

PETROGRAPHY OF CEMENT AND CONCRETE

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SYNOPSIS

Conventional petrography has developed as a technique for the study of rocks, mostly by means of thin sections as viewed under the light-polarizing microscope. The technique has served well in elucidation of mineral composition, structure, origin and history of natural rocks. In application to study of portland cement and clinker, certain unique features of the material have made necessary extensive supplement by the metallographic microscope and study of polished sections. In combination with this advantage, the technique of thin sections has been superseded largely by the easier preparation of powder mounts. Application to problems of concrete has required further broadening of the technique. The stereoscopic binocular is found to be the generally more useful and informative microscope, with aid of the petrographic and metallographic microscopes where higher magnification is specifically required. The amplified technique has proven of great advantage in working out problems in cement and concrete.

INTRODUCTION

Petrography, defined as a discipline in natural science, is a particular study of natural rocks. It is particular in the sense that observation and philosophy center about the facility and the technique of use of the petrographic microscope. Area and extent of the study is well described as the answer to two questions. (1), What is the rock made of? (2), How did the components come to be where they are? Finding the answer to the first question is obviously a matter of more or less precise measurement, of some sort. This area may therefore be called an exact science. Providing an answer to the second is a matter of interpretation of what is perceived. This area resembles philosophy more than exact science. It may be noted further that the basic inspiration is a matter of academic curiosity. The study represents an effort to learn more about our surroundings, the world in which we live.

The artificial world of portland cement and concrete has many features in com-

mon with materials and processes of the natural world. It is to be anticipated therefore that application of petrographic techniques may appreciably and profitably extend our practical knowledge of portland cement, its use, and its ultimate products.

The objective is that the application shall tell us something about properties that suit a building stone to structural use. In a practical sense these are three, namely strength, dimensional constancy, and durability. With natural building stones, these properties are more or less taken for granted and little attention has been given to derivation. Concrete, to be useful, must possess the same properties. With concrete, these desired properties derive from the processes by which concrete comes into existence as a structural material. Some knowledge of the processes of derivation therefore is of vital significance.

This paper attempts to review the accomplishments of this application of petrographic techniques to cement and concrete. Efficient appreciation requires some understanding of what is being applied and what it is being applied to, as well as the mechanics and potential means of application. The earlier part of the paper undertakes some amplification of these features. The later part attempts to answer some of the practical problems of portland cement and concrete.

THE PETROGRAPHIC MICROSCOPE

The petrographic microscope is an instrument of pre-eminent facility in the identification of crystalline substances. Visual distinction of a substance is by distinctive effects that the substance exerts upon the light by which it is perceived. The petrographic microscope essentially is an

ordinary compound microscope fitted with a rotatable stage, a pair of light polarizing prisms, and a few other accessories or refinements. The range of light properties thus made available to perception, analysis, and measurement is so broad that virtually no two substances are wholly identical. The qualifying adjective 'crystalline' imposes no significant limitation. The practical inference is that crystalline substances are substances with directional properties, of some sort, and the class of substances wholly free from directional features is very small. The unique feature of the petrographic microscope is its peculiar facility for perception and analysis of directional properties. It may be noted that the field of application is practically unlimited. It is applicable to all classes of substances, in both the organic and inorganic worlds.

OPTICAL CRYSTALLOGRAPHY

Optical crystallography is the name given to the science and technique of use of the petrographic microscope for substance identification. The facility of optical magnification is useful in more ways than simple revelation of occasional fine structure. There are two general classes of light effects. One of these is differential absorption (color). The other may be visualized as prism or edge effects, the property being generally known as refractive index. The edge effects actually are strongly damped vibrations, which fade out in about three wave lengths. Since the wave length of visible light is a small magnitude, magnification is required for perception and precise analysis of prism and edge effects.

Light deviation at boundaries of different refractive index is a function of the difference between the two indices. With a large difference, the deviations can be so wide as to leave some areas, of microscopic dimension of course, in darkness. It is customary, therefore, for clear viewing of an object to place it in a fluid medium in a refractive index fairly close to that of the object. Determination of refractive index of an object is accomplished by matching it against standardized fluid media. It is unnecessary here to point out the artful devices employed to locate optical directions and to determine refractive index corresponding to direction.

The process of identification consists in determining and tabulating all perceivable properties. The substance then is identified by ratification against some compendium of optical properties. If there is no matching set, if the substance has never been previously described, then identification can be a real problem.

MANNER OF DEVELOPMENT

The manner of development of the petrographic microscope is informative with respect to present day use. In ordinary vision, objects are seen by incident light. With the closer approach of increasing magnification, incident light is progressively shut out. There thus came into being the idea of the thin transparent section and transmitted light. The section has to be thin to transmit light. The section also must be thin to get away from overlapping units and to see fine detail clearly. That is the reason that for over two hundred years after its invention the compound microscope found use only in the biological world, with comparatively soft tissues easily reducible to thin films by squeezing or slicing.

It remained for a dentist, interested in the structure of teeth, to think, in about 1815, of making a thin slice by grinding away opposing faces of the tooth until only a film was left. Then the Nicol polarizing prism was devised about 1818 and a pair of prisms was first put on a microscope about 1827.

Realization of the potential advantage of combined thin section technique and polarized light microscopy came some years later. This apparently was first perceived by H. C. Sorby, whose 1858 monumental paper on rock description not only brought order out of capricious fantasy in the study of natural rocks but initiated the science now carried on as petrography.

SOME FEATURES OF TECHNOLOGY

In preparing thin sections, the specimen is ground to a smooth plane at the desired horizon. This face is then fixed by a resin to an object glass, and the specimen is ground away on the other side until only a thin film is left. The section is finished by covering this ground surface with resin and running this out to a thin film with a cover glass. The rock section thus is observed in the resin as the am-

bient medium, and air contact light effects are eliminated by the normal glass surfaces.

Three or four features fortuitously conspire to make the technique almost ideally suited to study of natural rocks. These merit special mention.

1. Considering mechanics and materials available, a thinness of 1/1000 inch is about the least that can be achieved. Even this achievement is an art.

2. The components of natural rocks are relatively resistant and long enduring. They are unaffected by water universally used as a grinding vehicle. Thin slices of soluble materials could not be expected to last very long.

3. In the igneous rocks, an average grain size is somewhat greater than 1/1000 inch. Thus in such a section the fine structure of the rock becomes more or less sharply defined, as a sort of delicate tracery. This in fact is the significance of 'graph' in petrography. The prefix 'petro' of course means 'rock', so the science is aptly named.

4. The only resin known was Canada balsam, which however was universally known and universally available. The refractive index of this resin is about 1.54. This is a close approach to 1.55 of quartz and 1.53 of feldspar. Quartz and feldspar are by far the more common and abundant components of igneous rock. With this close matching, light refractions are small and detail of composition and structure is most clearly defined.

5. It happens also that in quartz and feldspar the birefringence is low. The significance of this is that at a thickness of 1/1000 inch interference colors are well down in the first order, facilitating optical analysis.

6. At a thickness of 1/1000 inch, and grain size of similar dimension, a microscopical magnification of 100X suffices for resolution and easy perception of detail in most igneous rocks. This is accomplished with an objective lens and an eyepiece each of 10 power. While early lenses were really works of art, other features of construction as of that time made work at higher magnifications very trying. Fortunately, such magnifications

were not required for the usual study.

CLASSICAL PETROGRAPHY

Such then is classical petrography. In thin section the constituent particles of the rock are revealed in a manner permitting observation and appraisal of many optical properties and separate mineral identification thereby. Then the section is thin enough to reveal sizes and shapes and mutual relations of the constituent units, one to another. Consideration of these features, along with the mineral composition, leads to a philosophy of origin and history and orderly classification of natural rocks.

In general the philosophy part constitutes the science of petrography. Mineral identification of course is a prerequisite, but optical crystallography as such is considered only a tool, a means to an end, and its separate identity becomes somewhat submerged in pursuit of description and classification of rocks.

PETROGRAPHY OF PORTLAND CEMENT CLINKER

Classical thin sections of portland cement clinker quickly demonstrate several interesting features:

1. The refractive indices of all component minerals differ from that of Canada balsam by what are considered large amounts. Refraction shadows, so induced, seriously obscure fine detail.

Recognized mineral components of clinker, and their refractive indices, are about as follows:

C ₃ S*	1.72
C ₂ S	1.73
C ₃ A	1.71
C ₄ AF	1.96
MgO	1.73
CaO	1.83

The first two components usually make up about 80 per cent of the whole volume of clinker. The first three make up nearly 90 per cent of a Type I composition. It will be noted that the refractive indices for the first three are approximately the same. It may be expected therefore that thin sections of exceptional clarity might be made if the refractive index of the resin could be about this value. Such a resin, known as Hyrax, with refractive

*The abbreviated chemical symbolism now common in cement technology is used here, namely, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃.



Fig. 1—Portland Cement Clinker as Seen in Thin Section Prepared with Hyrax Resin, Refractive Index 1.71. Type II Composition.

index of 1.7135, is available but by no means generally known or used. Fig. 1 shows a section of a Type II composition clinker prepared with Hyrax resin. Compare this with Fig. 2, a section of the same clinker prepared with resin of refractive index 1.54, Canada balsam. The multitude of obscuring pepper spots over Fig. 2 are refractive index shadows. The effect is very much like trying to perceive detail through frosted glass, a very finely roughened surface. This effect explains in part the slow progress of conventional petrography in deciphering the mineralogy of clinker. In Fig. 1, the section has, of course, the same rough surface. Light deviations however are nearly eliminated by the contiguous resin of the same index. Increased clarity is notable.

2. The next thing one learns is that the conventional thickness of 1/1000 in. is too thick. It is about 30 microns. These sections are about half that thickness. Yet it is noted that detail is obscured by grain boundaries overlapping with depth, and that average size of the component mineral units is much less than 30 microns. It should be recalled that the mechanics of section grinding set what is almost a physical limit to attainable thinness somewhere in the neighborhood of 1/1000 inch. With specially sized grinding powders and very meticulous care, it is possible to go somewhat farther. If one can be content

with edge areas, these may persist down to 5 microns, on wedge-shaped sections.

3. Considering the small average grain size, it is evident that the customary lens system of 10X objective and 10X eyepiece is inadequate. Experience has shown that a 43X objective is very much better suited to study of clinker, and this is used in combination with a 20X eyepiece. In other words, a magnification of about 900X is required for easy perception of the usual features of portland cement clinker.

4. The next thing one learns is that some of the components are unperceivable even in the best and clearest sections and at high magnification. Refractive indices of C_3A , C_3S , and MgO are closely similar. In manner of occurrence, the grains of C_3S and MgO are enclosed essentially in a sort of envelope of C_3A . In this relation, the grains of C_3S are perceivable with crossed Nicols as weakly birefringent patches, but C_3A , being isotropic, is invisible with crossed Nicols and cannot be separately perceived in plane light. The same observations hold for MgO , except that once in a while diligent search may resolve a crystal outline.

5. In the meantime, one has learned that the portland cement minerals react with water. In some respects the rate may be slow enough for hydration to

introduce no significant alteration in the preparation of a section. In general, it is necessary to use a light mineral oil for a grinding vehicle. That is not an insurmountable difficulty, but it complicates the mechanics of specimen preparation.

It is seen that classical thin sections do not afford much help. They are informative only in a general way. The great French chemist LeChatelier, apparently taking his cue from Sorby, appears to have been the first to prepare sections of clinker. In 1883 he reported observing (a) clear, colorless, angular bodies, with low birefringence, (b) rounded, turbid, yellowish bodies with moderate birefringence, and (c) some dark brown intermediate substance of generally irregular and ragged form. From chemical considerations he identified these respectively as C_3S , C_2S , and a lime-iron aluminat assigned a composition close to the C_4AF formulated in 1929. From chemical considerations also he inferred the existence of C_3A .

LeChatelier's deductions as to composition of these bodies was long subject to doubt. For some time, responsible thought held no such compound as C_3S could exist. Even today, 80 years later, we are still attempting to devise proof as to precise composition of these bodies, which of course appear to us in the same general character perceived and described by LeChatelier.

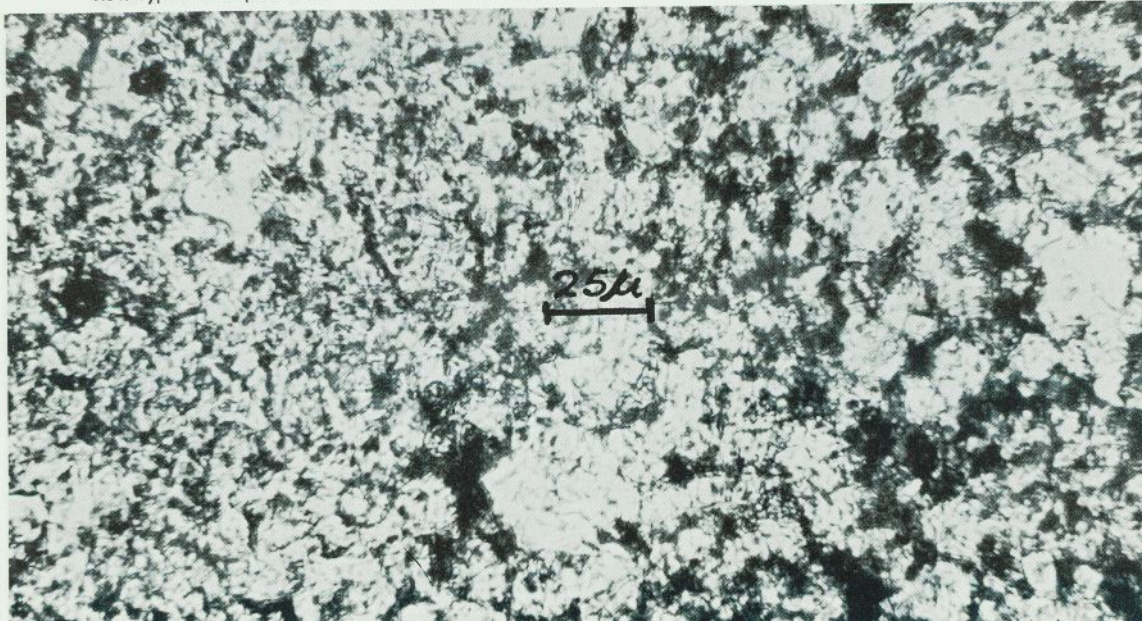
THE PHASE RULE

One approach to identification of a substance previously unknown or undescribed is synthesis from known compositions. The phase rule offers a comprehensive orderliness to this approach. First enunciated in 1876, it remained in classical oblivion till about 1890, when the first serious application was made to the study of aqueous salt solutions at ordinary temperatures. The thought of application to dry systems, i.e., melts at elevated temperatures, came some years later, and then at first with the object of determining the validity of the phase rule with respect to such systems.

In a practical sense, this is the beginning of the science of optical crystallography. It is here that the petrographic microscope has been of prime and extraordinary service.

The basic principle in graphical plotting of phase equilibria in a prescribed chemical system is simplicity itself. This is the plotting of primary phase fields, through examination of a wide orderly range of chemical compositions. At some composition the microscope reveals a single substance, and nothing else, through the whole temperature range. A compound thus is recognized, its chemical composition being that of the initial composition. The optical properties of this compound are described, by which it subsequently is recognized and becomes known. Then orderly

Fig. 2—Portland Cement Clinker as Seen in Thin Section Prepared with Canada Balsam Resin, Refractive Index 1.54. Type II Composition.



variations in the mix are introduced. Through a determinable range, the microscope reveals units of the compound, recognized by its optical properties, enclosed within an otherwise homogeneous material. The perceived units are called the primary phase. Eventually, variations in the mix lead to appearance of some other compound as the primary phase. In that manner the boundaries of the primary phase fields are delineated.

Essential mechanical details perhaps should be noted. The different mixes are heated to complete melts, as determined by instantaneous quenching and observation petrographically of one substance only, that is, a homogeneous isotropic substance, the melt, called, in its quenched solid condition, a glass. The same composition, quenched at progressively lower temperatures, eventually shows one other substance, the primary phase, in the glass.

The microscopic preparations are powder mounts, not thin sections. The quenched material is reduced to a powder, then successive portions are subjected to examination in progressively different refractive index oils, and the optical properties of the substances are thereby determined.

The formidable amount of time, labor, and equipment, and the meticulous care required in such investigation is obvious. On the other hand, practically all that we know about the constitution of portland cement clinker has been derived from such

investigation. Knowledge so accumulated underlies our present day computation of potential compound composition. Above all, it is to be noted that it all derives from optical crystallography and the facility of the petrographic microscope.

POLISHED SECTIONS

It was noted in an earlier paragraph that C_3A and MgO were not distinguishable as such in sections of clinker, because of peculiar optical properties and structural relations as viewed by transmitted light. Any other utilization of transmitted light, such as powder mounts, is attended by the same difficulty.

Another potential component that has come into considerable prominence in recent years seems to be in the same category. That is a glass, a solidified melt, that may be expected in a clinker that has been quickly cooled. Separately, it appears as an isotropic material with refractive index around 1.65. It is not, however, at all easily perceivable, if present, in clinker.

Recent years also have drawn considerable interest to measurement of proportions of the different mineral compounds in clinker. Mechanical attachments suited to this purpose are available for the microscope. That means nothing, of course, if the compounds are not perceivable. Furthermore, precise measurement requires sharp definition. As noted earlier, because of overlapping in depth, grain boundaries are not always sharply defined in thin

Fig. 3—Portland Cement Clinker as Seen in Polished Section, Etched with Distilled Water. Type I Composition. Large, Angular, Gray Areas Are C_3S . Somewhat Ragged Dark Patches Are C_3A . Scattered Silver-Bright Interstitial Material Is C_4AF .

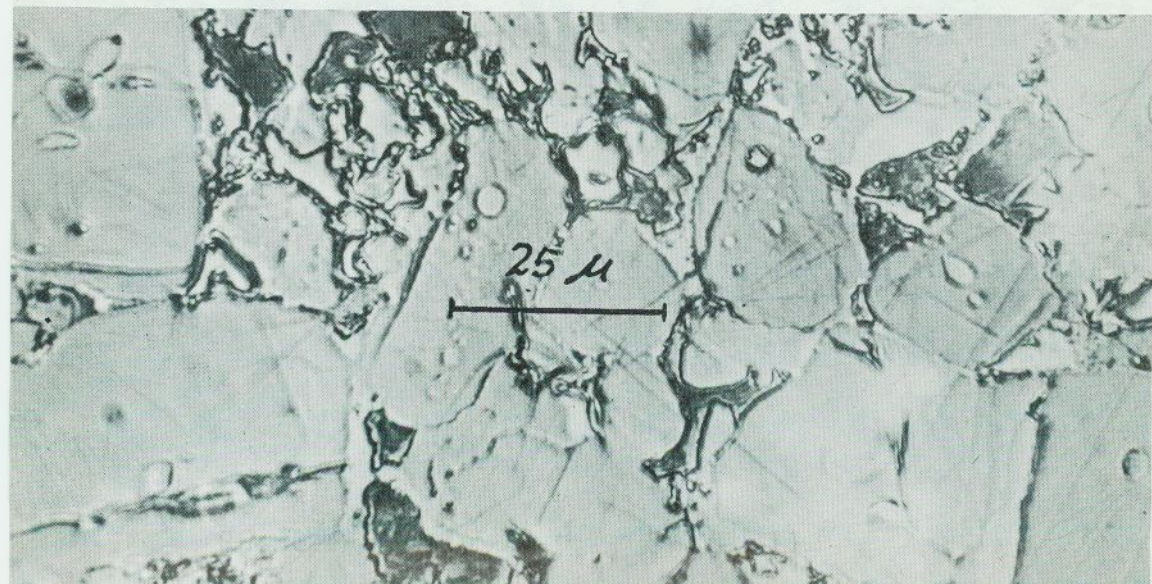




Fig. 4—Portland Cement Clinker as Seen in Polished Section, Etched with Distilled Water. Type II Composition. Angular, Gray Crystals Are C_3S . Rounded, Speckled Areas Are C_2S . Silver-White Interstitial Is C_4AF . Occasional Dark Interstitial Is C_3A .

sections. Obviously, powder mounts are inapplicable.

For sharpness of definition, the thought of the polished section seems to be eminently suited to requirements. Recent years have concentrated wide attention on this approach and a rewarding technology has been perfected. Specimen preparation is vastly faster and easier. The whole preparation can be completed in a few minutes, whereas the thin section can require hours of processing and meticulous care.

Admirable, sharp definition is secured for C_3S , C_2S , C_3A , C_4AF , MgO , and free CaO . Unfortunately, the glass component, if present, does not appear amenable to this technique either. There is some indication that it is not commonly present. We usually think that this is because the cooling rate was too slow. There is, however, plenty of evidence of extensive chemical reaction in the mix at the lower temperatures, and there is perhaps a possibility that not much melt ever was formed. Certainly there is no particular difficulty in distinguishing a light-burned clinker from a hard-burned clinker.

Clinker mineralogy as seen in polished section is shown in Fig. 3 and Fig. 4. The first shows a Type I composition, with a preponderance of C_3A over C_4AF , and C_3S in greater prominence than C_2S . In the second, the higher proportion of C_2S and lower proportion of C_3A are easily perceived. These sections were etched

with water to bring out the several components.

THE PHILOSOPHY

The preceding discussion has dealt almost exclusively with problems of substance identification — finding out what portland cement is made of. Very fair progress has been noted. But it has been noted also that progress required amplification and revision of classical petrographic techniques, and polished section microscopy has become an essential part of the compositional technology.

Little attention has been given to the interpretive side, the question of how the components got where they are. From our knowledge of the manufacturing process it seems evident that a philosophy different from that of natural rocks also is in order. To date, however, few criteria have emerged from which a philosophy might be developed.

Perhaps the closest parallelism might be the melts of phase equilibria studies and the melts of the igneous rocks, whereby the temperature experience of the clinker might be deduced from relative perfection of component crystals. This deduction is obscured by two considerations. For one thing, we know that some 80 per cent of the clinker, the great bulk of the C_3S and C_2S , remains solid throughout the entire heating process. No portland cement clinker starts with the 100 per cent melt of

phase studies. Actually, the usual mass production is composed of material of fairly broad heat experience. It is no particular trick to distinguish light-burned clinker from hard-burned clinker, partly on the evidence of differential bulk shrinkage.

For another interesting item, MgO, as periclase, has come in for much attention in recent years. Quick process cooling of clinker has resulted in markedly lowered autoclave expansions. The reason is thought to be reduction or absence of periclase by (1) solution of compositional MgO in the melt at burning temperature and (2) preservation of the melt as a glass by quick cooling. However, most clinkers with compositional MgO show MgO as periclase, and various features of the periclase units indicate that they are relicts from the raw material and never were in solution.

Another problem is of considerable practical import. Raw materials differ from place to place in what is referred to as "burnability". Some are hard burning, others are easy burning. No very good reason for the different behavior has been found. It should be possible to perceive some clue in the microstructures of the several clinkers, but so far the distinctive features or relations have not been distinguished.

HYDRATED CEMENT AND CONCRETE

Experience in the microscopy of concrete brings a realization of the desirability for further adaptation of the petrographic technique. The stereoscopic binocular becomes the central microscope, working at the comparatively low magnifications of 10X to 15X. The petrographic microscope provides essential support in substance identifications by use of powder mounts and the metallographic microscope lends assistance in resolution of fine structure through use of polished sections; but first reliance is placed in the stereoscopic binocular.

Necessity for such adaptation appears in two fairly well defined features. In the first place, the objective of the work is to answer practical engineering questions of strength, volume constancy, and durability of the concrete. These are problems of bulk properties, and usually they require a broader and more general survey than is

accomplished with the restricted areas of special preparations. Secondly, various features of concrete and unique properties of hardened cement make thin sections difficult and laborious to prepare and practically useless after preparation.

So the quick, and once in a while informative, approach is to note general features of the concrete by unaided eye or with the stereoscopic binocular. Where features of finer detail are encountered, these may be resolved by study at higher magnification as powder mounts or polished sections. The remainder of this paper will present some of the results of such study of a varied assortment of concretes.

STRENGTH

The basic importance of Abrams' water-cement ratio law has been amply confirmed by experience and empirical test. Microscopic study shows why this should be so. C_3S and C_2S are considered the essential hydraulic constituents of cement. Reaction with water, as can be seen in suitable preparations, generates two new substances, with however notably different habits. One of these is recognized to be calcium hydroxide, which starts to develop in open water space and tends to grow into large, clear crystals. Mineralogic identification of the other is not so easy. It is a precipitate, in very minute units, that forms on and adheres to exposed interfaces. In structure, the precipitate looks much like a random pile of uniformly sized spheres, hence with a significant bulk porosity, but all of a very minute detail. From this structure it is designated a gel.

The gel forms on surfaces of the cement particles and continues to form and adhere to itself. Thus the gel bridges the contacts between the cement particles thereby binding the initial suspension into a coherent unit. The gel forms on the surfaces of air voids within the concrete and against any other air interface, such as the exposed finishing surface. It is important not to overlook the calcium hydroxide. The microscope reveals that all of this time the hydroxide has been growing in crystal units out in the open space. It further shows that the gel has been forming on the surfaces of the hydroxide crystals, just as fast as they grew. The net result is a fairly uniform intergrowth throughout the whole initial water filled space. It is

readily understandable that bulk physical strength should show lower values, with more water space and less cement to fill it.

The intergrowth of gel and hydroxide shows why concrete can develop such high strength and apparent hardness, despite the unfavorable softness and perfect cleavage of the hydroxide itself. In this connection, it is important to note that, at least in the earlier periods, the water space is being filled by precipitates of calcium aluminates and sulfoaluminates, and that the gel apparently intergrows with these units as it does with the hydroxide. The calcium sulfoaluminates must be very minute and well distributed, for they have not yet been perceived. Neither have the calcium aluminate hydrates been certainly recognized. Their crystal properties are very similar to those of calcium hydroxide. There is, however, some evidence that aluminate hydrate intercrystallizes with the hydroxide and thus escapes certain separate recognition.

SOME FACTORS AFFECTING STRENGTH

It is obvious that strength is some function of time. At a given time, the strength will depend upon the proportion of cement hydrated at that time. This is best judged, by microscopic observation, from the proportion of the cement remaining unhydrated at that time.

Sometimes in concrete technology other powdered materials enter as components with attendant decrease in proportion of cement. Some examples are fly ash, blast-furnace slag, quenched or otherwise, and pulverized limestone. One may not conclude that such entry necessarily is adverse to strength development. However, adverse effect may sometimes be anticipated from what experience has shown about dilution with a particular admixture.

In practical microscopy the detection of such solid admixtures, and also unhydrated cement, is very simple and easily accomplished. If, for example, one wishes to hear a faint sound, his first thought is to restrict or eliminate all other sound. By analogy, if one wishes to see certain objects in a mixture, it helps to make all other objects invisible. With ordinary sight this could be cumbersome, but it is a simple matter in microscopy, in most applications. Refractive indices of calcium hydrox-

ide, and of the calcium aluminate hydrates, and of the gel, all are in the neighborhood of 1.54. So it is only necessary to make a pin-point mount of the hydrated paste in a 1.54 liquid. All of these substances fade into flatness, and the strange particles and the unhydrated cement stand out in unmistakable prominence. One pin-point mount usually tells the full story. Strange particles can be detected almost equally readily in a polished section, which also has some advantage in indicating distribution and in permitting estimates of proportion.

There have been occasional instances where the strength of the concrete was substantially zero. That is, the cement did not set at all. One powder mount in 1.54 sufficed to show that extent of hydration also was substantially zero. This is a result or effect that is typical of certain soluble organic compounds, which often interfere as powerful retarders. The point here is that the unhydrated cement can readily be made visible.

This may be a good place for a note on the bulk appearance of hardened hydrated paste, and its significance. It is a lusterless substance, in over-all color some shade of gray through light tan. These features are conferred by the minute porosity. Though the gel, and the hydroxide, and the aluminates can be seen at high magnification to be water clear and colorless, the abundant discontinuities in the structure refract the light in every direction, so the net return tends to be white, and no luster. This kind of fine structure can be inferred from simple observation of those features, even without a microscope.

As might be expected, high water-cement ratios induce a greater whiteness, partly because of more advanced hydration of the cement and partly because of greater refraction owing to large pores. Conversely, high cement contents and low water-cement ratios tend to make the concrete a dark gray. This is mostly the darkness of optical continuity, absorption of light, but some of it is contributed by a significant fraction of cement left unhydrated.

The practical reason for introducing these remarks is that these features serve to indicate relative cement contents and water-cement proportions. Much practical benefit could accrue from some method for

actual determination of cement and water proportions in concrete. There is no certain method, and we have to rely on qualitative appraisals of this kind. They work, after a fashion, but the peculiar hydration mechanics of spreading through the water space imposes very broad limits upon such appraisals.

It might be noted also that the hardness and strength of concrete evidently derive from the gel. As to the intrinsic hardness and absolute strength of the gel substance, we have no means of knowing. These properties would be interesting to know.

DIMENSIONAL CONSTANCY

It is readily apparent that matters of dimensional constancy must be closely related to properties of strength on the one hand and durability on the other. There is a particular area, however, that merits an attempt at separate consideration, inasmuch as within that area the petrographic microscope and associated techniques have rendered outstanding service.

Over-all dimensional constancy reflects a state of equilibrium, a stability, of the components of the material, both within as between the components and outwardly as between the components and the environment. With natural stones, both considerations are taken for granted, the more so perhaps for the inner equilibrium. In other words, conventional petrography has devoted little critical attention to these properties.

Concrete, however, comes into existence as a structural material through a profound and extensive series of chemical reactions. Initial solid substances in one way or another disappear as such and new solid substances come into being. It is a striking fact that these essential reactions occur with substantially zero change in external dimensions of the mass. Yet they do, and that behavior is the central feature of the concrete business.

Experience with cement and concrete has shown that not all of the possible reactions are benign, so to speak. Some reactions are attended with mechanically directional properties, which thereby may effect mechanical damage of the concrete. Among the longer known of such reactions are the hydration of free lime and of magnesia, which early led to restrictive specifications

and tests safeguarding the "soundness" of the cement.

It has proven convenient to distinguish reactions as accommodative and unaccommodative, respectively. In chemical terms, they respectively may be designated as reactions by hydrolysis and by simple hydration. The essential reactions in the transformation of the fresh concrete into a structural solid are hydrolitic and accommodative. They proceed by solution or partial solution of the old and concurrent precipitation elsewhere of the new. The new products fit themselves into available space. In contrast, the simple hydration is a change of one solid directly into another solid, without regard to available space, and hence unaccommodative mechanically.

Petrographic microscopy has learned how to spot the reaction products of unaccommodative transformation, mostly by means of strain shadows and fibrous structures.

This affords a facility which may well be incorporated within the philosophy of conventional petrography. The microscope provides a means for substance identification, which of course is a help in recognition of deleterious features, but the mechanical effects can be perceived without recognition of the particular substances involved.

There are some unaccommodative transformations that may not involve any chemical change or action, strictly speaking. For example, the destructive effect of "dusting" of C_2S is well known. This is a simple solid change from the beta to the gamma form of C_2S with attendant increase in volume. Experience of the writer shows no occurrence of gamma C_2S in cement as a commercial product nor of damage to concrete from the transformation. Optical properties and unaccommodative features of the gamma form make it readily recognizable.

Another non-chemical, unaccommodative transformation is the freezing of water. That concrete is widely subject to disintegration by frost action needs no comment here. Recognition of frost action as the damaging agent, however, is peculiarly difficult. For one reason, the secondary product, which is ice, eventually melts and thereafter is no longer present in place. For another reason, the unaccommoda-

tive mechanics are less easily visualized, since the initial phase is a liquid. By some means or other, escape of the liquid is hindered, but particulars of the hindrance usually are not clearly defined.

There is one kind of frost effect that is very easy to read. Freezing of a fresh concrete, within a few hours of mixing, leaves radiated bladed voids popularly called "crow's feet". This occurs, however, only with frost action before a firm set has been acquired.

DURABILITY

Durability of concrete is a property concerning which there is little in the way of absolute knowledge. Long experience has revealed a concrete technology requisite to long endurance in a relative sense. Most of this knowledge has been acquired from study of concretes that have not endured. Here again is a field in which the petrographic microscope and associated techniques has rendered notable service. But here again to function effectively that service had first to develop those landmarks or visual criteria by which causes of mechanical damage, referred to in the preceding paragraph, can be recognized. In other words, petrographic microscopy has done very well in looking at poor or failed concrete to learn why it was poor or had failed. Looking at good concrete to learn why it is good is a more difficult problem.

In general, the question is one of stability either of the components within or of the components against the environment. As examples of the former, the hydration of free lime and magnesia already has been noted. As examples of the latter, one may note disintegration in sulfate water, rusting of reinforcing steel, and frost action. In general, the secondary substances (i.e. reaction products) can be identified as such. Proof of mechanical damage is not always afforded by identification alone. Usually some feature or expression of directional force must be found associated with the damaging agent to afford proof that it has effected damage.

For many agents the visual approach to identification, including microscopy, can be relatively easy. That is because the secondary substances, and commonly some residual primary as well, remain in place and can be found to tell the story. Percep-

tion, however, is not always simple, by virtue of three or four principal complications. (1) With frost action the secondary substance, ice, melts and does not remain in place. (2) Practically all substances have some solubility. In moist exposure, and insofar as the secondary substance dissolves, mechanical effects become less marked. (3) The size of the offending unit is a significant factor in ultimate mechanical expression, since a hydrated cement paste is subject to plastic deformation. (4) Damage by one agent usually opens the way for damage by others. Thereby it may become difficult to perceive which one was the prime offender.

These observations introduce a further paragraph of pre-eminent significance in concrete technology. The fact that one agent may open the way to damage by others leads to the conclusion that deterioration of concrete is subject not only (1) to active agents, intrinsic sources of energy, but also (2) to permissive factors, conditional features, which may permit or promote, or avoid, damage by potential active agents.

Long experience in the examination of concrete has shown that malperformance is traceable almost wholly and in almost every case to such conditional features. These may be noted as (1) slighting of cement content, (2) excess mix water, (3) aggregate that is unsuitable, with respect to gradation, absorption, cleanliness, or composition, (4) improper placement or finishing, (5) improper protection against early freezing, (6) lack of air entrainment, etc. These features are too well known for further comment here. For the most part, however, these features hold the practical answer to problems of durability. Even these features are subject to visual perception, but the implicating evidence may well call upon large scale field inspection.

CONCLUSION

The discussion has shown that the fields of petrography and concrete technology hold much of common interest. This is perhaps necessarily so, since both deal with effective building stone, the one of natural origin, the other artificial.

On the other hand, distinct differences are noted in respect to constituent substances, processes of origin, and objectives of study. It has been found therefore that,

in application to concrete, conventional petrography requires extensive adaptation in respect to techniques, instrumentation, and philosophy. The discussion has pointed out the specific needs and accomplishments in this adaptation through which petrography has well served the interests of cement and concrete.

At the same time, application to the study of cement and concrete has well served the interests of conventional petro-

graphy, though the service is far less well recognized. Mechanical features of chemical reactions constitute a subject of vital significance in the field of concrete. This area is practically unknown in conventional petrography. What has been learned in this area from study of concrete can well broaden knowledge of the origin and properties of natural rocks, particularly with respect to considerations of durability in constructional exposure.

