larger clinker grains can be distinguished from the distribution of the surrounding coarsely crystalline calcium hydroxide. If curing conditions are appropriate or water is able to penetrate into the concrete over a long period of time, the residual unhydrated clinker particles become pseudomorphed with secondary hydrates with a resultant change in optical properties such that the particle appears to be isotropic in thin section and composed of felted microcrystallites in reflected light. The small clinker particles (<20 µm) tend to be fully converted into hydrates during the normal setting process. If moisture is available from external sources, relict unhydrated clinker particles may become progressively hydrated with shells of hydration product being formed from the external surface inwards. If wetting and drying is cyclic it may be possible to detect the number of cycles and assess the age of the concrete. This is very difficult, however, as the hydration shells are usually only two or three micrometres thick and are usually found in the outer 20 mm or so where other alteration processes such as carbonation may be predominant.

Portlandite

A major component of normal hydrated Portland cement paste is portlandite (calcium hydroxide), typically amounting to 30% of the hydrated paste although there is probably slightly more in concretes made with higher water/cement ratios. However, there are differences and the distribution and occurrence will also vary according to the initial water/cement ratio. At higher water/cement ratios the calcium hydroxide crystals become larger and more clearly defined and

are often clustered whereas at lower water/cement ratios they tend to be smaller and more uniformly distributed through the paste. In all concretes calcium hydroxide is precipitated onto the surfaces of aggregate particles. It tends to be most conspicuous on the surfaces of the siliceous fine aggregate particles but sporadically develops as thin pellicles or clusters of coarse crystals on the surface of the coarse aggregate particles. The amount of calcium hydroxide precipitated in this way is to some extent dependent on the aggregate type and siliceous aggregates such as cherts and quartz grains may accumulate relatively thick layers of calcium hydroxide whereas in carbonate rocks they are thin and impersistent. Rocks such as serpentinites also frequently develop thick haloes of calcium hydroxide which may be sufficiently large to be visible on the core surface as white shells around the aggregate particles and can be confused with the products of alkali-aggregate reaction. In general the finer the sand the greater the amount of portlandite development, but various cement replacement phases also influence the amounts and distribution of portlandite significantly. Larger PFA and slag particles are often coated with the hydroxide while rather less portlandite occurs co-existing around the fine aggregate surfaces. Silica fume appears to reduce the amount of calcium hydroxide visible in sections.

If the concrete is factory-made pre-cast material, the calcium hydroxide tends to occur in slightly smaller crystals and be much more uniformly distributed throughout the cement paste than is found for in situ concrete. In steam-cured concrete very coarse portlandite occurs which may be intergrown with ettringite or found in cracks and voids as a secondary product.



FIG. 18. Particles of fly ash in a Portland cement paste with needle-like crystals of calcium silicate hydrates linking the spheres to the hydrated gel.

Hydrated gel

The structure of the calcium silicate hydrates and aluminates and hydrated ferrite complex, usually referred to as gel, is very difficult to make out in detail with the optical microscope and indeed, in many cases, with the electron microscope. Though structure can be seen with the optical microscope, the electron microscope shows this to be composite, further detail being made out with the transmission electron microscope. A number of features are evident in thin section, often relating to particular processes of deterioration. Where moisture passes through concrete or the water/cement ratio is high, the calcium silicate hydrates tend to appear lighter in colour, more transparent and of coarser texture than paste of low hydration state. Against a dark background such material shows dark zones along cracks where the material has been recrystallized and possibly leached by the passage of moisture through the concrete. Concomitantly, ettringite or related phases such as thaumasite may be formed within the calcium silicate hydrates as spherulitic collections of needles or as dispersed needles.

The hydrated gel has a capillary porosity which is most voluminous where the water/cement ratio is highest. This is readily detected by impregnation of the paste with a fluid resin containing a fluorescent dye.

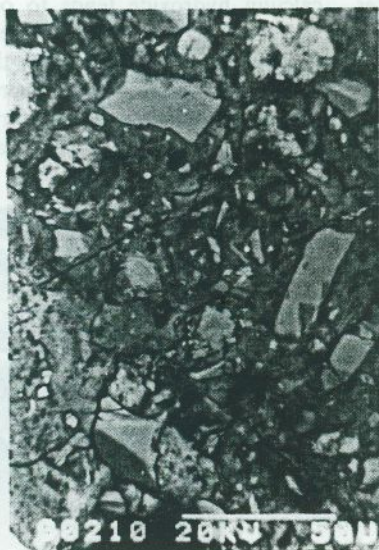


FIG. 19. Typical angular pieces of ground granulated blast furnace slag in combination with a Portland cement paste.

Slag and PFA

These two materials are dominated by silicate glasses as angular shardy pieces in the case of the slag, or spheres and ellipsoids in the case of PFA. These particles remain visible and unaffected for many years.

Both types of grain commonly have $\text{Ca}(\text{OH})_2$ on their surfaces and needles of calcium silicate hydrates frequently connect PFA spheres with the surrounding Portland cement paste.

There are no obvious chemical changes in the preserved particles which may be as small as $5\ \mu\text{m}$, or less in the case of PFA. The larger grains can be seen in thin section but it is usually not possible to assess the amount of PFA or slag without the aid of a scanning electron microscope. Some of the most robust concretes contain both slag and PFA.

Secondary changes

Moisture passing through concrete tends to leach calcium hydroxide from the hydrates and there is some evidence that this also affects the calcium silicates. Calcium hydroxide crystals which develop on aggregate surfaces may be removed from the paste in the vicinity of joints and cracks from which moisture issues and be deposited on the surface of the concrete or in the cracks, becoming visible as a white 'lime' deposition. This lime is usually built up in layers which may become carbonated immediately or very soon after their formation so that calcium carbonate (calcite) is produced. The calcium silicate hydrates within the concrete may also lose calcium into the percolating moisture so that they develop a high silica-to-calcium ratio and often form blade-like crystals with little cementitious value. This process occurs very rapidly below ground if tidal water enters and leaves concrete on a regular basis and where run-off from bridge decks or other surfaces can penetrate through concrete or along cracks or joints. In this situation the aluminates are frequently converted into ettringite which may become a major component of the cement paste. It is often precipitated in voids and cracks and ultimately leads to substantial weakening of the concrete. If there is 5% of gypsum in the original cement some 15% of ettringite can be produced (by weight of cement or 20% by volume) representing some 8% by volume of the whole cement paste.

Portlandite is also deposited in voids and cracks through secondary change and is not infrequently found intergrown with ettringite (the term is used here for solid solutions including iron-bearing members). It is also found that various intermediate compounds are formed which have lower SO_3 than stoichiometric ettringite. Silica can also be included in the solid solutions. Where the needle-like phases occur in carbonated paste thaumasite may be the predominant phase. Thaumasite has also been found in paste damaged by water penetration and here possibly the water contains dissolved CO_2 . Ettringite also forms in alkali-silicate gel (produced by alkali-aggregate reaction) through reaction between the gel and cement paste. It may sometimes be a primary constituent of the gel but

more often replaces the gel. Complete replacement can occur locally.

The importance of moisture penetrating through concrete is frequently underestimated as a cause of damage to the concrete. It can be an extremely deleterious process and, coupled with damage due to freeze/thaw processes, can produce rapid disintegration of surface concrete, with crack development reminiscent of that produced by alkali-aggregate reaction.

A high moisture content can be generated by condensation in the surface layer of concrete which has been coated with tiles or metal. The effect of the condensation is again to produce abundant ettringite with concomitant expansion and cracking.

Carbonation

The paste of the external surface of concrete is usually more strongly hydrated than that of the heart of the concrete. It reacts with atmospheric carbon dioxide to produce vaterite and calcite as very small crystallites (Figs 10, 12 & 20). It is sometimes suggested that only the calcium hydroxide becomes converted into calcite, but in practice it is usual to find that the calcium silicates alter to carbonate as readily as the hydroxide. Even the larger residual unhydrated clinker particles

become altered in the carbonation process, the effect on the silicates and aluminates being to liberate gel-like phases rich in alumina, silica and iron which form an interstitial phase to the carbonate. In thin section it appears that the outer part of the concrete is converted into a layer of very fine-grained calcium carbonate, the depths of both complete and partial penetration of carbonation being readily detectable. Usually carbonation penetrates to a depth of a millimetre or so along a general front but more extensively along aggregate surfaces or cracks; fine cracks extending from the surface frequently allow carbonation to penetrate directly to the reinforcement.

The extent to which carbonation penetrates into concrete depends on the quality of compaction and the microporosity of the hydrated binder. The degree of compaction is the more important parameter and is most easily assessed by measuring the total amount of void. In cores taken from concrete structures rather than experimental concretes the depth of penetration of carbonation is most closely related to the total void content of the concrete, particularly that in the outer part, correlation with the water/cement ratio of the material being much poorer. In experimental concretes made with the same degree of compaction and of the same aggregate types, there is substantially increased

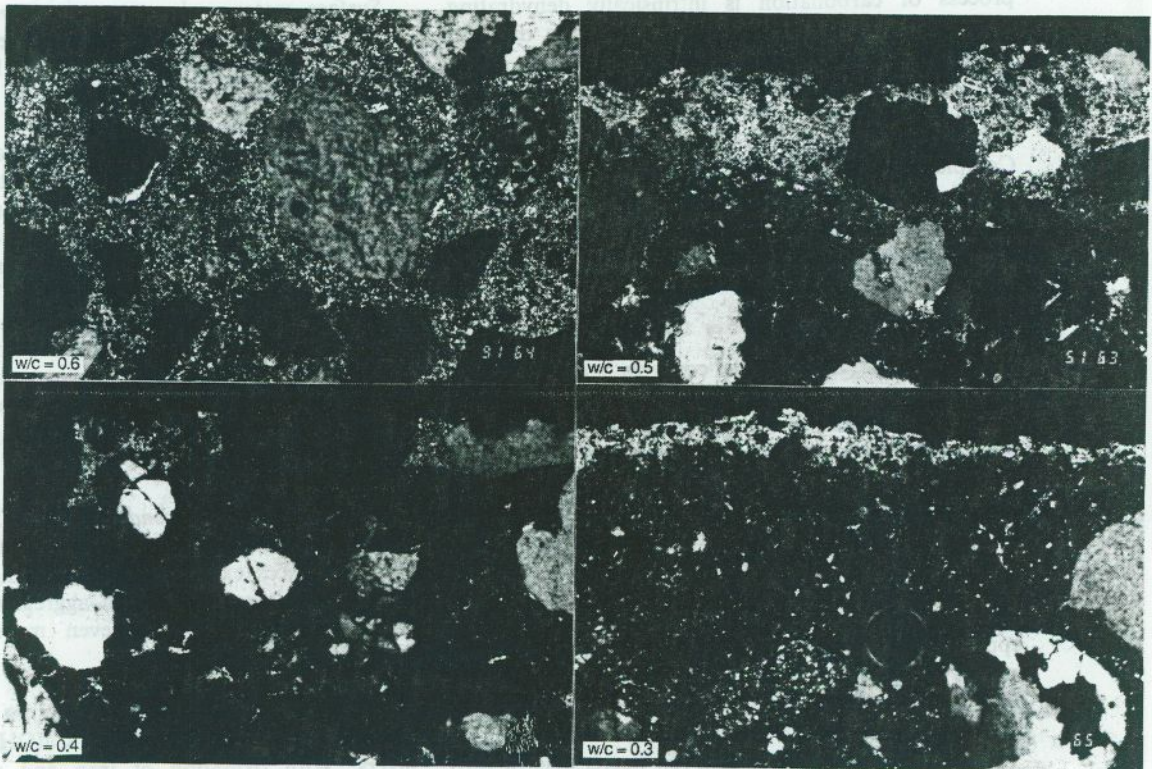


FIG. 20. This photograph illustrates the relationship between the depth of carbonation and the water/cement ratio for standard concretes. The carbonated zone occurs along the top of each thin section and appears light in tone. The photographs were obtained when the concrete was approximately two months old. Width of photograph = 0.7 mm.

carbonation with increased water/cement ratio. At a water/cement ratio of 0.38 the carbonation of test cubes is only a fraction of a millimetre in several months whereas at a ratio of approximately 0.6 the penetration of carbonation can extend to 3 or 4 mm in only a few days. Cores taken from relatively low-grade concrete have shown extensive carbonation. Experiments to monitor the rate of carbonation from the freshly sawn surfaces of relatively low-grade concrete with new surfaces being created from time to time can show carbonation penetrated from the sawn core surface into the uncarbonated paste at the rate of several millimetres in a week if the concrete was poorly compacted. In the worst cases the alteration extended throughout the full length of the core sample. Where the cement has a low iron content the rate of carbonation penetration is greatly enhanced and apparently sound concrete made with white cement, for example, can sometimes be extremely deeply carbonated despite its apparently normal structure.

The process of carbonation of unhydrated or pseudo-morphed residual clinker particles can lead to the development of very high silica concentrations in the locations of the original alite and belite particles, the carbonation leaving the structure of the clinker particle apparently unchanged but producing profound chemical alteration of the silicates and aluminates. As the process of carbonation is intrinsically dehydrating, moisture is lost from the concrete and it is therefore essential to check samples for carbonation before chemical analyses are carried out for determination of cement content or water/cement ratio by the conventional BS 1881: Part 124: 1988, chemical procedures. Complete carbonation may be detected using phenolphthalein on the concrete core surface but partial carbonation is less easily identified by chemical tests and is best seen in thin section.

Effects of setting at low temperatures

If the surface temperature of concrete is about 16°C it is usual to remove props to slabs about 10 days after placement. If the placement temperature of 0°C is maintained, however, the props may need to remain for some 25 days as the lower temperature retards strength gain and hydration reactions. Examination of concrete placed at 0°C shows that the paste contains a much larger number of unhydrated clinker particles than are normally present at a given water/cement ratio. From the residual clinker the material may appear to have a water/cement ratio of about 0.4 when in fact it was made with a ratio 0.6 or above. Conversely the cement gel is more porous than usual implying a high water/cement ratio.

If the temperature drops to a few degrees below zero for a sufficient length of time, small amounts of water in capillaries freeze, forcing water into air voids and

leading to the development of a zone peripheral to the void which has more remnant clinker than the remainder of the paste. Conversely calcium hydroxide may develop in the voids or, more usually, on the surface of the void and in the immediately surrounding paste. Differences in coefficient of thermal expansion between aggregate and paste coupled with the forces generated by freezing water in capillaries can lead to the development of microfractures on aggregate surfaces. In addition shrinkage of the paste during the cooling process before ice formation commences will also generate stresses between paste and aggregate. Using petrographic procedures to identify this process and the other features associated with high temperatures discussed above it is often possible to determine the conditions under which the concrete set.

Principal deleterious changes in binder

The main causes of deterioration of paste include the following.

Carbonation. This causes slight shrinkage but may increase strength. Deeper penetration of carbonation can lead to reinforcement corrosion and consequent cracking of the paste.

Surface water and water penetrating along joints. This leads to solution of the paste especially if the water is acidified by solution of CO₂. Portlandite may be removed at an early stage from the surfaces of aggregate particles. The hydroxide can also be precipitated from this solution into cracks and possibly in voids near the cracks. When the solution issues onto the concrete surface, layers of calcium-rich material are deposited. There may also be stalactites and stalagmites beneath horizontal surfaces and curtains of 'lime' on vertical surfaces near cracks. This material is usually calcite and may be deposited as such or possibly may form as Ca(OH)₂ which is rapidly converted into CaCO₃. The removal of the calcium from the cement paste leads to progressive alteration of the calcium silicate hydrates with loss of strength and cementitious value.

Seepage of water or condensation. This leads to the formation of significant amounts of ettringite and in some instances expansion and cracking. The process can be as damaging as alkali-aggregate reaction with numerous fine cracks or even macrocracks being generated.

Heating of hardened concrete e.g. fire damage. This causes dehydration with loss of Ca(OH)₂ in the outer layers. With oxidation of iron and manganese the paste becomes brownish or pink and certain aggregate types may also become discoloured. Microcracking

and fine cracking are generated parallel to the thermal front and in the paste surrounding reinforcement (Concrete Society Report No. 15). It is often possible to detect the depth to particular isotherms by petrographic observation, particularly using colour changes in the paste and aggregate. As the fabric of the paste is also changed once the temperature exceeds approximately 100°C the thermal profile can sometimes be deduced.

Overheating. Overheating of the paste in the wet condition leads to abundant portlandite and ettringite development.

Undercooling. This leads to microcracking on aggregate surfaces, shrinkage, excessive porosity of the hydrates and enhanced amounts of residual unhydrated and pseudomorphed clinker.

External sulphates. In solution these cause replacement of calcium hydroxide and the aluminates and some silicates of the cement paste. Gypsum and ettringite are formed and the paste becomes cracked, friable, weak and porous (see, e.g. BRE Digest 174). The rate and depth of alteration depend mainly on the degree of compaction of the concrete and its microporosity, some porous honeycombed materials being altered throughout within months or a few years while dense high quality concrete might be altered for only a few millimetres on the surfaces over many years.

Sea water damage. This relates mainly to penetration of magnesium and chloride ions into the paste, producing pinkish zones a few millimetres from the surface, mainly of extremely weak magnesium silicate hydrates. The surface layers tend to spall, allowing further penetration of the deleterious ions. Penetration of chloride produces calcium chloro-aluminates and some chloride salts may also be precipitated into voids and capillaries. With carbonation the chloride ions are removed from the paste and may be driven deeper into the concrete during progressive carbonation with a concentration maximum being produced that may correspond with the location of the reinforcement. The sodium released in these processes may enter the pore fluid and enhance the potential for alkali-aggregate reactions so that coastal examples of severe ASR are not uncommon. Sea water included in cement paste changes the hydration reactions with chloro-aluminates becoming important and alkalis being released into the pore fluid. In thin sections, clearly defined changes indicate that less of the original cement powder becomes hydrated and there is less pseudomorphous hydration of the larger clinker grains but the tendency to development of shrinkage microcracking in the more porous hydrated gel is enhanced.

Road salts. Similar effects are produced to those of sea water except that damage from magnesium is not marked. There is an enhanced potential for ASR in surface layers of the concrete and the tendency for solution of $\text{Ca}(\text{OH})_2$ may also be accentuated with the formation of large amounts of calcite on external surfaces. Sulphates in the paste may become recrystallized with the formation of ettringite-like phases but evidence of sulphate attack from external sources is generally lacking. The principal mode of deterioration is reinforcement corrosion as a result of the chloride penetration.

Cracking in concrete

A principal mode of deterioration is through the development of cracks of various sizes. All concrete is cracked to some degree, with cracks being associated with the location of reinforcement or on aggregate surfaces, or near voids as a result of shrinkage or differential thermal effects even in concrete of very good quality. The most obvious deleterious cracks produced by non-structural processes are summarized in the Concrete Society Report No 22. Cracks of all types can be studied using the various microscopic methods and it may be possible for the origin of both structural and non-structural cracks to be established and their nature studied. In making the microscopic examination the cracks should be examined in transverse sections, using both thin sections and polished surfaces, and by direct examination of crack surfaces. The latter can be particularly important in establishing the age and nature of macrocracking.

Problems exist with respect to the nomenclature of crack systems as seen in samples taken from concrete structures, particularly concerning the dimensions of cracks. It is common for example to refer to the cracks generated by alkali-aggregate reaction as microcracks, despite the fact that the cracks are often readily visible with the naked eye in cores. Cracks can conveniently be allocated to four size ranges: cryptocracks, microcracks, fine cracks and macrocracks. Microcracks are visible only with the optical microscope, either in reflected light looking at polished surfaces or in transmitted light using thin sections. Fine cracks can just about be made out with the unaided eye, or with a hand lens. They are often detected by their effects on the sawn surfaces of cores or the occurrence of a deposit within the crack such as gel, calcium hydroxide or ettringite. Macrocracks are readily visible with the naked eye and may have substantial infill deposits. Cracks which are visible only with the electron microscope are referred to as cryptocracks.

Cracks of all sizes may exist with no significant opening or gap. The opening of the cracks may occur

on release of constraint when the core is extracted. In many cases there may be extremely fine cracks which may only be detected by staining procedures.

Typically microcracks have openings of less than about $10\ \mu\text{m}$ and can be followed in thin sections for between a millimetre and a few centimetres. Fine cracks may have openings of up to $100\ \mu\text{m}$ and may extend for 200 to 300 mm. Macrocracks commonly have openings of around 0.2 mm but range up to very large open cracks which often exceed several millimetres and extend for several metres through the concrete.



FIG. 21. This photograph shows a fine crack across the centre. The paste on either side of the crack has been recrystallized as a result of the passage of moisture along the crack. Width of photograph = 0.5 mm.

Diagnosis of the origin of crack types can be difficult and most of the following information will be required:

- form, distribution and size of cracking;
- crystal or gel lining or infill material;
- relationship to aggregate;
- relationship to concrete configuration;
- details of the adjacent paste;
- details of contaminants occurring on crack surfaces;
- details of efflorescence or exudation from crack openings;

Microcracks

Microcracks (Fig. 23) are a normal feature of concrete and do not necessarily indicate deterioration. Experi-

ence shows that microcrack frequency varies with water/cement ratio, the effects of temperature and deleterious processes as well as the mass and dimensions of the concrete. Stress release is of less importance than for other crack sizes. Frequency is measured by counting the microcracks over specified areas (e.g. each cm^2 of a thin section) or along mutually orthogonal lines of traverse or mapping of selected areas of the section. Typical values of crack frequency in cracks/metre measured on thin sections or polished plates are given in Table 2.

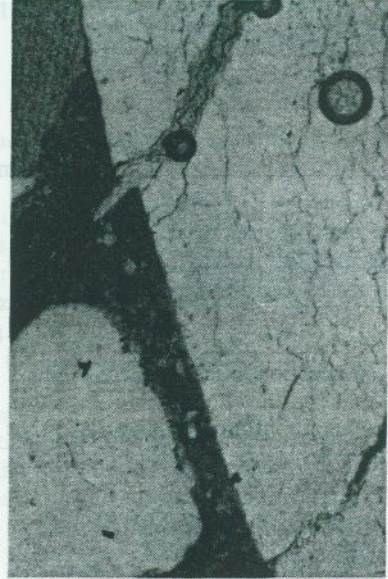


FIG. 22. This photograph shows to the right a metaquartzite particle containing various cracks. Towards the top of the photograph one of the cracks is open and contains alkali-silicate gel. Along the crack surface is a zone of finely recrystallized or granulated quartz which appears to be the reactive component of the quartzite. Width of photograph = 0.5 mm.

Microcracks are most easily seen on polished surfaces which have been impregnated using a soluble dye particularly a fluorescent dye. Microcracks may not be visible in thin section unless a dye is used in the impregnated resin. Care is obviously needed to ensure that the cracks are not induced in cutting and polishing and that materials are not removed from the sections during the preparation. The largest number of microcracks per metre of traverse is of the order of 1500, usually following the surface of fine aggregate and bridging the gaps between nearest fine aggregate particles. This type of cracking probably relates to shrinkage but can be substantially enhanced if there are temperature oscillations or the concrete is subject to low temperatures on placement; the development of ice within the paste being one likely cause. The orientation of microcracks oblique to the plane of the

TABLE 2. Typical values of crack frequency in cracks/metre

Water/cement ratio	Sound concrete	Concrete showing slight signs of deterioration such as slight AAR or shrinkage cracking	Concrete showing obvious deterioration	Concrete exhibiting exceptionally high frequency of microcracking short of disintegration of the concrete
0.35-0.45	0-20	20-60	60-200	> 200
0.45-0.55	0-40	40-120	120-400	> 400
0.55-0.65	0-60	60-200	200-600	> 600

thin section tends to make them appear more open than they are. This effect can be detected by observing any change in the position of the crack with change in focus. Microcracks generated by shrinkage tend to meet at triple junctions in the paste, to radiate from aggregate surfaces, run along parts of aggregate surfaces and initiate on voids. Sometimes three or four cracks radiate from a single small void. Microcracks also tend to occur in seams of paste which have high levels of portlandite, are coarser in texture and of different colour from the remainder of the paste. These are probably generated during the setting reactions and may reflect the development of an uneven distribution of water where the water/cement ratio is moderate to high.

Fine cracks

Fine cracks (Figs 21 & 22) occur in the surface zone of concrete as a result of crazing or minor shrinkage, or sometimes as a result of thermal damage, but are most commonly due to processes of expansion within the concrete, including alkali-silica reaction, alkali-silicate reaction or alkali-carbonate reaction. They may also be a consequence of the development of ettringite in cracks produced by the passage of water through concrete or sulphate attack of external origin. Occasionally fine cracking is seen in association with reinforcement, when they may be infilled with reinforcement corrosion product. As with microcracks they can be recorded by crack mapping or counting. Relationships with aggregate types are assessed by mapping.

The frequency of occurrence of cracks within a particular volume of concrete is inversely proportional to the crack size, hence the number of fine cracks encountered is substantially less for a given level of damage than is the case with microcracking. A frequency of 100 fine cracks per metre would represent extremely severe deterioration. The size will depend on the process of deterioration. In the case of alkali-aggregate reactions (Fig. 22), for example, the smaller

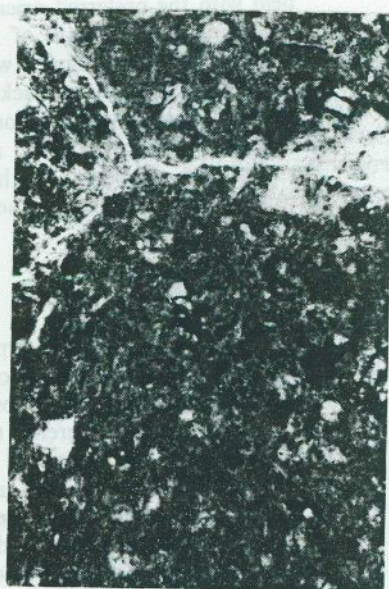


FIG. 23. Portland cement paste containing fine shrinkage microcracks which form a triple junction pattern. Width of photograph = 0.5 mm.

the reactive aggregate particles the finer and shorter are these cracks. Alkali-aggregate reaction in structures as distinct from experimental concrete tends to be most damaging when the aggregate is several millimetres or more in diameter. In the case of alkali-silicate reactions, the greatest size range may produce the main cracks which may be large and penetrative, but relatively widely spaced compared with cracks generated by alkali-silica reaction.

The distribution of the cracks is governed by constraints of the structure, including the form of the structural unit, its size and the position of the cracks with respect to the external surface. In real structures the cracks generated by alkali-aggregate reaction, for example, vary from the surface inwards; cracks in the outer 60 mm or so being mostly at right angles to the external surface, large and spaced out. Those within

the heart of the concrete tend to have random orientation, although this may be influenced to some extent by the location of reinforcement. There is often an interface between these two sets of cracks in which the majority of cracks are sub-parallel to the external surface. This zone may occur at a depth of from perhaps 60 to 120 mm from the external surface. Similar patterns can be identified wherever the damage is due to expansive processes operating in the heart of the concrete. They would be expected where the paste is altered with the production of large amounts of ettringite, where abundant sulphides react with aluminous phases to produce ettringite or where fairly small amounts of gypsum are present within the aggregate.

In fine cracks the crystals sometimes grow in a stress field with the preferred orientation of elongation often indicating the direction of maximum extension. This often occurs, for example, where ettringite develops in the cracks. Similarly, crack orientation and opening may reflect the overall distortion of the structural unit and there can be value in mapping fracture patterns and degree of opening in three dimensions using thin sections and polished surfaces as well as field observations.

Macrocracks

The description and interpretation of macrocracks from microscopic examination can be difficult because the amount of the crack observed in the core sample may be small and reference to data obtained from the structure will be required. However, the field data itself may be enhanced by information obtained from examination of crack surfaces as well as the relationships between the crack and aggregate particles, and between the main crack and co-existing microcracks and fine cracks. Of particular importance is the occurrence of carbonation on the surface of such cracks. This may penetrate very deeply into concrete and in the case of concrete cracked by alkali-aggregate reaction, frequently reaches the reinforcement. The surface cracks generated by the internal expansive forces tend to be open at the surface and, even though they may be coated with gel, are nevertheless carbonated for considerable depth. Examples have been found where carbonation has penetrated for 150 mm or so into the concrete along such cracks. In addition surface cracks induced by alkali-aggregate reaction often penetrate directly to reinforcement, their position being related to the location of the reinforcement. Reinforcement corrosion is therefore likely to develop after relatively minor alkali-aggregate reaction. Damage due to the passage of moisture through concrete or freeze/thaw processes may also occur after development of cracks due to the alkali-aggregate reaction. Both fine cracking and macrocracking may therefore be due to several causes in any one structural member.

Quantitative analysis

Semi-quantitative analysis using petrographic procedures can be carried out using rapid routine techniques. More elaborate but more precise procedures can be applied to give more fully quantitative results. In routine work on a substantial batch of cores, for example, it may be sufficient to determine the compositions of the samples on single polished plates representing areas of about 70 cm². Such observations are useful if the maximum aggregate size is 20 mm or less. Careful point count analysis can provide an indication of the volume percentage of aggregate and paste with a standard error of approximately 1%. Use of combined data from several cores may then give quantitative data on the larger mass of concrete. If three similar polished surfaces from a single core are examined the standard error is reduced to approximately 0.6%. Significant differences between the slices may also be observed and the composition of the individual sample can be calculated.

The various quantitative procedures discussed here are:

- (i) water/cement ratio;
- (ii) cement content;
- (iii) aggregate content and composition;
- (iv) void content and parameters;
- (v) cement type;
- (vi) granulated slag/Portland cement ratio;
- (vii) PFA/Portland cement ratio.

Water/cement ratio (Figs 24 & 25)

Perhaps the most important and difficult measurement is that of the original or apparent water/cement ratio of the concrete. BS1881: Part 124: 1988 provides details of the chemical methods used to determine, separately, cement and water content. The method used for determination of cement content provides reproducibility at the 95% confidence level of approximately 60 kg/m³ where the cement content may be in the range 240 to 425 kg/m³ (BS1881: Part 124: 1988); the repeatability is about 40 kg/m³. The amount of water will normally be approximately half that of the cement (by weight) but no standard error is given for this determination. BS 1881 specifies that the method is only suitable for concrete which is sound and has suffered no chemical alteration. The complexity of the method is such that it is doubtful if the results for the water content can be more precise than those for the cement content. Since the water/cement ratio is obtained from these two measurements, the standard error is very large and for a single determination is unlikely to be better than ± 0.08 at the 95% confidence level at a water/cement ratio of 0.5.



FIG. 24. Polished surface of concrete which is coated with gel which appears white. The gel issues onto the polished surface through fine cracks which occur on the aggregate surfaces. To the bottom and right of the photograph white gel can be seen along the aggregate surfaces in the fine cracks. Width of photograph = 60 mm.

It is slightly misleading to describe this determination as a measurement of the water/cement ratio, equating it with the original free water/cement ratio. The result obtained relates to the hardened concrete and may be affected by a number of factors connected with the history of the concrete. A distinction should be made between water/cement ratio as a mix design criterion, determined or recorded for fresh concrete and the *apparent* water/cement ratio obtained from analysis of hardened concrete.

The chemical determination of cement content requires the measurement of the weight percentage of CaO and SiO₂ for the concrete and the separate aggregate. If the calcium content of the aggregate is high, the calcium method is vitiated and if the aggregate contains soluble silica, the silica method is unsatisfactory. The author recently examined a concrete in which the aggregate was largely soluble in dilute acid and had a composition almost identical with that of Portland cement. Consequently the chemical method is not of general application without recourse to numerous corrections and frequently the only aggregate (or cement) available for analysis is that in the sample being analysed. As it is then necessary to assume a composition for the aggregate and the cement it is always advantageous to study the concrete in thin section before undertaking the chemical tests.

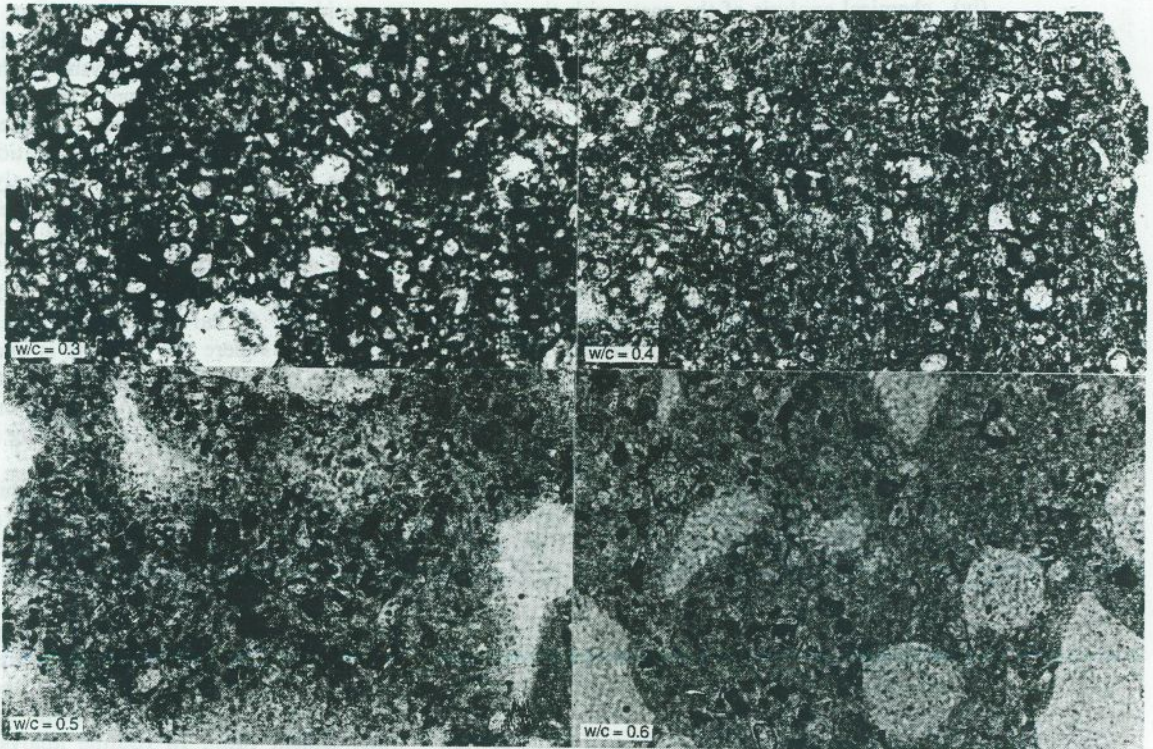


FIG. 25. Photomicrographs of thin sections of concrete having differing water/cement ratios. Decrease in the amount of residual unhydrated clinker and increase in the microporosity of the paste with increasing water/cement ratio is evident. Width of photograph = 0.7 mm.

The determination of the water content by the standard method also requires data on the water content of the aggregate. If it contains a minor amount of clay mineral then a significant contribution may be obtained from the sheet silicates. Many rocks have 2 or 3% of combined water while typical values for the cement paste are equivalent to water contents of only 6 or 7% in the concrete. Problems can arise with a number of rocks due to hydrothermal alteration. For example the presence of serpentine minerals adds substantially to the determined water content. Problems of this kind can be evaluated and avoided by a proper petrographic analysis before chemical analysis is attempted.

There are several approaches to the direct determination of apparent water/cement ratio by petrographic observation, most of which rely on the assumption that the concrete was cured at normal temperatures and in a normal manner. They include:

- (i) assessment of the capillary porosity of the hydrated paste using impregnation with fluorescent resin;
- (ii) determination of the amount of unhydrated clinker by point counting;
- (iii) determination of the number of residual clinker particles per millimetre traverse of paste;
- (iv) chemical analysis of the paste with the electron microprobe;
- (v) determination of the weight of paste by assessment of the aggregate density and measurement of the concrete density.

Method (i) is widely practised, particularly in Scandinavia. Results may show a considerable scatter and occasional wild values are obtained. This may reflect the difficulty of ensuring that the concrete is made under standard conditions and that penetration of the fluorescent dye during sample preparation is uniform.

Method (ii) (Ravenscroft 1982) requires a detailed point count analysis of the cement paste. It is time consuming and requires very careful preparation of the sample which is examined in reflected light, with etching as necessary to allow recognition of the unhydrated clinker particles. In addition because the volume proportions of fine aggregate and clinker in the hardened concrete are compared with those of the original mix proportions, some knowledge of the intended mix proportions is required.

Method (iii) is that preferred by the writer and is based on comparisons with standard concretes made with particular water/cement ratios and a range of different aggregate types and proportions. The method is very simple using direct comparison of fields of view of standard thin sections. It follows from the relationship that the cement content rises as the water/cement ratio falls. It can be quantified by measuring the

number of unhydrated clinker particles encountered on a traverse of the paste. In routine work it is usually necessary to traverse at least 120 mm of paste. At a water/cement ratio of about 0.6, some five or six particles will be encountered in the traverse while at a ratio of 0.4 some 60 to 70 particles would be anticipated. Linear calibration is obtained with data from standards (Fig. 26). Although it may appear crude, in fact this method is very robust and gives very satisfactory results; experience indicates a standard error of ± 0.02 . The most important sources of error are the incorrect identification of residual clinker grains and of cement type and those practising the method need to establish their own wide range of standard materials and study them carefully in order to obtain the maximum benefit.

Method (iv) depends upon the chemical analysis of the Portland cement paste with the electron microprobe. A sample of the concrete is prepared with two pieces each about 20 mm square containing as little coarse aggregate as possible. These are mounted in resin and polished using diamond dust to give a high quality finish before analysis using the EDS attached to the electron microscope. The equipment must be standardized using standard cement paste so that analytical accuracy is assured. Analyses are then made of the hydrated paste in the unknowns, taking care to avoid dust or aggregate particles. Because of the chemical separations that take place in the hydration reactions, the chemical analysis of the cement paste varies with the water/cement ratio; for example the SiO_2/CaO ratio of representative areas of paste increases with water/cement ratio. Ratios of oxides can then be used in conjunction with analyses of standard concretes made with given water/cement ratios to calculate the apparent water/cement ratio. The method has the advantage that differences between the results obtained using particular ratios can indicate that deterioration due to carbonation or other processes has taken place. Where the concrete is unaffected by such processes, the standard error attached to the method is considered to be ± 0.02 . Again the method is dependent on the concrete under test being made under the same conditions as the standards.

Method (v) is indirect and determines the volume percentages of the paste and various aggregate types. The density of the concrete is measured after vacuum saturation in water by weighing in water. The density of the aggregate components is assessed either from the literature or by direct measurement. The weight of the paste can then be determined directly. This leads to the establishment of a value for the density of the paste which is directly dependent on the apparent water/cement ratio. In routine analysis, the methods based on clinker grain counting and on density determination are both carried out. The quality of the results can then be judged by the correspondence of

results obtained by the two methods. Where further confirmation is called for these two methods are combined with that based on the electron microprobe microanalysis.

One advantage of petrographic methods for the evaluation of water/cement ratio and concrete composition is that they can be applied over relatively small areas. Use of the electron microprobe or unhydrated clinker grain counting for example can be adapted to measure gradients of water/cement ratio from the surface of concrete inwards. The outer 20 mm to 50 mm or so of concrete usually has a higher water/cement ratio than the main mass of the material. In some kinds of concrete placement, additional cement is added to the external surface reducing the water/cement ratio and increasing the clinker count. The change in hydration state of the Portland cement paste from the surface inwards may relate to bleeding as water migrates towards and onto the external surface or to rehydration during finishing. This can also be observed using petrographic techniques.

Cement content

Petrographic methods can also be used for the determination of cement content in a rapid and repeatable manner. Point counting on polished surfaces or large thin sections measures the total amount of binder with an error of less than 2%. As the volume of paste is determined by the amount of the original cement powder and the quantity of water employed, in volume terms the percentage of paste gives a direct measure of water plus cement. If the apparent water/cement ratio can be determined, the paste content then gives a direct measure of both the apparent cement and apparent water content of the mixture.

With the establishment of the apparent water/cement ratio and the measured paste content by volume, the cement content can be determined from

$$C = V/(W/C + 1/D)$$

where C is the cement content in kg/m^3 , V the volume of paste, W/C is the apparent water/cement ratio, and D is the density of the cement. The water content in kg/m^3 is then found from the water/cement ratio. This gives the actual composition of the concrete which may differ from that specified because of the presence of voids. Some correction may therefore be required to allow for the void content if the designed mix proportions are to be matched.

In point count analysis to determine the volume percentage of paste it is important that a sufficiently large area is covered, the number of points counted being less significant than the size of the area covered. Sometimes it may be more accurate to determine the ratio of fine aggregate to paste and of coarse aggregate to fine aggregate. ASTM C-457 gives tables indicating the area to be covered and the number of points to be obtained for particular aggregate sizes. The spacing of points is chosen according to the particle size of the materials, but is usually approximately 2 mm between both the points and the rows of points. If the procedures are properly carried out and care taken in the counting, the method gives results which are at least as good as those obtained by the chemical procedure and experience suggests are usually a lot better. The method also has the advantage that it can be used where the conventional technique is inappropriate; it being possible, for example, to determine the paste content of carbonated concrete providing islands of uncarbonated material are available. A further advantage is that the method can be repeated if necessary since the samples are not destroyed. As an example, analyses were performed on three separate cores taken from a single large mass of concrete containing a crushed limestone aggregate which was also siliceous. The concrete was reported to have been made with a water/cement ratio of 0.50 and a cement content of 330 kg/m^3 (Table 3).

The paste content of normal concrete has a very limited range. If it exceeds 35% the material will either have a very high cement content or high workability whilst with less than 25% paste it can be difficult to compact unless the water/cement ratio is high.

TABLE 3. Analyses of three separate cores taken from a single large mass of concrete

	Analysis 1 (kg/m^3)	Analysis 2 (kg/m^3)	Analysis 3 (kg/m^3)	Mean (kg/m^3)
Coarse aggregate	1304	1327	1354	1328
Fine aggregate	586	569	566	574
Cement	340	331	314	328
Water	177	161	166	168
Total	2407	2388	2400	2398
Measured density	2399	2401	2401	2400
Water/cement ratio	0.52	0.49	0.53	0.51
Aggregate/cement ratio	5.60	5.70	6.10	5.80

TABLE 4. Illustrative values for concrete compositions

Volume % of paste	w/c ratio	Water (kg/m ³)	Cement (kg/m ³)	Aggregate (kg/m ³)	Total (kg/m ³)
40	0.4	223	557	1560	2340 *
35	0.4	195	487	1690	2372
30	0.4	167	418	1820	2405
25	0.4	139	348	1950	2437 *
40	0.5	244	489	1560	2293 *
35	0.5	209	428	1690	2362
30	0.5	183	367	1820	2396
25	0.5	153	306	1950	2409
40	0.6	261	435	1560	2256 *
35	0.6	228	381	1690	2299
30	0.6	196	327	1820	2343
25	0.6	163	272	1950	2385

* In practice these are extreme compositions unlikely to be encountered because the water content is either too high or too low. The density of the aggregate is taken to be 2600 kg/m³ and the cement 3140 kg/m³.

Illustrative values for concrete compositions at given water/cement ratios and paste contents are as given in Table 4.

The advantages of the petrographic methods of determination of concrete composition over the chemical method are summarized as follows:

- the petrographic methods are independent of the chemical and mineralogical composition of the aggregate;
- providing the concrete was made under normal conditions, the standard error is less than that for the chemical method;
- it may be possible to identify whether concrete was placed or cured in other than normal conditions;
- the effects of secondary alteration can be observed and need not affect the result;
- the measurements can be repeated fairly rapidly and the prepared samples are not consumed;
- the methods can be applied to cracked or damaged concrete.

If the BS chemical method is to be carried out the petrographic method gives guidance on the selection of the appropriate chemical techniques.

Determination of aggregate composition

The point count method allows direct determination of the volume proportions of the various types of aggregate. The composition of fine aggregate is best determined on the thin section using point counting with the points being approximately 1 mm apart. If grains

are also counted on lines of traverse the aggregate spacing, mean particle size, and specific surface of the fine aggregate can be established (see ASTM C-457). The bulk density of the fine aggregate can be obtained from the volume proportions of the individual constituents and the library of information on rock densities.

The composition of the coarse aggregate is determined on polished plates using a counting strategy with point spacings between 2 and 5 mm depending on the aggregate size. The bulk density of the coarse aggregate is calculated as for the fine aggregate except that account has to be taken of the intra-particle variability of the rock. It is often useful to determine the volume proportions of a particular lithology, even though that may be only a component of the individual aggregate particles. For example, the amounts of secondary calcite or calcareous fossils or interstratified limestone may be determined. This would be useful in the calculation of the density of the aggregate and for correction of the determination of cement content by the chemical method as well as evaluating the potential for deterioration through aggregate/paste reactions or the possibility of continued reaction. The pessimum effect (French 1980) is well known and the approach to the pessimum value may be determined by the volumetric analysis.

Void content

Air voids in concrete typically range from a few micrometres to several millimetres. Voids less than 1 mm in diameter are often referred to as entrained air voids and those greater than 1 mm as entrapped air voids.

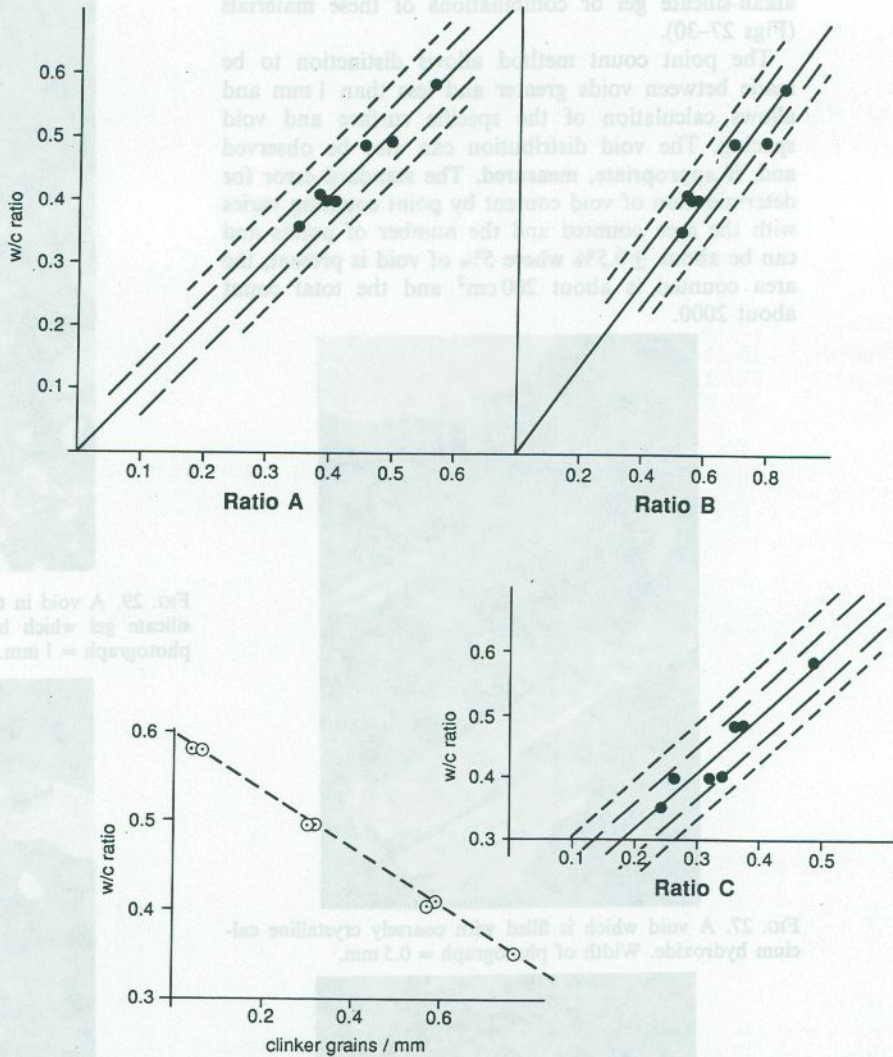


FIG. 26. Determination of the apparent water/cement ratio. These diagrams are based on data obtained from standard concretes. The parallel lines represent the errors to be expected at 1 and 2 standard deviations for the chemical methods given in BS 1881. The w/c ratio is the free water to cement ratio of the standard concretes. Ratio A = SiO_2/CaO of the bulk hydrated paste, Ratio B = $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MgO})/\text{CaO}$ for the bulk paste, and Ratio C = $(100 - T)/T$ where T is the analytical total.

Air deliberately entrained may form some 4 to 5% of the concrete by volume with a further 1% or so of larger voids being regarded as entrapped air. Normal concrete with no deliberately entrained air nevertheless has a significant proportion of voids less than 1 mm in diameter. Concrete which is very well compacted typically has some 0.5% by volume of small air voids, similar to that in well made cubes. Much concrete has around 1 to 1.5% of voidage, but in cases of honeycombing it can locally range up to as much as 30%. Excess voidage is that present over and above the percentage found in the same concrete which has been as fully compacted as is normally possible. The excess

voidage is assessed by (i) comparison with standards or standard photographs (Concrete Society Technical Report No. 11); (ii) by measurements of the test cube density and actual density and (iii) by point counting using the methods given in ASTM C-457. Method (iii) is far more reliable than the others, (i) being very approximate while (ii) depends on knowledge of the comparable cube density which may not be available. There may also be doubt as to the amount of void filled with water in the two density measurements.

Voids often provide useful information on the quality of concrete. They may contain various secondary phases such as ettringite, thaumasite, portlandite or

alkali-silicate gel or combinations of these materials (Figs 27–30).

The point count method allows distinction to be made between voids greater and less than 1 mm and allows calculation of the specific surface and void spacing. The void distribution can also be observed and, if appropriate, measured. The standard error for determination of void content by point counting varies with the area counted and the number of points and can be about $\pm 0.5\%$ where 5% of void is present, the area counted is about 200 cm^2 and the total count about 2000.



FIG. 27. A void which is filled with coarsely crystalline calcium hydroxide. Width of photograph = 0.5 mm.



FIG. 28. A typical view of Portland cement paste exhibiting air entrainment. Width of photograph = 20 mm.



FIG. 29. A void in the lower part which is lined with alkali-silicate gel which has been deposited in layers. Width of photograph = 1 mm.



FIG. 30. A void which is infilled with needles and blade-like crystals of calcium hydroxide. Width of photograph = 0.5 mm.

Cement type

A method is described for the determination of cement type in BS 1881: Part 124: 1988 which is based on optical microscopy. The sample is mounted, polished and etched to allow diagnosis of the C3A content of the cement clinker. At least 20 large clinker particles must be examined and the proportion of C3A in the

interstitial matrix phase determined. With use of the electron microscope, the matrix phases can often be analysed with the EDS system. Sometimes the matrix material is in zones which are too narrow to allow a reliable analysis but nevertheless the ratio of C3A to C4AF in the matrix phase can be calculated using the Bogue normative process. Further data can also be obtained on the composition of the paste by analysing areas. It is not normally considered good practice to measure the compositions of areas with the EDS system on the electron microscope but by standardizing the method using concretes prepared from standard cements it is possible to obtain satisfactory analyses for areas of the paste. Care must be taken to ensure that aggregate dust is avoided. The types of dust present can usually be identified and analysed. The analyses of the bulk paste must also be corrected for the effect of the hydration process; however, as these affect the amounts of both the Al_2O_3 and the Fe_2O_3 content they do not significantly affect the normative C3A. If there is adequate residual clinker, analyses are also made of large clinker particles. Three approaches can therefore be made to the recognition of the cement type:

- identification of the matrix phase in unhydrated clinker particles;
- chemical analysis of the bulk paste;
- chemical analysis of large clinker particles

As with the water/cement ratio the result should strictly be described as the apparent cement type because the amount of C3A determined is based on a normative calculation. Any significant chemical changes occurring in the concrete with time could invalidate the determination. The results normally obtained fall into three categories: those indicating that the C3A content is high, typically around 10%, implying the cement is an ordinary Portland cement; those in which the C3A content is very low with the cement having the unambiguous composition of a sulphate resisting type; and an intermediate group where the spread of results is such that the mean result is ambiguous. The result is therefore reported using Student's *t* Test to indicate the probability of the composition corresponding with one or other of the main cement types.

Slag/(Slag + OPC) and PFA/(PFA + OPC) ratios

The use of PFA and ground granulated blast furnace slag in concrete appears to be increasing and with it a greater demand for measurement of the proportions present in the paste. Suggested methods are given in

BS 1881: Part 124: 1988 but they are prone to some serious and often unknowable errors. The determination of the proportion of slag in the binder, for example, is dependent mainly on the determination of the sulphide content in the concrete. Information is then required on the sulphide content of the slag itself and of the aggregate. The aggregate may have much more sulphide than the slag so that the method can be extremely imprecise. Moreover oxidation of sulphide in the aggregate and the slag may occur and the extent of this in any hydration reactions may be sufficient to produce significantly low results in the slag determinations.

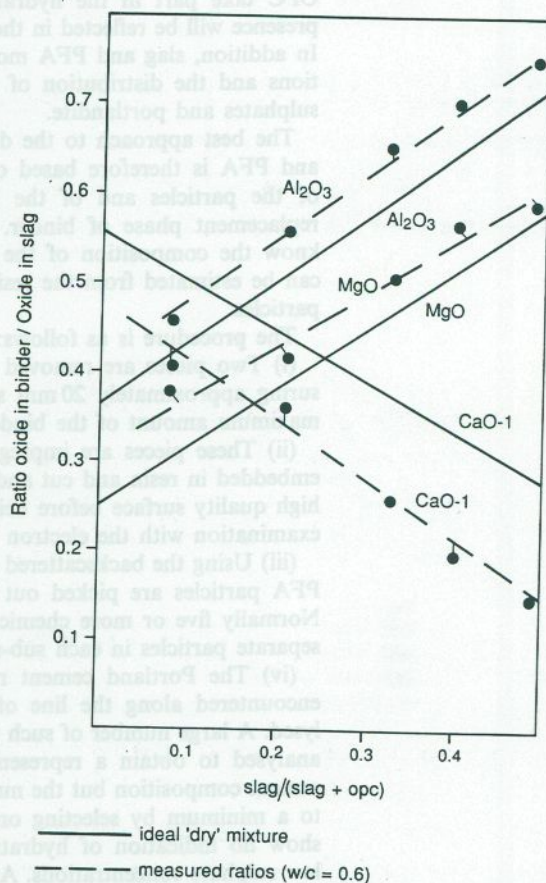


FIG. 31. This diagram shows the relationship between the composition of the cement paste containing ground granulated blast furnace slag and the amount of slag. The full lines represent the ideal compositions obtained by mixing OPC and slag. The broken lines give measurements of hydrated mixtures.

At first sight it seems a simple matter to determine the slag content from the polished surface or thin sections. It is almost always possible to recognize when slag and PFA are present and estimates of the required ratios can be made. However, the grading of the PFA

and slag may vary from sample to sample and, as only the larger glass particles can be identified unambiguously, the determination of the proportions from the thin section is of dubious accuracy. In the case of PFA the iron-rich particles are the most conspicuous but the least representative of the globules present. With the electron microscope the particles of slag and PFA are much more readily recognized and a visual impression can be obtained of the amounts present. An image analysis of a high-quality polished surface of paste containing slag and PFA will therefore produce a result related to the slag/(OPC + slag) and PFA/(PFA + OPC) ratios. However, the slag, PFA, and OPC take part in the hydration reactions and their presence will be reflected in the composition of the gel. In addition, slag and PFA modify the hydration reactions and the distribution of compounds such as the sulphates and portlandite.

The best approach to the determination of the slag and PFA is therefore based on the chemical analysis of the particles and of the bulk combined OPC + replacement phase of binder. It is also necessary to know the composition of the Portland cement which can be estimated from the residual unhydrated clinker particles.

The procedure is as follows:

(i) Two pieces are removed from the concrete measuring approximately 20 mm square and containing a maximum amount of the binder.

(ii) These pieces are impregnated with epoxy resin, embedded in resin and cut and polished to give a very high quality surface before being coated in carbon for examination with the electron microscope.

(iii) Using the backscattered electron image, slag and PFA particles are picked out along lines of traverse. Normally five or more chemical analyses are made of separate particles in each sub-sample.

(iv) The Portland cement residual clinker particles encountered along the line of traverse are also analysed. A large number of such particles may need to be analysed to obtain a representative indication of the cement composition but the number of analyses is kept to a minimum by selecting only large particles which show no indication of hydration and have extremely low sulphate concentrations. As obtaining the Portland cement analysis is the most difficult part of the task it may be more satisfactory to assume that the cement has a standard normal composition once the cement type is identified. In practice, variations in cement composition make relatively little difference to the determination of the desired ratio.

(v) Along the lines of traverse areas of paste containing no dust and no aggregate are analysed. The areas chosen are normally 100 μm square. The number of analyses made varies, but the minimum required is five, and enough analyses are made to obtain a reliable bulk composition for the binder. Although a reliable

indication of linear composition can usually be obtained over the areas measured, because the hydration process involves separation of elements into different parts of the binder, the measured binder composition differs slightly from the true binder composition. The principal difference is related to the water/cement ratio and slightly high values for the determination of the required ratios will be obtained unless corrections for the separation of phases are applied.

(vi) The area analysis must be standardized using standard mixtures of Portland cement paste and the method as a whole is controlled by the use of standard paste mixtures containing PFA or slag together with Portland cement.

Because special compounds may be present in the PFA and/or the slag, the bulk analysis of the areas may be affected for certain oxides.

For example, the presence of metallic particles can greatly affect the amounts of manganese, titanium and iron that are present. Conversely, the presence of carbonaceous particles in PFA cannot be detected in the microprobe analysis. In order to take account of these factors the apparent ratio should be obtained using all constituents and the standard deviation to be attached to the determination measured for each constituent. The elements used for the determination are then selected as those showing the maximum range between the replacement material and the Portland cement and the maximum ratio of range to standard deviation. The chemical analyses of the mixtures, the replacement phases and the Portland cement are then recalculated to 100%, excluding the unsatisfactory components. This use of ratios obviates problems arising from the presence of the constituents which cannot be analysed in a representative way. For the determination of slag it is almost always found that the most satisfactory constituents are CaO, Al_2O_3 , and MgO. For the determination of the PFA content the most satisfactory components are SiO_2 , CaO, and Al_2O_3 .

The differences between the results calculated for each of the individual main components are used to assess the corrections needed, particularly for separation of calcium hydroxide from the binder onto the aggregate surfaces (Fig. 26).

When the concrete is of high quality and can be polished to give a very good surface, the method is repeatable from sub-sample to sub-sample with a standard error of ± 0.03 for the required ratio. Analysis of standards shows that this can also be regarded as an indication of the accuracy of the method. However, because concrete can be changed with time as various deterioration processes affect the composition of the paste, once again the ratio obtained should be regarded as the apparent ratio only. The method based on examination of the sample with the electron microscope has the advantage that the slag and PFA can be seen so that at least minimum values for the replace-

ment phase can be obtained using point counting or image analysis procedures.

Conclusions

Although the microscopic evaluation of cements and concrete has been used for several decades its value has not always been appreciated and insufficient attention has been directed to improving methods of observation and measurement. This paper draws attention to its potential but there is still room for very substantial development and improvement of both the qualitative and quantitative techniques. The paper highlights what should be present in the requirement of a full routine study of hardened concrete and the substantial amount of useful data relating to the quality of concrete and processes of deterioration which can be obtained rapidly and economically by an appropriate petrographic study. It is also possible to discuss reasons for low strength or low modulus of elasticity, to evaluate the effects of fire on concrete, to observe the penetration of external agencies and carbonation, and to assess the potential for further deterioration.

Petrographic examination should always precede the chemical analysis of concrete so that the appropriate chemical procedures can be selected. Possibly more importantly, the petrographic approach (principally via point counting or image analysis) can provide quantitative data relating to the composition of concrete including the following:

- (a) determination of water/cement ratio;
- (b) determination of cement content;
- (c) determination of the total mix proportions, including the ratios of slag to OPC and of PFA to OPC;
- (d) determination of apparent cement type;
- (e) determination of aggregate grading.

Properly carried out, many of these methods of determination are superior and more widely applicable than the standard chemical procedures. In addition because the methods of determination are inter-related, it is usually possible to determine parameters expeditiously and economically.

References

- ANDERSON, K. T. & THAULOW, N. 1989. The application of undulatory extinction angles (UEA) as an indicator of alkali-silica reactivity of concrete aggregates. In: OKADA, K., NIGHIBAYSHI, S. & KAWAMURA, M. (eds) *Proceedings of 8th International Conference on Alkali-Aggregate Reaction, Kyoto, Japan*, The Society of Materials Science, Japan, 489-492.
- AMERICAN SOCIETY OF TESTING MATERIALS 1989. *Annual Book of ASTM Standards, Part 14, Concrete and Mineral Aggregates; Manual of Concrete Testing*. Especially standards C-294, C-295, C-457, C-823 and C-856.
- BARNES, P. & GHOSE, A. 1983. The microscopy of unhydrated Portland Cement. In: BARNES, P. (ed.) *Structure and Performance of Cements*. Applied Science, London, 139-203.
- BRITISH STANDARDS INSTITUTION 1975. *Methods of Sampling and Testing Mineral Aggregates, Sands and Fillers: BS 812*.
- 1981. *Code of Practice for Site Investigations: BS 5930*.
- 1988. *Testing Concrete: BS 1881 Part 124, 1-21*.
- BUILDING RESEARCH ESTABLISHMENT 1968. *Shrinkage of Natural Aggregates in Concrete, Digest 35*.
- 1975. *Concrete in Sulphate-Bearing Soils and Groundwaters, Digest 174*.
- 1988. *Alkali Aggregate Reaction in Concrete, Digest 330*.
- CAMPBELL, D. H. 1986. *Microscopical Examination and Interpretation of Portland Cement and Clinker*. Portland Cement Association, Construction Technology Laboratories, Stokie, Illinois, 1-128.
- CEMENT AND CONCRETE ASSOCIATION 1976. *Hydraulic Cement Pastes; Their Structure and Properties*.
- CONCRETE SOCIETY 1976. *Concrete Core Testing For Strength*. Technical Report No. 11.
- 1978. *Assessment of Fire-Damaged Concrete Structures and Repair by Gunite*. Technical Report No. 15.
- 1982. *Non-Structural Cracks in Concrete*. Technical Report No. 22.
- 1987. *Alkali-Silica Reaction, Minimizing the Risk of Damage to Concrete. Guidance Notes and Model Specification Clauses*. Technical Report No. 30.
- DEPARTMENT OF TRANSPORT 1986. *Specification for Highway Works*. HMSO, London, 1-32.
- DOLAR-MANTUANI, L. 1983. *Handbook of Concrete Aggregates, a Petrographic and Technological Evaluation*. Noyes, New Jersey.
- FRENCH, W. J. 1980. Reactions between aggregates and cement paste: an interpretation of the Pessimism. *Quarterly Journal of Engineering Geology*, 13, 231-247.
- & CRAMMOND, N. J. 1980. The influence of Serpentinite and other rocks on the stability of concretes in the Middle East. *Quarterly Journal of Engineering Geology*, 13, 225-280.
- GRANDET, J. & OLLIVIER, J. P. 1980. Nouvelle method d'etude des interfaces ciment-granulats. In: *Proceedings of the 7th International Congress of Chemistry of Cement, Paris*, 3, 85-89.
- GRATTAN-BELLEW, P. E. 1987. Is high undulatory extinction in quartz indicative of alkali-expansivity of granite aggregates? In: GRATTAN-BELLEW, P. E. (ed.) *Concrete Alkali-Aggregate Reactions*. Noyes, New Jersey, 434-438.
- JAWAL, I., SKALNY, J. & YOUNG, J. F. 1983. Hydration of Portland Cement In: BARNES, P. (ed.) *Structure and Performance of Cements*. Applied Science, London, 237-318.
- LAMA, R. D. & VUTUKURA, V. S. 1978. *Handbook on the Mechanical Properties of Rocks*, 2. Transtech, Clausthal, Germany.
- LEA, F. M. 1970. *The Chemistry of Cement and Concrete*. 3rd Edn. Arnold, London.
- LE CHATELIER, M. 1883. *Constitution of Hydraulic Mortars*, McGraw-Hill, New York.

MANGER, G. E. 1963. *Porosity and Bulk Density of Sedimentary rocks. Contributions to Geochemistry, Geological Survey Bulletin 1144-E*, Geological Survey of America, Washington.

MATHER, K. 1966. Petrographic examination of hardened concrete. In: *Symposium on Significance of Tests and Properties of Concrete and Concrete Making Materials*, ASTM 169A, American Society of Testing Materials, 125-143.

MIELENZ, R. C. 1962. Petrography applied to Portland Cement concrete, In: FLUHR, T. & LEGGET, R. F. (eds)

Reviews in Engineering Geology, Geological Society of America, GAEGA, 1, 1-38.

NIXON, P. J. 1986. *Changes in Portland Cement Properties and their effects on Concrete. Building Research Establishment, Information paper. P3/86*, 1-5.

RAVENS CROFT, P. E. 1982. Determining the degree of hydration of hardened concrete. *Forum*, Jan/Feb, 4.

WRIGHT, P. J. F. 1955. A method of measuring surface texture of aggregate, *Magazine of Concrete Research*, 7, No. 21.

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Property carried out, many of these methods of determination are superior and more widely applicable than the standard chemical procedures. In addition because the methods of determination are inter-related, it is usually possible to determine parameters expeditiously and economically.

References

BRIDGEMAN, R. T. & THORNTON, N. 1989. The application of ultrasonic extinction angles (UEA) as an indicator of alkali-silica reactivity of concrete aggregates. In: *Proceedings of the International Conference on Alkali-Aggregate Reaction*, Kluwer Academic Publishers, Dordrecht, 1-10.

CHAPMAN, M. 1983. *Compendium of Methods for the Microscopical Examination of Concrete*, McGraw-Hill, New York.

GRANT, I. & OLLIVER, J. P. 1980. Nouvelle méthode des interfaces ciment-granulats. In: *Proceedings of the 7th International Congress of Chemical Engineering*, Paris, 1, 83-89.

GRATTAN-BILLW, F. E. 1987. Is high industrial efficiency in quartz indicative of alkali-reactivity of aggregates? In: *Grattan-Billw, F. E. (ed.) Alkali-Aggregate Reaction*, McGraw-Hill, New York, 432.

JAWAL, I., SKALIY, J. & YOUNG, J. F. 1983. *Hydroxyl Content of Concrete*, P. (ed.) *Structural Performance of Concrete*, Applied Science, London, 318.

LAMA, R. D. & VUTURIA, V. S. 1978. *Handbook of Mechanical Properties of Rocks*, J. Turner, C. G. Hoek, G. G. Schuster, McGraw-Hill, New York.

LEA, F. M. 1970. *The Chemistry of Cement and Concrete*, 2nd Edition, Butterworths, London.

LE CHATELIER, M. 1853. *Compendium of Methods for the Microscopical Examination of Concrete*, McGraw-Hill, New York.

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CHAPMAN, M. 1983. *Compendium of Methods for the Microscopical Examination of Concrete*, McGraw-Hill, New York.

GRANT, I. & OLLIVER, J. P. 1980. Nouvelle méthode des interfaces ciment-granulats. In: *Proceedings of the 7th International Congress of Chemical Engineering*, Paris, 1, 83-89.

GRATTAN-BILLW, F. E. 1987. Is high industrial efficiency in quartz indicative of alkali-reactivity of aggregates? In: *Grattan-Billw, F. E. (ed.) Alkali-Aggregate Reaction*, McGraw-Hill, New York, 432.

JAWAL, I., SKALIY, J. & YOUNG, J. F. 1983. *Hydroxyl Content of Concrete*, P. (ed.) *Structural Performance of Concrete*, Applied Science, London, 318.

LAMA, R. D. & VUTURIA, V. S. 1978. *Handbook of Mechanical Properties of Rocks*, J. Turner, C. G. Hoek, G. G. Schuster, McGraw-Hill, New York.

LEA, F. M. 1970. *The Chemistry of Cement and Concrete*, 2nd Edition, Butterworths, London.

LE CHATELIER, M. 1853. *Compendium of Methods for the Microscopical Examination of Concrete*, McGraw-Hill, New York.