PETROGRAPHIC EXAMINATION

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Petrography is the scientific description of the formation and composition of rock, including the systematic classification of rocks. Petrographic examination of hardened concrete—a man-made rock—is the examination of concrete by the techniques used in petrography, to determine the formation and composition of the concrete and to classify it as to its type, condition, and serviceability.

This paper is intended to show that petrographic examination provides information useful in evaluating hardened concrete, to note the problems inherent in its use, to outline what it involves, to describe the kinds of information that it can produce, and to show how this information can be applied.

The questions that materials testing and evaluation tries to answer are: (*a*) "How will this material behave in use?" or (*b*) "Why did this material behave in use in the way it did?" The first question is never unequivocally answered except after-the-fact, by determining how the material did behave in use. The most useful method for developing practical information upon which to make decisions that depend on prediction of probable behavior of materials is the study of why materials behaved in use as they did.

Testers of materials are unable to compress time or to anticipate and reproduce the environment that the material will experience. Generally they use standardized procedures not directly related to the specific environment or that do not determine the particular properties relevant to performance in the specific instance. Thus, testing construction materials amounts to obtaining certain kinds of information about certain samples in specified conditions and extrapolating to the conditions of intended use insofar as they can be predicted.

Petrographic examination of hardened concrete is included among the subjects in this volume because it helps to improve the extrapolation from test results to performance in use. It offers direct observational information on what is being tested and what is in the structure, giving another way of appraising the relation between samples and materials in use and judging how similar the two are.

COMMUNICATION PROBLEMS

A petrographic examination of concrete ordinarily begins and ends with a problem of communication between the person who requests the examination (usually an engineer) and the person who makes it (usually a petrographer). Unless the two succeed in producing a clear, mutually understood statement of the problem, they cannot expect a clear, useful answer to be economically obtained. The engineer who asks for an

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examination of a particular concrete suspects that the concrete is unusual; the more clearly he defines the features prompting his interest, the more he directs the petrographer toward the important aspects. The engineer may not be familiar with the techniques that the petrographer may use or with his approach; the petrographer may not realize the engineer's responsibility for decision and action, may not find out all the engineer could tell him about the concrete, and may not realize which petrographic findings are useful and relevant. The petrographer should not expect petrographic results to be taken on faith; the rationality of the techniques producing them should be demonstrable. Both should remember that the essentials of petrographic examination of concrete are practiced anytime anyone looks intelligently at concrete either in a structure or as a specimen and tries to relate what he can see to the past or future performance of the concrete. On this basis, it is clear that many most useful petrographic examinations are made by inspectors, engineers, chemists, physicists—anyone concerned with the production or use of concrete. No one should hesitate to examine concrete with all available means; all, from novice to expert, should question the indicated conclusions and verify them in as many ways as possible.

METHODS

A recommended practice for petrographic examination of concrete aggregates has been standardized [*1*].[2] Techniques of petrographic examination of hardened concrete have been described and discussed [*2–25*]. They have not been standardized for several reasons including: the considerable variety of techniques that are used in different laboratories, the wide variety of purposes for which examinations are made, the rapidly increasing uses in the recent past of a variety of instruments, and kinds of data clearly applicable in petrographic examination of cement paste and hardened concrete but not yet available in many laboratories in which petrographic examinations of concrete are made.

At present I know of no laboratory where petrographic examinations of concrete are made that is equipped to use all the methods that have yielded useful information and no one person who has digested the available approaches and developed the ability to choose the particular combination of techniques best suited to each problem encountered. Concretes are more complex than most rocks used as aggregates; their constituents are less well known; concretes change through time more rapidly than most aggregates. All of these circumstances combine to make each petrographic examination of concrete unique and thus to make the methods harder to generalize and standardize. Each examination presents some new facet for the petrographer who is willing to learn.

Between 1950 and 1955 remarkably rapid advances in knowledge of the calcium silicate hydrates [*26–28*] were brought about in part by work sponsored by the Building Research Station. J. D. Bernal and his students, then working at Birkbeck College, and others in the United Kingdom, proceeded by synthesis of compounds and study of naturally occurring minerals, making use of X-ray crystallographic methods, optical methods, and static dehydration. The interest thus aroused among mineralogists and chemists, especially in the United Kingdom and the Soviet Union, has led to a greatly increased knowledge of natural and synthetic calcium silicate hydrates [*29*], recently summarized by Taylor [*30, 31*] and from another approach by Belov and co-workers [*32*].

In 1955 differential thermal analysis had been usefully applied [*24,25*] but not widely investigated. The use of electron microscopy in the study of portland cement hydrates had not advanced very far in the United States, and differences of opinion on proper specimen preparation and ambiguities in interpretation made it difficult for persons not expert in the field to assess the value and meaning of the results. The potentialities of these methods and others for characterizing calcium silicate hydrates, calcium aluminate hydrates, and other phases in hydrated cement paste could be recognized, but most laboratories where petrographic examinations of hardened concrete were made were not equipped with instruments more sophisticated than the polarizing microscope and were not yet prepared to relate and to combine the information available from visual observation and light microscopy with that available from X-ray diffraction, differential thermal analysis, and electron microscopy and diffraction.

These newer techniques and the results they yield offered an opportunity to understand in much more detail than previously had been possible the chemical reactions that had gone on in a concrete being examined, because they suggested that it would soon be possible to characterize the hydration and reaction products more clearly and thus to reconstruct in detail the chemical reactions of normal hydration or abnormal deterioration or both in the concrete, and to evaluate, with much more certainty than is possible without fairly complete identification of the reaction products, the relative roles of chemical attack and physical attack in producing deterioration. The goal of relating better established and more familiar techniques in petrographic examination of hardened concrete to the more intimate and detailed insights made possible by the newer techniques remained to be achieved, and while progress since 1955 is considerable, the task is not complete.

The term, petrographic examination of hardened concrete, does not imply that a microscope or any other particular instrument necessarily is used; it does imply examination to discover what recognizable constituents are present and how they are arranged in space. Often it implies an evaluation of quality and condition of the concrete—an evaluation sometimes based on quantitative information.

ASTM Test for Compressive Strength of Concrete Using Portions of Beams Broken in Flexure (C 116 – 65 T) and Test for Compressive Strength of Molded Concrete Cylinders (C 39) requiring observation of "type of failure and appearance of the concrete" and "type of fracture if other than the usual cone," respectively, implicitly require partial petrographic examination—the part dealing with defects and departures from the norm—but offer no instructions on how to conduct it. Several specifications under the jurisdiction of ASTM Committee C 13 on Concrete Pipe include as one basis for rejection "measurements and inspection" to ascertain whether the product conforms to the specification as to design and freedom from defects (Specification for Concrete Sewer, Storm Drain, and Culvert Pipe (C 14), section 35; Specification for Reinforced Concrete Culvert, Storm Drain, and Sewer Pipe (C 76 – 65 T), section 27; Specification for Concrete Pipe for Irrigation or Drainage (C 118 – 65 T), section 20; Specification for Reinforced Concrete Low-Head Pressure Pipe (C 361 – 65 T), section 32; Specification for Concrete Drain Tile C 412), sections 16, 17; Specification for Perforated Concrete Pipe (C 444 – 65 T), sections 13, 19; Specification for Precast Reinforced Concrete Manhole Sections (C 478 – 65 T), sections 24, 27; Specifi-

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

TABLE 1—OUTLINE FOR EXAMINATION OF CONCRETE WITH EYE AND HAND LENS.

Coarse Aggregate	+ Fine Aggregate	+ Matrix	+ Air	+ Steel
CONSTITUENTS				
Maximum dimension, in inches, in the range——>d>——[a] *Type:* 1. Gravel 2. Crushed stone 3. Mixed 1 and 2 4. Other (name) 5. Mixed 1 +/or 2 +/or 4 If 1, 2, or 4, homogeneous or heterogeneous	type: 1. natural sand 2. manufactured sand 3. mixed 4. other 5. mixed 1 +/or 2 +/or 4 if 1, 2, or 4, homogeneous or heterogeneous	color, by comparison with National Research Council Rock Color Chart (1948) *color distribution:* 1. mottled 2. even 3. gradational changes	more than 3 per cent of total, predominantly in spherical voids less than 3 per cent of total, abundant nonspherical voids color differences between voids and mortar?	type, size, location
Lithologic types Coarse aggregate more than 20, 30, 40, 50 per cent of total			voids empty, filled, lined, or partly filled	
FABRIC				
Shape Distribution Packing Grading (even, uneven, excess, or deficiency of size or sizes) Parallelism of flat sides or long axes of exposed sections, normal to direction of placement +/or parallel to formed and finished surfaces[b]	distribution particle shape grading preferred orientation } as perceptible	distribution	shape distribution grading (as perceptible) parallelism of long axes of irregular voids or sheets of voids: with each other; with flat sides or long axes of coarse aggregate	voids below horizontal or low-angle reinforcement
CONDITION				
Does it ring when hit lightly with a hammer or does it give a dull, flat sound? Cracks? How distributed? Crack fillings? With cores or sawed specimens: did aggregate tear out in drilling or sawing?				rusty or clean? put in rusty or corroded later?

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[a] A substantial portion of the coarse aggregate has maximum dimensions in the range shown as measured on sawed or broken surfaces.

[b] Sections sawed or drilled close to and parallel to formed surfaces appear to show local turbulence as a result of spading or rodding close to the form. Sections sawed in the plane of bedding (normal to the direction of placement) are likely to have inconspicuous orientation. Sections broken normal to placement in conventionally placed concrete with normal bond tend to have aggregate knobs abundant on the bottom of the upper piece as cast and sockets abundant on the top of the lower piece as cast.

TABLE 2—OUTLINE FOR EXAMINATION OF CONCRETE WITH A STEREOMICROSCOPE.

Coarse Aggregate	Fine Aggregate	Matrix	Voids
Lithologic types and mineralogy as perceptible Surface texture Within the piece: grain shape grain size—extreme range observed, mm median within range —— to —— mm textureless (too fine to resolve) uniform or variable within the piece From piece to piece: intergranular bond porosity and absorption[a] If concrete breaks through aggregate, through how much of what kind? If boundary voids, along what kind of aggregate? All? All of one kind? More than 50 per cent of one kind? Several kinds?	lithologic types and mineralogy as perceptible shape surface texture grading distribution	color fracture around or through aggregate contact of matrix with aggregate: close, no opening visible on sawed or broken surface; aggregate not dislodged with fingers or probe; boundary openings frequent, common, rare width empty filled cracks present, absent, result of specimen preparation, preceding specimen preparation fly ash[b]	grading proportion of spherical to nonspherical nonspherical, ellipsoidal, irregular, disk-shaped color change from interior surface to matrix interior surface luster like rest of matrix, dull, shining linings in voids absent, rare, common, in most, complete, partial, colorless, colored, silky tufts, hexagonal tablets, gel, other underside voids or sheets of voids uncommon, small, common, abundant

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[a] Pore visible to the naked eye, or at ×——, or sucks in water that is dropped on it.

[b] Dark solid spheres or hollow-centered spheres of glass +/or magnetite recognizable at × 9 on sawed or broken surfaces. Other mineral admixtures with characteristic particles visible at low magnification should be recognizable.

Condition: When it is examined at × 6 to × 10 under good light, the freshly broken surface of a concrete in good physical condition that still retains most of its natural moisture content has a luster that in mineralogical terms is subtranslucent glimmering vitreous.[1] Thin edges of splinters of the paste transmit light; reflections appear to come from many minute points on the surface, and the quality of luster is like that from broken glass but less intense. Concrete in less good physical condition is more opaque on a freshly broken surface, and the luster is dull, vitreous going toward chalky. A properly cured laboratory specimen from a concrete mixture of normal proportions cured 28 days that has shown normal compressive or flexural strength and that is broken with a hammer and examined on a new break within a week of the time that it finished curing should provide an example of concrete in good physical condition.

Under the same conditions of examination, when there is reasonable assurance that the concrete does not contain white portland cement or slag cement, the color of the matrix of concrete in good physical condition is definitely gray or definitely tan, except adjoining old cracks or original surfaces.

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[1] E. S. Dana, *Textbook of Mineralogy*, John Wiley & Sons, New York, N. Y., 4th edition, 1932, pp. 273–274; revised by W. E. Ford.

cation for Nonreinforced Concrete Irrigation Pipe with Rubber Gasket Joints (C 505 – 65 T), section 26; Specification for Reinforced Concrete Arch Culvert, Storm Drain, and Sewer Pipe (C 506 – 65 T), sections 26, 29; Specification for Reinforced Concrete Elliptical Culvert, Storm Drain, and Sewer Pipe (C 507 – 63 T), sections 26, 29). These provisions for visual inspection and measurements are also requirements for a partial petrographic examination; a person qualified to make the inspection and measurements needs to be familiar with the products specified, because the instructions provided are not detailed. Tables 1 and 2 give outlines for examining concrete as a material but do not refer to dimensions or to quality of formed or finished surfaces.

PURPOSE AND APPROACH

Purpose:

A petrographic examination attempts to answer two general objective questions: "What is the composition?" and "How is it put together?" The first question refers to the recognizable individual constituents present on the scale at which they are considered. The second question refers to structural fabric, that is, the articulation or packing in space of the component elements making up any sort of external form [*33*] or heterogeneous solid body. Both questions may be answered on any useful scale by choice of technique or techniques of appropriate resolving power. The resolving power needed differs depending on the specific questions to be answered.

Approach:

Step one, in any case, is to define the problem in order to find and ask the right questions, those that need to be answered to solve the problem that caused the examination to be requested. These right questions should be answered insofar as they can be in the context, limited as it will be by money, time, instrumentation, and the state of the art. The best petrographic examination is the one that finds the right questions and answers them with maximum economy in minimum time, with a demonstration clear to all concerned that the right questions were answered with all necessary and no superfluous detail. In practice the approach to the ideal varies depending on the problem, the skill with which the questions are asked, and the skill of the petrographer. One measure of the petrographer's skill is knowing when to stop, either because the problem is adequately solved, or, in some cases, because it has been shown to be insoluble under the circumstances.

FABRIC AND COMPOSITION

Fabric—the packing of component elements in space—is the heterogeneity obvious as one looks at a weathered concrete structure or at a broken or sawed surface of concrete. Fabric includes all of the structural elements, ranging in scale from gross to atomic, and comprises both structure and texture as those terms are used in rock description. The fabric appears on the scale of the lift or course or batch or the structural crack, on the scale of the coarse aggregate, on the scale of the sand grains or the air voids in the mortar or the "microcracks," on the scale of the residual unhydrated cement or the calcium hydroxide crystals, on the scale of the hydrous calcium aluminates and the scale of the poorly crystalline hydrous calcium silicates in the hydrated cement paste, or on the scale of the atomic structure of any crystal forming a part of any of the structural components. Rocks, fabricated metals, and yeast-raised bread are other examples of substances with fabric. The closest naturally occurring analogue among rocks to the fabric of concrete is graywacke conglomerate with abundant matrix. The closest naturally occurring analogue to hardened cement paste is silty clay.

Fabric and composition together define, characterize, and form the basis for descriptive classification of solid multicomponent substances. Composition and fabric are so closely interrelated in concrete that they cannot be clearly separated.

One important decision in a petrographic examination is the decision whether the request for the petrographic examination was made because of problems created by the physical structure of the concrete or because of problems created by its chemical composition. Problems arising from the physical structure or fabric include inadequacies in mixing, consolidation, and inadequacy of the air-void system to provide frost resistance. Problems arising from the chemical composition include those resulting from errors in batching, reactions between cement and aggregate, reactions between a contaminant and cement paste, and reactions between cement paste and solutions from external sources. Were the construction practices employed suitable for producing concrete capable of giving satisfactory service in the particular environment and exposure? Were the materials that were chosen susceptible to participation in chemical reactions that have deleterious consequences? Was there a failure to modify the environment, for instance, by improving the drainage so as to increase the ability of the concrete to survive it? Is the difficulty principally physical or principally chemical? Usually several causes have interacted, but one is probably the originator; if it can be identified, the appropriate techniques are more clearly pointed out.

Investigating composition and fabric provides a specific, unique definition of what is being examined. The standard tests do not always supply information that permits discrimination between one piece of concrete and another, but direct observation on the relevant scale does. There are *n* possible concretes all having 2-in. slumps, with air contents of 5 per cent, with 4500-psi compressive strength at 28 days, but the No. 2 cylinder in the set of 3 broken on Day A in Laboratory B is unique and different, perceptibly and logically, from Nos. 1 and 3 and from all the members of the other possible sets, and its top is different from its bottom as cast. The salient lesson from the study of composition and fabric of concrete is the individuality and uniqueness of each structure or part of a structure, of each specimen and each thin section; this individual combination of fabric and composition reflects the history and conditions the future performance of the concrete. What is investigated at any time is particular concrete, not concrete in general. Each structure and each part of a structure is unique in terms of composition, fabric, history, and exposure.

COMPARISONS

To say that each structure and specimen is unique does not mean that comparisons are useless or impossible; they are essential, and concretes can be rationally grouped and usefully compared within classes and between classes, if the basis for the grouping is objective. Each comparison is an abstraction that leaves out of account some characteristics of the things compared, so that it is necessary to bear in mind that the accidentally or deliberately omitted factors may prove to be important. Paste, mortar, or concrete of known proportions, materials, age, and curing history offer the logical basis for comparison and extrapolation; laboratory specimens made to be examined or salvaged just after having been tested for strength provide a good source of such comparative material. Specimens exposed to laboratory air outside the moist room or curing tank for more than a few hours are much less suitable, because specimens that are cracked or that have slender cross sections sometimes carbonate very rapidly. Specimens exposed to simulated weathering tests, or wetting and drying cycles, or prolonged drying are not to be considered as representative of normally cured or of naturally weathered concretes. Natural weathering differs from part to part of a structure, as well as from climate to climate and subgrade to subgrade.

INTERPRETATION OF OBSERVATIONS

Normal Concrete:

For this discussion, "normal" constituents and fabrics are defined as those present in serviceable concrete of the class and age in the region. "Serviceable" is used instead of "undeteriorated" because it is possible to tell whether concrete in a structure is serving as it was intended to, but the criteria that distinguish inevitable chemical and physical changes from deterioration in concrete 20 or 50 years old have not been well established.

The most valuable information that can be obtained by petrographic examination of concrete comes from the examination of normal concrete; only by comparison with the range of constituents and fabrics in normal satisfactory concrete can that which differs from the normal be recognized and its differences specifically defined. Unless it can be demonstrated that the constituents, or the proportions of constituents, or the fabric, depart from those found in serviceable concrete of the age and class in the region, there is no logical basis for assuming any connection between constituents, or proportions, or fabric, and service behavior. Even when it can be shown that a concrete has a peculiar service record and some unique feature or features not shared by a dozen others of comparable class, age, and provenance, it remains to be seen whether the known unique feature and the peculiar service record are causally connected, or whether both are related to some third or *n*th factor that is the effective cause of the abnormal behavior.

Class of Concrete:

The restriction to concrete of one class is necessary because changes in cement content, water-cement ratio, and maximum size of aggregate large enough to change the class entail such large changes in properties that no close comparison will be significant. If, for example, the criteria for paving concrete are applied to mass concrete, all mass concrete appears very inferior, which it is not for the purpose it is intended to serve. Class of concrete is important in the definition as it implies relative homogeneity in mixture proportions, particularly in water-cement ratio, cement factor, and maximum size of aggregate. It is possible by microscopic methods to sort mass concretes that are fairly homogeneous in cement content and water-cement ratio in order of increasing age, or it is possible to sort mass concretes fairly homogeneous in age in order of increasing cement content. In terms of the ability to sort mass concrete microscopically, "fairly homogeneous" in cement content and water-cement ratio means a maximum difference in cement content between concretes of about 0.5 bags per cubic yard, and 0.1 by weight in water-cement ratio.

Age of Concrete:

Some restriction on the ages of concretes compared is necessary unless age is the variable being studied. Unless the age is known or unless one has younger and older concretes of otherwise comparable characteristics, so that the age of the unknown may be estimated in relation to the knowns, it may be impossible to judge the significance of observations. For example, in one case calcium sulfoaluminate was found in many voids as far as 5 in. from the outer surfaces of a concrete pavement of high flexural and compressive strength and of unknown age. In other field concrete from the region, calcium sulfoaluminate is commonly present in concrete over five years old made with Type I or Type III cement, but it is not abundant and is confined to voids near outer surfaces. If the concrete of unknown age is in fact five or seven years old, it differs conspicuously from others of comparable age and class in the region and the difference probably justifies some concern about its future; if it is 15 years old, it is peculiar, but the peculiarity is probably of less practical importance.

Provenance of Concrete:

Restriction to one region assists rational comparison from several points of view. The aggregates economically available in an area are determined by the regional geology and consequently show some homogeneity of composition resulting from similarity of origin and history. In a particular region, cements and aggregates economically available are used in making concrete which is exposed to the climate characteristic of the region—the prevailing temperature range and temperature frequency distribution and the characteristic amount and sequence of precipitation. The extent of a region of comparable concrete may vary from a few square miles to many thousands, depending on variation in: (1) *regional geology*—as it determines quantity and uniformity of aggregate supply; (2) *topography*—a region of low relief and generally uniform slope such as the Great Plains, or the Atlantic or Gulf Coastal Plain, has widespread, essentially comparable range and distribution of temperature and precipitation, but in a region of high relief and broken slopes, temperature varies considerably with altitude, and precipitation with orientation to prevailing winds, making important differences in exposure over short distances; and (3) *patterns of distribution of aggregates and cement from competitive sources*—in some areas, only one type of natural sand and gravel is available; no manufactured aggregate is produced, and synthetic aggregate sources are not common. Metropolitan marketing areas served by water transportation usually have available a selection of natural coarse and fine aggregates, manufactured coarse aggregates, and synthetic aggregates. All variations between the two extremes just mentioned can be found in availability of aggregates.

Cement plants per state range from none in New Hampshire and Vermont to 22 in Pennsylvania [*34*]. Ports and coastal areas may be served in periods of high construction activity by overseas and domestic cement sources.

An additional influence that may appear is a prevailing engineering opinion, in an organization placing concrete in a large area, on what is desirable in mixture proportions or methods of placing or consolidation. In building gravity dams the Corps of Engineers restricts the height of a single lift to 5 to 7½ ft [*35*] while the Hydroelectric Power Commission of Ontario has placed gravity dams up to 70 ft high in one continuous operation [*36*]. The intention in the first case is to minimize heat generation and in the second to eliminate horizontal construction joints. Such differences in emphasis entail differences in mixture proportions, plant, and construction practice that are bound to affect the fabric and character of the concrete. The existence of satisfactory structures built in many different ways underlines the need to define "normal" concrete in objective and restricted terms.

EXAMPLE

Although the most important kind of petrographic examination of concrete is the examination of normal concrete, usually the concrete that a petrographer is asked to examine has behaved in an unexpected way. Before and during the early stages of the examination, the information on the history and behavior should be considered and the following questions asked:

1. What process or processes could produce the described results?
2. What observable traces could the process or processes leave in the concrete?
3. Would such traces be unique and specific evidence of what is supposed to have happened?

Consider, for example, two 6 by 12-in. cylinders made at a field project during the winter; the 28-day strengths were 885 and 1025 psi, less than 25 per cent of the strengths obtained from earlier and later cylinders made, cured, and tested under presumably similar conditions; the resident engineer suspects an overdose of air-entraining agent.

Processes that Could Produce the Results:

Several distinct processes were considered that could have produced the observed results. Increasing the air content does reduce the compressive strength; the observed reduction is so drastic, however, as to require an increase in air content of at least 15 per cent of air to be a sufficient cause. Mistakes in batching, such as too little cement or too much water or damage due to early freezing, also could produce the observed results.

Traces that These Processes Could Leave:

Excessive air content can be recognized at low magnification and verified and quantified by comparison with concrete of known air content and by count. ASTM Recommended Practice for Microscopical Determination of Air-Void Content, Specific Surface, and Spacing Factor of the Air-Void System in Hardened Concrete (C 457 – 60 T) describes procedures for determining parameters of the air-void system.

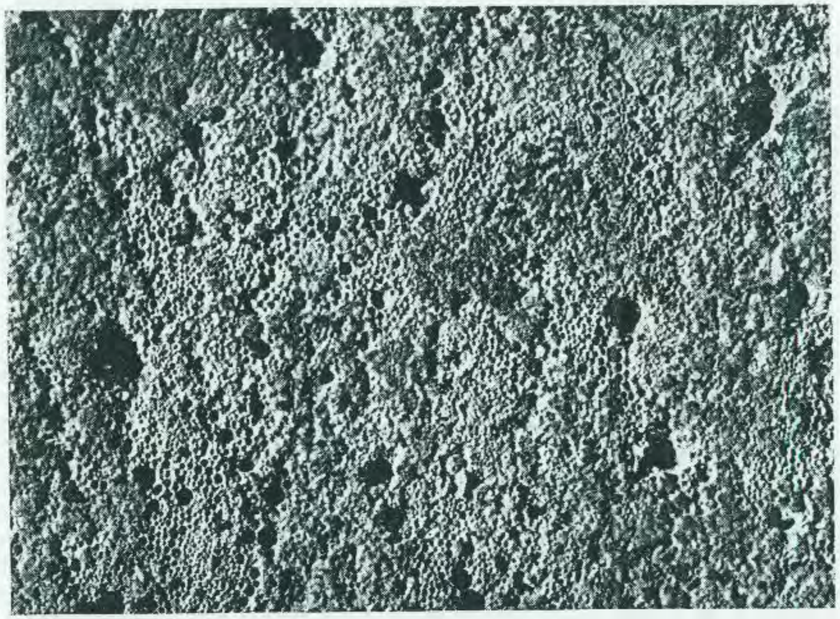
Too little cement can be demonstrated by comparing thin or polished sections from cylinders of normal strength and the same mixture and age, with sections from these cylinders, and finding substantially less cement in the low-strength cylinders.

Too much water produces sedimentation even in air-entrained concrete, and may be demonstrated by comparing finely-ground surfaces of axial slices of cylinders of normal strength and those of reduced strength, and finding wider underside separations between paste and aggregate in the cylinders of reduced strength; the result may be inconclusive. More complete demonstration would result from comparing thin sections cut parallel with the placing direction from cylinders of normal strength, of the same mixture and age with sections cut in the same orientation from these cylinders, and finding probably a little less unhydrated cement with a large development of calcium hydroxide rims along the undersides of aggregate in the low strength cylinders.

Freezing before final set may leave imprints of ice crystals recognizable at low magnification. Freezing immediately after set may produce closely spaced fractures parallel to surfaces exposed to the low temperature [37].

Unique and Specific Evidence:

Lacking the necessary comparative material—cylinders of normal strength and similar age and history from the same mixture—it is very difficult to show petrographically that a large part of the cement was left out or that a large excess of water was put in. By making three sets of specimens from one mixture, one set with normal proportions, one with reduced cement, one with added water, curing all three in standard conditions, breaking part in compression, and sectioning companion specimens, a strong presumption might be established that one of the two working hypotheses was correct; it would not be conclusive proof. Axon's method [38] of determining original mixture composition, by micrometric determinations of aggregate content, paste content, and air content, supplemented by measurements of total evaporable water and evaporable water in aggregate, permits a calculation of cement content of the original concrete, if the age of the concrete can be approximated. Axon [38] and Mielenz [4] have used the method successfully.



NOTE—This is the surface as received, with most of the surface skin rubbed off in handling. Th void walls can be broken with a fingernail The sides of the cylinder show the same condition wit finer bubbles in some areas.

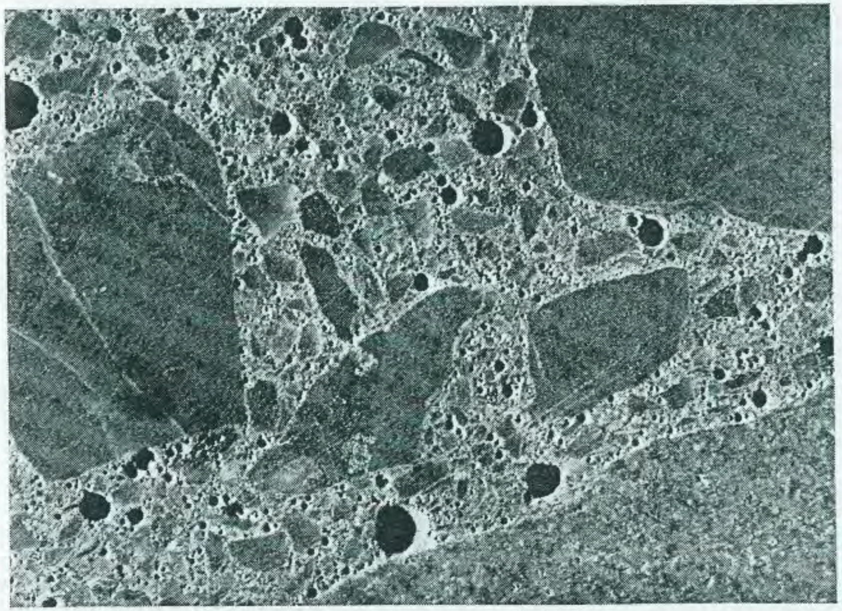
FIG. 1—Void size and distribution in the cement paste just inside the surface skin, bottom o low-strength cylinder (×6).

Demonstration that the concrete froze before final set would depend on finding the imprint of the ice crystals. Excessive air content, on the other hand, can be qualitatively and quantitatively demonstrated without ambiguity.

Let us hope that the resident enginee in our example is right, for the other possibilities that suggest themselves woul be harder to establish. Examination o broken surfaces, outer surfaces, an sawed slices did show that the air conten of the concrete was phenomenally high around 25 per cent (Fig. 1) by comparison with concrete of known air conten

(Fig. 2). The air content was so high and the thin walls of paste between the air voids so fragile that the low strengths were explained adequately by this evidence alone.

This example illustrates how one goes about asking relevant questions that can be answered by petrographic evidence.



NOTE—The air content of the plastic concrete determined by pressure meter was 5.3 per cent; the air content of this hardened beam by micrometric count was 5.7 per cent. This surface is smoother than the surfaces in the other photograph, but this concrete obviously has less than a third of the air content of the other.

FIG. 2—This diamond-sawed and ground slice of air-entrained concrete provides a comparison with Fig. 1 (×6).

The general question in examination of hardened concrete with peculiar behavior is: "Does this concrete differ significantly from comparable normal concrete, with respect to one or more properties that may be shown to be causally connected with its behavior?" The generalized form of the null hypothesis is that the concrete falls within the normal range in respect to a certain property or properties.

Of the four mechanisms considered, three should produce recognizable traces in amounts that can at least be approximated. The freezing-before-final-set hypothesis was poorly defined in effects and their magnitude. The ability to be quantitative and the ability to obtain confirmation by nonmicroscopic means differed in the three hypotheses. Air content is specified in a numerical range, in this case, 4 to 7 per cent measured at the mixer.

Brown and Pierson [*39*] have shown and others confirmed that measurements of the air content of freshly mixed concrete and micrometric determinations of the air content of the same concrete allowed to set undisturbed agree very closely. If concrete with 7 per cent air were produced and if a generous allowance for field and laboratory error is made, it would still be most surprising to find more than 10 per cent air in a supposedly normal cylinder from this project. The low strengths were in the range of strengths of moist-cured foamed neat cement [*40*]. With this background we conclude that unless the low strength cylinders have a total air content above 20 per cent, the excessive air hypothesis could not be accepted as an adequate explanation of the strengths. The hypothesis can be quantitatively expressed, and the quantities can be measured in more than one independent way; the magnitudes involved can be distinguished by anyone who can see through a stereoscopic microscope and ask, "What relation does the air content of A bear to the air content of C?"

The quantitative aspects of both forms of the batching-mistakes hypothesis are not so well explored, and data are less easily verified by independent means. The volume of cement in the original mixture and the volume of calcium hydroxide at a given stage in hydration can be calculated making certain assumptions, which in this example could not be confirmed. However, given comparable cylinders of normal strength, the omitted-cement hypothesis could be checked by comparing sections from the normal concrete with sections from the low-strength concrete to see whether there was a difference between the amounts of unhydrated cement per unit area. If the difference were to provide a satisfactory explanation, it would be fairly large and should be perceptible to an observer able to recognize unhydrated cement in thin or polished sections. Some petrographers might choose to count a group of 300 to 500 points on a section of each kind in order to obtain a result that can be expressed as a number, with the under-
standing that the sample was not ad
quate; others would prefer to look
several areas and express the results
"more than . . ." "less than . . . ,"
"no difference recognized." The proc
dure in checking the extra-water h
pothesis is similar but would concern t
development of calcium hydroxide rir
along undersides of fine aggregate.

The simple, orderly example just d
scribed involves a problem that can
solved without techniques more elabora
than those normally used in several co
crete laboratories in this country in 194
The simplicity and order arise becau
the concrete examined was two te
specimens, and both the history ava
able and the total age of the specime
made it clear—and examination of t
concrete adequately confirmed—that
chemical attack on cement paste h
taken place and that reactions betwe
the particular aggregates and ceme
could not have developed, in the ti
available, to a degree that could renc
them significant effects on the strengt

RECONSTRUCTION OF HISTORY OF FIELD CONCRETE

To pass from consideration of su
petrographic examinations as that
scribed in the previous example to t
petrographic examination of concre
that has aged and perhaps deteriorat
in service, introduces two important n
unknowns—time and the precise
vironment of the structure. The effe
of the passage of relatively short peri
of time on the constituents present
several cement pastes of known wat
cement ratio stored under laborato
conditions have been investigated [*41,4*
but anomalies remain [*43*] in the resu
although both the composition of
pastes and the nature of the envir
ments were known and controlled
more thoroughly than the composit
and environment of any field concret

Composition:

If the changes in composition through time of cement paste in laboratory conditions were known for a representative number of cement compositions and water-cement ratios, effects of both cement-aggregate interactions and of environmental influences would be easier to recognize and could be more usefully interpreted.

Environment:

Why do exposed vertical walls of chert-gravel concrete in the vicinity of St. Louis, Mo., generally have fewer popouts than apparently similar walls in the vicinity of Memphis, Tenn.? The winters are colder in St. Louis, but the mean annual rainfall is lower; and in Memphis a larger proportion of the higher mean annual rainfall occurs in winter. The difference may be that the chert gravel in the Memphis walls is more likely to be critically saturated when it freezes. The Weather Bureau's climatological data for the location are a valuable source of information that can assist in many petrographic examinations of hardened concrete.

The discovery in Mississippi of several highway pavements and associated structures affected by sulfate attack and by combined sulfate and acid attack [47] emphasizes the need to make use of available information on the composition of foundations and subgrades.

Thus, the examination of samples of field concrete after extended service involves an increase in complexity, a decrease in available information, and a decrease in the confidence that may be placed in the answer, as compared to examinations of laboratory test specimens of hardened concrete.

It does not belittle the petrographer to admit that he cannot make bricks without straw; neither can the chemist, the physicist, or the engineer; sometimes the petrographer can recover evidence not accessible by other approaches. Several reasons make reconstructions of the history of deteriorated field concrete difficult; in any particular instance it may be important and impossible in the present state of our knowledge to decide what weight belongs to each.

Deteriorated field concrete that is referred to a laboratory or to a petrographer is almost never concrete that has performed abnormally for one single obvious cause; such simple cases can be and are explained on the spot to the satisfaction of those concerned. The field concrete that is examined by a petrographer is concrete that has worried some responsible person enough to make the effort and expense of sampling and testing appear justified. There is thus a built-in bias in the sampling process. Normally the concrete that a petrographer sees as part of his assigned duties is controversial concrete sent in by organizations with alert conscientious concrete technologists. In practice, this generally means that he sees only the poor concrete produced with better than average control. The worst concrete is rarely sampled and sent to a petrographer; good concrete is rarely controversial.

Furthermore, the older the concrete the less information is likely to be available about materials, proportions, conditions of placing, and the characteristics that undeteriorated comparable concrete would have. Although one can deduce from the concrete that water-cement ratio was high or low, and usually that cement factor was high or low or medium, and the general quality of the workmanship, one cannot reconstruct the alkali content of the cement. Aggregate sources, particularly of natural sand and gravel, can be located from their composition—the constituents present and their size

distribution are diagnostic of the region and sometimes of the particular source.

Finally, deteriorated field concrete usually shows superimposed traces of several processes, with at least one in an advanced stage. The most advanced process may conceal the evidence of others that were more important in effect. Frequently the most conspicuous process is carbonation of outer surfaces and along the borders of old cracks.

Laboratory test exposures are simplified compared to natural exposures by the exclusion of some factors and the regulation of those retained and often are "accelerated" by altering some factor so as to remove it from the range possible in nature. Consequently, a laboratory procedure often results in symptoms different from symptoms encountered in a field example of the process the test is intended to simulate.

Samples of field concrete, when examined using light microscopy, frequently are found to contain secondary calcium carbonate near their outer surfaces, along old cracks, and sometimes in the interior. Such calcium carbonate, when examined by optical methods, is generally found to be calcite, rarely aragonite, and almost never vaterite, the form-birefringent spherulitic calcite with interstitial water. Vaterite, however, was found by optical methods to be common on mortar bars that had been tested according to ASTM Test for Potential Alkali Reactivity of Cement-Aggregate Combinations (C 227) and had been found on concrete specimens tested for resistance to freezing and thawing according to ASTM Test for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water (C 290 – 63 T). The use of X-ray diffraction to examine cement-paste concentrates from field concrete has revealed that vaterite, not recognized by optical methods, is frequently a major constituent of the secondary calcium carbonate [48], especially on samples from seawater exposures or from other wet environments. Vaterite is known to persist for several months in laboratory specimens stored in room conditions. The sequence from poorly crystallized vaterite, calcite, and aragonite to well-crystallized calcite in the carbonation of pastes and mortars has been clarified by Cole and Kroone [49], and vaterite is now known as a natural mineral [50].

Accelerated freezing and thawing in water according to ASTM Method C 290 produces a characteristic loss of surface skin and loss of mortar, which is not like the condition of specimens exposed on the mean-tide rack at Eastport, Me. [51]. Some field concrete, deteriorated by natural freezing and thawing, develops sets of subparallel cracks normal to the placing direction of the concrete or deteriorated regions parallel to the nearest free surface. These phenomena are not reproduced in accelerated freezing and thawing in water.

Field concrete that has deteriorated primarily because of the alkali-silica reaction usually has much more advanced and conspicuous internal symptoms of this reaction than are found in mortar bars of expansive combinations examined after test according to ASTM Method C 227. On the other hand, some field concrete regarded as undeteriorated has shown a range of evidence of alkali-silica reaction.

Alkali-carbonate and alkali-silica reactions exist together in varying degrees of development in some concretes [18], and inconspicuous degrees of reaction may be the only recognizable peculiarities in cases of unsatisfactory service with possibly expensive consequences [52]. The several alkali-carbonate reactions [53] include dedolomitization and rim-forming reactions [17,53,54]. The effects of rim-forming reactions are as yet inadequately known, although they appear to reduce strength [53].

CLOSURE

It was true in 1955 and still is that we do not yet know enough about the hydrous calcium silicates that hold concrete together, the other compounds associated with them, and the varying successions of compounds in laboratory and field hydration of concrete. For instance: hexacalcium aluminate trisulfate hydrate [55]—more usually known as "high sulfate sulfoaluminate" or ettringite—is a normal early hydration product of most cements. It is not stable in the presence of tricalcium aluminate when hydration can continue, and frequently disappears from cement pastes after longer curing. If it is found in a 20-year old concrete, does it indicate some abnormality? Calcium aluminate monocarbonate (or monocarboaluminate) [15,55] is found in laboratory cement pastes and in field concrete [18,48]. In the laboratory it can be produced by accidental carbonation or by the addition of finely ground calcite to the freshly mixed paste [55]. Hadley [53] recognized it at the interface of dolomitic limestone and cement paste in dedolomitization. What is its effect in field concretes with and without carbonate aggregates [56]?

The measure of progress and the results of the use of newer techniques including X-ray diffraction, differential thermal analysis, electron microscopy and electron diffraction are that the questions listed above, and others, are obvious to me in 1965, although I could not have formulated them in 1955. "Things which are seen"—concrete and mortar—"were not made of things which do appear" [57] to the eye and to the light microscope. The use of the newer techniques mentioned and of the electron probe and infrared spectroscopy, in conjunction with the observing eye and the light microscope, still offers the chance of sorting out the qualitative and quantitative differences in hydration products and in submicroscopic fabric that are related to serviceable and deteriorated concrete.

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