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DIAGNOSING CONCRETE FAILURES

by

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DIAGNOSING CONCRETE FAILURES

INTRODUCTION

It was with great pleasure that I accepted the invitation extended by Professor Charles T. G. Looney to present the second lecture of the Stanton Walker Lecture Series on the Materials Sciences here at the University of Maryland. Not only is this opportunity a great honor, but I am grateful for the privilege to participate actively in extending this tribute to a man who has contributed so much to an understanding of concrete, its production, control, and use. There are no narrow confines to the part he played; we have known him in the laboratory, the office, the plant, the jobsite, the conference room, the speaker's rostrum, the classroom—a consistent force promoting greater knowledge, improved practices, and responsible performance.

With such a man before us it is not surprising that we stand in tribute to him. But, a stranger may wonder why we should talk about failure of concrete at such a time. The hero's acclaim should not recount the battles lost! More still, we here heap our testimony upon that of Dr. Bates, who last year pointed to failure of concrete and to careless ways of many who make and use concrete. Let us tell the stranger though: These are the foe! These are the things that Stanton Walker probed and fought against! Would we could say he had conquered. He did not—though he made advances that are now secure.

Our task now is to more clearly define and identify the causes of failure and abnormal behavior of concrete and to further his efforts to bring them under control.

This lecture covers examination and analysis of hardened concrete to determine its composition and to reconstruct causes of abnormal behavior. In this context reference is made to failure and abnormal service of concrete as a material, rather than failure or inadequate service of structures and pavements that arise in appropriate design of members or of the structures themselves or in defects of foundations or other environmental conditions that impair performance by unexpected loading, impact, lack of support, or other unanticipated conditions of stress.

Failure of concrete is performance not meeting the established or implied criteria for particular work under the conditions of service imposed. Failure of concrete may relate to defects of quality that impair the soundness and structural competence of the material, or it may be lack of or progressive loss of esthetic qualities that are significant with respect to the architectural value of the work. Consequently, to some extent, the conclusion that concrete has failed or is in danger of failure is a matter of subjective judgement and, in

any event, must be reached only with due recognition of the specifications under which the concrete was formulated and manufactured. What is failure to one engineer or architect may not be failure to another, and failure in one situation is not failure in another situation.

Deterioration of concrete is progressive loss of those qualities that are necessary for adequate performance under the conditions of service imposed in relation to the established or implied criteria for the work. In speaking of deterioration in this sense, one should always imply "excessively rapid" deterioration inasmuch as portland cement mortar and concrete are only metastable under even natural atmospheric conditions and their deterioration in a long-range sense is inevitable.

In general, either of two circumstances serve as a basis for an investigation of concrete, namely, (1) determination of the properties of concrete in order to establish its ability to perform properly under the anticipated conditions of service and (2) determination of the cause of observed failure. Although the former is very important and the more common basis for testing and analysis of concrete, it is the objective of this paper to examine the latter subject, that is, to review procedures that are or can be employed to establish the cause or causes of failure of concrete in service. Such an investigation may be undertaken for a variety of reasons, such as to establish remedial measures that may be necessary to render the concrete into a condition that will withstand the destructive processes in a satisfactory manner, to determine responsibility for the defects that promoted the failure, or to obtain information that will permit avoidance of a recurrence of failure in this or other construction. The objectives of the investigation will dictate the procedures and the extent of the methods of testing and analysis that are likely to be most effective.

THE PROCESS OF DIAGNOSIS

Diagnosis of abnormal behavior of hardened concrete is the identification of a deleterious process that has acted against the concrete to produce unsatisfactory performance. The concrete as such may or may not have been defective as a material; for example, well-proportioned and well-placed concrete may be destroyed by early freezing. On the other hand, a deficiency may exist without the occurrence of abnormal behavior, either by reason of the degree of deficiency or because the defect was not put to the test. In most instances, examination, testing, and analysis of hardened concrete will reveal some defects, such as improper protection and curing, excessive water content, incorrect air content, excessive water-cement ratio, unsound constituents in aggregate, a cement-aggregate reaction, and so on. But also, by the same token, many of these defects will not be pertinent to an observed failure or other aspect of abnormal behavior. On the other hand, failure may arise only be-

cause of the coincidence of a deleterious process and a succession of defects that, together, establish the condition of failure. That is to say, the concrete, under the conditions of service imposed, could have provided adequate performance if only improper curing or protection or improper finishing or excessive water-cement ratio were to be sustained.

The definition indicates that the diagnosis involves discovery of a deleterious process. In order that the concrete will be disrupted or decomposed, the necessary levels of energy must be provided. The defects mentioned above establish a level of permissiveness or susceptibility, but the failure is accomplished only through the performance of work by physical or chemical processes.

Listed below are defects of hardened concrete, their origin, destructive processes that are at work on concrete, and phenomena of failure. In any instance of failure or abnormal behavior of hardened concrete, the diagnostician should attempt to tie these factors together into a coherent history. Examples of features associated with various types of failures and abnormal behavior of concrete are shown in accompanying Plates 1 through 21.

Defects of Hardened Concrete

- Excessive absorptivity
- Excessive permeability
- Inadequate air-void system
- Low strength
- Low abrasion resistance
- Excessive volume change with wetting and drying
- Excessive volume change with heating and cooling
- Chemical instability of the constituents
- Nonuniformity
- Discoloration of surfaces or efflorescence

Origin of Defects of Hardened Concrete

- Defective concrete-making materials or combinations
- Defective proportioning
- Defective batching and mixing
- Defective transportation procedures
- Defective placing and compaction
- Defective forming and finishing
- Defective protection and curing

Deleterious Processes Affecting Hardened Concrete

- Excessive loading
- Excessive impact
- Drying
- Carbonation
- Freezing and thawing

Cement-aggregate reaction
Autogenous, expansive reactions of aggregates
Autogenous, expansive reactions of contaminants
Deleterious hydration reactions of cement
Deleterious reactions of cement and admixtures
Deleterious reactions involving substances from external sources
Temperature changes

Phenomena of Failure

Surface staining
Excessive wear
Spalling, scaling, or popouts
Cracking
Excessive expansion
Excessive shrinkage
Excessive deflection

PRELIMINARY INVESTIGATIONS

Manifestations of Failure

The first phase of any such investigation is to establish that a failure has indeed occurred. As is indicated above, subjective judgements are important in individual situations. Any such questions should be resolved and a decision made on the significance of the defect that has been observed. That is, is the blemish, the crack, the low indicated strength, the observed disintegration such as to justify investigation. Second, is the defect real, that is, for example, is the low strength observed in testing of a control cylinder representative of the quality of the concrete in the structure or is it spurious as a result of improper sampling of the concrete, mishandling or improper protection and curing of the sample, or improper testing.

Assembly of Records

Any significant investigation of a failure of concrete should be preceded by assembly and review of records pertaining to the specifications, the construction operations, and the concrete-making materials. Of course, minor defects might most efficiently be studied prior to such research so as to pinpoint their nature and probable causes. Such records should establish the nominal requirements for the materials and for the work and may reveal circumstances or conditions that are the cause or have contributed to the subsequent failure of the concrete. Of particular importance are concrete-control reports, test data on aggregates, cements, and admixtures, and reports by inspectors and engineers.

Under some circumstances, it is helpful to confer with suppliers, contractors, and project engineers, or to interview workmen to obtain detailed information that is not included in the records. The information so obtained is occasionally startling. Additional valuable information that aids in explanation of the failure may frequently be obtained by conversations with owners and occupants, especially as to the development of symptoms of distress and failure and any circumstances that seem to have been associated with the onset of failure, such as the ambient conditions and conditions of service.

Field Investigations

Field investigations of significant failures comprise three steps, namely, (1) visual examination of the affected concrete to establish the nature and extent of the failure, (2) field tests and surveys to evaluate the extent of failure and to define the condition of the structures involved, and (3) taking of samples to be employed in laboratory tests.

The visual examination should be such as to permit location of all affected structures or portions of structures, description of the external aspects of failure, description of environmental and service conditions that appear to be pertinent to the condition of the concrete, and examination of sources of supply of the concrete or concrete-making materials. Such examinations should include detailed photography of pertinent features of the construction, its environs, and the indications of failure.

From the findings of the visual inspection, any necessary field tests and surveys can be outlined. This stage will include surveying to establish alignment and grade of structures that appear to be displaced, measurement and location of defects, establishing of reference points and initiation of measurement of volume change or continued movement of structures, evaluation of the quality of concrete in place such as by loading tests, use of the sonoscope and impact hammers, core drilling of structures to evaluate foundation conditions or to determine the location and extent of cracking or other features, and geologic study of aggregate sources, insofar as these are germane to the failure.

Taking of samples of concrete or of other materials for laboratory testing and analysis presents great problems of judgement in order that the samples are truly representative of the conditions to be studied, that they are sufficient in number to exemplify the range of conditions that exist, but so that they are not excessive with respect to the technical requirements, the value of the potential findings, or the authorized budget appropriated for the investigation. It is not completely facetious to note also that the sampling should not be so extensive as to endanger the stability of the structure that remains thereafter.

Sampling should be done with complete objectivity so that the suite of samples is not weighted with either the unusually poor or the unusually sound materials. Samples demonstrating unusual or extreme conditions may be of value in identification of causes of distress or failure and so may be worthy of special study, but they should be kept apart from samples that are randomly or systematically taken to statistically exemplify the materials under study.

In securing the samples care should be taken to avoid disturbance or contamination of the materials in ways that may either prevent adequate testing or analysis in the laboratory or even contribute to misinterpretation. For this reason, coring in place is preferable to sampling by other means because the concrete is disturbed to a minimum, whereas use of sledges or air hammers may induce internal fracturing or may so disrupt the concrete as to make it difficult or impossible to describe its structure accurately and in detail.

The sampling should include both near-surface concrete and concrete at depth inasmuch as they may differ substantially in development of cracking, deterioration of the cement paste, progress of cement-aggregate reactions, and other features.

The samples should be sufficient in size and number to permit application of all necessary laboratory procedures. That is to say, the planning of the sampling program and of the laboratory investigation should be coordinated beforehand so that the physical tests, petrographic examination, and chemical analytical procedures individually can be applied to representative and undisturbed material that is available in sufficient quantity to yield valid data. For example, the petrographic examination is more difficult and less thorough and reliable if it must be performed on concrete that has already been subjected to a compression test or to a freezing and thawing test.

Samples should be identified and oriented by painted or inked markings on the material itself, if feasible, and should be packed so as to be properly protected from damage. Concrete should be wrapped and sealed so as to preserve the moisture content existing when the sample was taken. Complete data on the location of the source of the sample, the direction of drilling, the depth from which the core was taken, and other pertinent information should be transmitted to the laboratory.

LABORATORY TESTING

Receipt of Samples in the Laboratory

Cores and groups of samples received at the laboratory should be examined visually and described (logged) so that all features and variations of composition and internal structure are recorded. This

description should include: superficial effects, such as pattern cracking, scaling, popouts, staining, carbonation; general deterioration; secondary deposits; evident variation in composition and grading of the aggregate; segregation; variation in color of the cement; variation in distribution of voids; and related phenomena. Photographs of the samples are usually helpful supplements to the descriptive record.

This cataloguing of the samples and any possible classification of the samples into groups based upon their source and characteristics, afford a basis for selection of portions to be subjected to individual tests and analyses.

Laboratory tests typically are of three types, namely, (1) tests to establish the physical properties of the samples, (2) visual and microscopical examination, that is, petrographic examination to establish the nature of the concrete and its constituents and to describe features of interest, and (3) analytical techniques by which the composition of the concrete may be determined in whole or in part.

Physical Tests

ASTM and other methods of testing provide means by which the properties and characteristics of samples of hardened concrete can be determined. These methods permit evaluation of such features as strength, elasticity, creep, unit weight, volume change with wetting or drying, thermal properties, permeability, resistance to freezing and thawing, and expansion in storage. Similarly, samples of the individual concrete-making materials, if available, can be subjected to physical tests to establish their quality and characteristics.

These procedures are well standardized and the literature contains abundant information concerning interpretation of the results. Hence, they will not be discussed further here.

Petrographic Examination of Hardened Concrete

Petrographic examination of concrete is visual and microscopical examination of samples directed to description of the constituents, the proportioning and distribution of the constituents, the external surfaces, and the internal structure of the concrete^{(1)*}. The procedures include inspection with the unaided eye, use of a hand lens usually at magnification ranging from 10 to 20 diameters, use of a stereoscopic microscope usually at magnification ranging from 10 to 150 diameters, and use of petrographic or metallographic microscopes, usually at magnifications in the range from 100 to 1000 diameters.

Visual inspection and examination by means of the stereoscopic microscope can provide valuable information when applied to original

* Numerals in parentheses refer to references listed at the end of the text.

exterior surfaces, surfaces of fractures, voids, and surfaces of fresh fractures through the cement paste and aggregate. During this examination the following features can be studied and described in some detail.

- Composition and condition of the aggregate
- Cement-aggregate reactions
- Deterioration of aggregate particles in place
- Hardness and denseness of the cement paste
- Tenacity of the cement paste-aggregate bond
- Homogeneity of the concrete
- Occurrence of settlement and bleeding of the fresh concrete
- Depth and extent of carbonation
- Occurrence and distribution of fractures
- Characteristics and distribution of voids
- Presence of contaminating substances
- Occurrence and identity of secondary chemical deposits

As a part of this examination, noteworthy portions of the concrete, secondary deposits, or particles of aggregate are separated for more detailed microscopical study or for chemical, x-ray diffraction, or other types of analysis. If pertinent to the investigation, the aggregate can be analyzed petrographically by breaking down a representative portion of the concrete.

Formed or finished surfaces should be examined in detail visually and under the stereoscopic microscope to identify and describe any features that are pertinent to the observed distress and failure of the concrete. Such an examination will reveal lack of proper strength and abrasion resistance of the superficial mortar, presence of laitance, the spacing and nature of any cracks, evidences of deterioration or disintegration of the cement paste, degree of bond of the near-surface mortar to the concrete at depth, features related to pits, spalls, and staining, the identity and location of exudations from the concrete, efflorescences, or other surface deposits, presence and identity of coating materials applied to the concrete, and other significant features related to the placing, exposure, and service history of the concrete.

As part of the stereoscopic microscope study, it is helpful to prepare sawed and finely ground surfaces, preferably from the formed or finished surface inwardly across the planes in which the concrete was deposited. Such surfaces reveal details of the texture and composition of the near-surface cement paste and any variations in these characteristics with depth in the concrete. Also, the interface between aggregate particles and the cement paste can be examined in

detail and any reaction rims or secondary deposits or separations can be discerned. Details of textural and compositional changes in the peripheral portion of aggregate particles and the adjacent cement paste frequently can be made visible by acid-etching of the ground surfaces. The presence of fractures and their distribution can be observed in relation to the exposed surfaces, particles of aggregate, or locations exposed to concentrations of stress or aggressive chemicals. Also, inhomogenities, such as channels created by bleeding of water, development of concentrations of air voids, segregation of constituents of the fresh concrete, or remixing and retempering of stiffened concrete, can be observed. During this phase of the examination, specific areas may be selected for thin sectioning or preparation of polished and etched surfaces.

As will be described below, sawed and finely ground surfaces of concrete are used in microscopical analysis of concrete, both to determine the air content and various parameters of the air void system in accordance with ASTM Recommended Practice C 457⁽²⁾ and to establish the relative proportions of the coarse and fine aggregate, cement paste, and air voids by microscopical traversing by the linear traverse or point-count procedures.

Examination of surfaces of fractures produced in the laboratory is a valuable means to establish qualitatively the strength and denseness of the cement paste and the quality of bond that exists between the cement paste and the aggregate. Sound, well-cured concrete of low water-cement ratio that has been properly cured is tough and compact. Internal fractures are sparse. Intense carbonation extends inwardly from the surface in a superficial zone that is usually less than 1/8 inch thick but this zone is tough, dense, and continuous with the cement paste and mortar matrix at greater depth. Such carbonation results from slow interaction of the hardened cement paste with carbon dioxide of the atmosphere.

On fresh fractures, sound cement paste is gray, vitreous in luster, and amorphous in appearance. At magnification of about 100 diameters or greater particles of partially hydrated clinker are visible and, under ordinary conditions of curing and service, are common to abundant in the cement paste, indicating a substantial capacity of the concrete for continued strength gain and rehealing of microfractures under moist conditions. New fractures intersect many sound particles of both fine and coarse aggregate, a fact that demonstrates good quality of bond of the cement paste to the aggregate. Aggregate sockets and air voids are gray and are free from secondary deposits, except for occasional platy crystals of calcium hydroxide. Any reaction rims on aggregate are faint and have created no fracturing either within the aggregate particles or in the adjacent cement paste. Discoloration of the cement paste in shades of blue-green or green is typical in concrete containing blast furnace slag

aggregate or portland-blast furnace slag cement, and may also develop in pavements laid upon slag base-course aggregate as a result of upward movement of moisture.

With increase in water-cement ratio, decrease in compaction, inadequate curing, inadequate protection from drying or freezing before hardening or at very early ages, or initiation of deterioration of the concrete for any of many reasons, the firmness and denseness of the cement paste and the quality of cement paste-aggregate bond are decreased. The cement paste is less firm, softer, lighter in color, more porous, internally fractured, and less vitreous and possibly somewhat granular in appearance, in contrast to properly cured cement paste of low water-cement ratio. Voids commonly occur at the periphery of aggregate particles; these voids are concentrations of small spherical bubbles of entrained air around the perimeter of coarse aggregate as well as both large, well-defined air voids and irregular voids representing accumulation of bleeding water beneath particles of coarse aggregate in the fresh concrete. Openings at the periphery of aggregate particles and air voids are commonly partially or almost completely filled by secondary deposits of calcium hydroxide, calcium carbonate, calcium sulfoaluminate, or other substances.

When concrete of inferior quality or concrete affected by some process of deterioration is broken, the fractures tend to pass around particles of aggregate, rather than through them. As a result, the concrete may appear to be deficient in aggregate upon superficial examination. Aggregate sockets that are so revealed commonly are very light gray or white because of the presence of secondary deposits. Careful examination may reveal fine, ramifying microfractures in the cement paste, such fractures can be observed at the periphery of air voids, where a thin membrane of brittle cement paste is present. The fractures may be empty or they may contain secondary chemical deposits resulting from deterioration of the cement paste, attack of aggressive waters on the cement paste or aggregate, or cement-aggregate reactions. Occasionally, near-surface fractures contain intrusions of paint, curing compounds, sealers, waxes, or other materials applied to the surface of the concrete that will indicate the age and history of development of the crack system.

Specimens for detailed petrographic examination should be selected on the basis of the study at low or intermediate magnification under the stereoscopic microscope. Such specimens may be typical portions of the cement paste, examples of cement-aggregate reactions, secondary deposits in voids and cracks or other features. The detailed examination is conducted by use of granular mounts in immersion oils, thin sections, or polished and etched surfaces, or a combination of these methods. Granular mounts in oils can be rapidly prepared and, with experience, can be used to

determine the relative abundance of unhydrated cement, the kind of cement (i.e. portland cement, portland-blast furnace slag cement, or portland-pozzolan cement), presence of mineral admixtures or diluents, degree of carbonation of the cement paste, identity of many secondary deposits, identity of selected aggregate particles, and so on. Immersion mounts allow determination of index of refraction of substances and other optical properties so that identification is more sure. Stains and dyes are a valuable aid in this type of examination.

Petrographic thin sections permit thorough examination of concrete because all details of texture and structure are preserved. Such sections are slices of concrete, mortar, aggregate, or similar materials that are cemented to a small glass plate, usually about 1-1/16 by 1-13/16 inches in area, and then are ground thin enough that they will readily transmit light. In order that details of texture and structure are clearly evident in the cement paste and in very fine-grained particles of aggregate, the sections should be no more than about 15 microns or .0006 in. thick. When so prepared, the sections can be examined under the petrographic microscope at magnifications up to about 1000 diameters, or with oil immersion objectives to about 2000 diameters. The composition of the fine and coarse aggregates can be established and evidences of cement-aggregate reactions can be determined. The proportion and some features of composition of unhydrated granules of the cement can be observed, together with any cracking that may be related spacially to granules that include partially hydrated free lime or magnesia. A quantitative determination of the proportion of unhydrated granules of cement in the cement paste matrix can be made by point-count or linear traverse methods. Examination of the cement paste reveals details of its microstructure, presence of mineral admixtures or additions to the cement, alterations of the hydration products, and the identity and distribution of products of cement-aggregate reaction that may have penetrated the cement paste. Secondary deposits in air voids usually can be identified readily.

Polished surfaces also are employed in the study of concrete and mortar. Such surfaces permit application of microchemical tests and etching techniques that are especially valuable in identification of constituents of unhydrated granules of cement. Hence, considerable information can be obtained about the composition of the cement unless the cement has been completely or almost completely hydrated or otherwise altered. Crystals of tricalcium silicate, dicalcium silicate, calcium oxide, and magnesium oxide can be identified, and the nature of the interstitial phase within the granules of cement can be described. Masses and individual crystals of calcium hydroxide are clearly evident in the cement paste following proper etching of polished surfaces.

Determination of Cement Content by Chemical Analysis

Although hardened concrete may be subjected to chemical analysis for any of many reasons the most common is determination of the proportion of cement used in the mixture. ASTM Method C 85⁽²⁾ and variants of it are usually employed for this purpose.

These methods are based upon the fact that portland cement and its products of hydration are more readily decomposed and dissolved in dilute hydrochloric acid and caustic soda than are materials that are commonly employed as aggregate. Accordingly, a representative sample of the concrete, suitably prepared, is subjected to sequential digestion in dilute solutions of the acid and caustic soda and the proportions of released calcium and silica are determined. By knowing or assuming the composition of the cement and assuming that all of the soluble calcium and silica were derived from the cement, the cement content of the concrete can be estimated. Any contribution of calcium or silica by aggregate or admixtures creates spuriously high values of indicated cement content. The actual calcium and silica contents of the cement should be employed in the calculation if they are known. If samples of the aggregate and admixture are available, correction factors can be derived by application of the test to these materials; however, the probable validity of the result decreases as the magnitude of the correction increases. Limestone, dolomites, slags, and fly ash contribute calcium to the result whereas slags, cherts, some volcanic rocks, some lightweight aggregates, and many mineral admixtures contribute substantial proportions of alkali-soluble silica.

The test is designed especially for use with portland cement mixtures, but it may be applied where other hydraulic cements are involved if reliable samples of the cement, aggregates, and admixtures are available for use in standardizing the data. However, again, the precision of the result grows less as the magnitude of the correction factors increase.

In general, the indicated cement content is in good agreement with the actual proportion of cement or, if no correction for the effect of the aggregate is made, is higher. In cooperative tests reported by Kriege,⁽³⁾ excellent results were obtained in analysis of a range of concrete mixtures, the maximum deviation being about 0.7 per cent of the actual cement content. However, Ford,⁽⁴⁾ based on an independent study of ASTM Method C 85 and two other similar chemical procedures, concluded: " * * * none of these methods may, apparently, be depended upon to give results closer than within 10 to 20 per cent of the known cement content * * * " of concrete or mortar. Similarly, Polivka *et al*⁽⁵⁾ report an average error of 11.3 per cent in indicated cement content when adjustment is made

for the contribution by the aggregate and the actual composition of the cement or 9.0 per cent when this adjustment is not made. Comparable results are being obtained by others.

The magnitude of possible error, the usual lack of suitable samples of the concrete-making materials, and the general unreliability of the test in analysis of concrete containing cements other than portland cement, pozzolans, or certain aggregates has led to uncertainty about interpretation of the results in many instances. Especial care must be given to sampling inasmuch as there is commonly differential loss of cement paste and mortar in contrast to the coarse aggregate if the concrete is in a state of deterioration or has been subjected to prior laboratory testing. Cores or sawed specimens are to be preferred over random fragments for this reason. Also, molded or formed specimens must be sampled in such manner as to avoid the bias that will result unless account is taken of the higher proportion of cement paste and mortar that is present close to the outer portion of the concrete, where the typical packing of the coarse aggregate does not occur.

Method C 85 is now in process of revision by Subcommittee III-1 of ASTM Committee C-9. One defect in the procedure that should be removed is the lack of a standard method for converting the indicated cement content as a per cent by weight of the concrete to a weight or number of sacks per cubic yard so as to compensate for the yield obtained from the batch of fresh concrete.

An as-yet unpublished procedure developed by the Turkish Highways Department⁽⁶⁾ is reported to determine the cement content of hardened concrete by non-destructive techniques. Total water content is determined by neutron scattering and capillary water is determined as a function of electrical conductance. The water combined in hydration products is calculated by difference and is assumed to bear a constant ratio to cement content. Consequently, the cement content is readily calculated. Data on accuracy and precision of the method are not available. The assumptions are such as to cast doubt on the reliability of the method.

Determination of Chemical Admixtures in Hardened Concrete by Chemical Methods

It would be of value to have available quantitative or qualitative chemical methods to determine the presence and concentration of water-reducing admixtures, set-controlling admixtures, accelerators, and air-entraining agents in hardened concrete. However, among all the substances used as admixtures of these types there is only one of significance whose concentration in hardened concrete can be determined by available methods. This is calcium chloride, which is determined as equivalent chloride ion by either titration or precipitation with silver nitrate from a nitric acid solu-

tion obtained by digestion of the concrete. The method should yield an accurate measure of the proportion of chloride ion in the particular sample under analysis. However, the value thus obtained does not necessarily represent an accurate estimate of the amount of calcium chloride as such which was added to the concrete mixture. Aside from the difficulty of obtaining a truly representative sample, each constituent of the concrete (cement, aggregates, and mixing water) might also contribute chloride ion, which in some instances can total to an amount of chloride greater than is ordinarily employed as an accelerating admixture. Moreover, chlorides may be introduced from external sources if the concrete has been in service, especially through use of de-icing salts. Also, chlorides other than the calcium salt may be involved, so that determination of acid-soluble alkalis, especially sodium, may be worthwhile in particular instances.

If an admixture containing two or more constituents in known proportions has been used, and calcium chloride is one of these constituents, then, in principle, the proportion of this admixture in hardened concrete can be computed from a determination of the chloride content. However, considering normal rates of use of chemical admixtures, the determination requires great precision and the result is open to question if any appreciable proportions of chloride ion could have been introduced otherwise.

A qualitative test for detection of lignosulfonate in hardened portland-cement pastes has been developed by Swenson and Thorvaldson.⁽⁷⁾ In this method, a water extract of the hardened paste is obtained and the presence of lignosulfonate and vanillin is determined spectrophotometrically. Vanillin is one of the reaction products of a lignosulfonate and a cement paste. This method can be used to determine presence of a lignosulfonate or its reaction product in hardened concrete. However, in its present form, the method is not quantitative, although it should be possible to demonstrate whether a lignosulfonate admixture is present and if it is present in proportions greatly in excess of the amount usually recommended.

Substances formed by degradation of lignosulfonate in portland cement mixtures can be detected by characteristic fluorescence of water solutions produced by acid extraction of hardened concrete, mortars, or pastes at ages as great as at least two years. Although not quantitative in its present form, the method is sufficiently sensitive to indicate the presence of lignosulfonate employed in amounts equivalent to less than 0.1 per cent by weight of the cement.

No generally-applicable methods are available for detection, either quantitative or qualitative, of the many other organic compounds that are being used as chemical admixtures in concrete. However, with research, it should be possible to adapt heretofore-

developed chemical procedures to detection and identification of classes of organic compounds that are employed as chemical admixtures, particularly at early ages and when the admixtures have been added to the concrete at unusually high rates. Problems of detection and quantitative determination are very great because (1) the admixtures are used in very small amounts relative to other constituents of concrete so that there is a very unfavorable ratio of material sought to diluent, and (2) complex organic compounds that are the most important constituents of such admixtures are rapidly destroyed or are converted into other substances by interaction with cement. That is, even when we know the identity of the compound or compounds added, we do not, in general, know what compounds to look for in the hardened concrete. A further difficulty derives from the fact that multicomponent chemicals frequently are used as constituents of admixtures. In principle, if the admixture contains one substance normally foreign to concrete detection of that substance would permit a computation of the amount of admixture originally used, regardless of its chemical fate in the concrete. For example, a determination of the element nitrogen might be used to establish the amount of an amine that had been added to the concrete (assuming that no other nitrogen-containing compound had been used). However, products of differing nitrogen assay are used in practice, rather than chemically pure compounds, so that the analyst is frustrated in this approach.

Considering the various difficulties touched on above, dependable quantitative methods for detection of organic admixtures in hardened concrete are not likely to be developed in the near future.

Chemical Analysis of Concrete for Contaminating Substances

Concrete may contain any of a wide variety of organic or inorganic substances, either as contaminants in the concrete-making materials or the fresh concrete or because they were absorbed into the hardened concrete. Inorganic chemicals can be determined by classical analytical methods, although sampling may present a substantial problem and interpretation of the results may not be clear-cut. For example, determination of sulfate to establish the existence of substantial sulfate attack must take into account the sulfate present as calcium sulfate in the original cement and the effects of leaching that may have removed substantial proportions of the cement paste and secondary sulfate following partial deterioration of the near-surface concrete. Detection and quantitative determination of organic substances present individual problems that are commonly insolvable from a practical standpoint on the basis of chemical procedures. Circumstantial evidence available at the jobsite might present the solution to problems of attack of aggressive chemicals upon hardened concrete.

QUANTITATIVE ANALYSIS OF CONCRETE BY
MICROSCOPICAL METHODS

Procedures

The work of Verbeck,⁽⁸⁾ Brown and Pierson,⁽⁹⁾ and others⁽¹⁰⁾ demonstrate the feasibility of determining the air content and parameters defining the size and spacing of air voids in concrete by microscopical methods applied to finely ground surfaces of concrete. The analyses can be made routinely by either linear traverse or point-count procedures. The techniques for evaluation of the air void system in hardened concrete are covered by ASTM Recommended Practice C 457.⁽²⁾

These same methods can be applied to analyze the concrete for the volumetric proportions of aggregate, cement paste, and air voids.

For these procedures, sections are sawed through the concrete, preferably across the layers in which the concrete was deposited. By means of a succession of abrasives plane, smooth surfaces are prepared. If the concrete is weak or significantly fractured or if friable particles of aggregate are present, the concrete should be impregnated by carnauba wax or other suitable materials to permit completion of the plane surface. The wax must be removed from the near-surface concrete by means of a solvent before the microscopical analysis is made.

In the linear traverse method, as applied to evaluation of the air void system, the surface is traversed along a sequence of lines and the length of intercept across each section of an air void encountered is determined by means of a suitable micrometer device. Upon completion of the analysis, the following data are available (1) number of voids intersected, (2) summation of the lengths of the intercepts across the void sections, and (3) the total length of void-free concrete traversed. From these data, based upon several simplifying assumptions, air content, the average size of the voids, and the spacing of the voids in the cement paste can be calculated. The calculation of the spacing factor requires that the cement paste content of the concrete be known. The proportions of cement paste and aggregate are determined similarly.

The point-count procedure utilizes identical specimens and equivalent traversing procedures, but the analysis is accomplished by counting the number of voids intersected by the line of traverse and by observing the presence or absence of an air void only at regularly-spaced points on the line of traverse. The procedure provides the following experimental data: (1) Total points observed, (2) points superimposed on voids, and (3) number of voids intersected by the line of traverse. From these data, the air content, average size of the voids, and, if the cement paste content is known, the spacing factor

of the air void system can be calculated. The procedure also can be employed in total analysis of concrete.

Considerable care must be taken in preparation of surfaces for microscopical traversing to assure that small voids are not obliterated and that edges of air voids and boundaries of aggregate particles are preserved with a minimum of breakage and rounding. The indicated content of air voids and cement paste can be modified substantially by the fortuitous occurrence of large sections of coarse aggregate or concentrations of mortar, such as adjacent to forms and at the sides and bottoms of molds.

Air Void Content

In the microscopical determination of the parameters of the air void system in hardened concrete, all microscopically visible openings in the cement paste matrix or adjacent to particles of aggregate are classified as air voids. Voids within aggregate particles are not included. Air voids that are included in the determination are those that are commonly designated as entrapped air voids as well as those that are usually said to be entrained. In actuality, all air voids in the matrix of concrete literally are entrapped by any of several mechanisms; however, the term "entrapped" air void may be used conveniently to designate those voids that are sufficiently large to be irregular in shape and to be molded against the adjacent particles of aggregate. Frequently, these voids represent bubbles that were in process of escape from the concrete at the time of initial stiffening. They are characteristically larger than 1 mm in diameter. Although the inclusion of these voids in the microscopical determination of the air void system may greatly increase the indicated air content, their presence ordinarily does not significantly modify the indicated spacing factor, which is the primary measure of the value of the air void system in protecting hardened cement paste from the effects of freezing and thawing.

"Entrained" air voids are typically spherical in shape or nearly so and typically 10 to 1000 microns in diameter. They are retained within the fresh concrete by mechanical entrapment among the granular structure of the aggregate, by the viscosity of the cement paste, and by adhesion to particles of cement and to particles of aggregate possessing chemically active surfaces.

As a whole, air voids constituting the microscopically visible void system of concrete produce a "grading" of size comparable to the "grading" of aggregate. The minimum size of void present is controlled mainly by the rapid rate at which air voids of small size dissolve in the mixing water before hardening of the cement paste. Consequently, air voids less than about 7 microns in diameter are essentially non-existent. The frequency of air voids of large size is controlled by numerous factors, the main ones being the kind and

concentration of air-entraining agent, the water-cement ratio, and the compactive effort applied during placing of the concrete. The average size of void tends to increase with decreasing concentration of the air-entraining agent and with increase of water-cement ratio and slump.

The air content of hardened concrete determined microscopically usually corresponds closely with that determined by standard methods on the fresh concrete or by high-pressure meter on samples of hardened concrete. However, the air content of the hardened concrete can be substantially lower than that indicated on the fresh concrete if the concrete upon which the microscopical determination is made was subjected to greater compactive effort than was applied to the fresh concrete used in the test of air content. Such a reduction of air content is not harmful to freezing and thawing resistance of concrete if the fresh concrete was adequately air-entrained.

Similarly, the air content in the uppermost part of a concrete slab, particularly within $\frac{1}{2}$ inch of the finished surface, is characteristically less than that in the concrete at greater depth because the manipulation removes a large proportion of the larger voids. This action may decrease the air void content of the topmost $\frac{1}{16}$ inch to one-third or less of the air void content of the concrete as a whole. Nevertheless, if the concrete was originally adequately air-entrained, the spacing factor is not significantly modified. On the other hand, the specific surface of the void system is increased substantially because of the elimination of the large voids.

Conversely, air content of hardened concrete may be significantly higher than that indicated in the fresh concrete by the physical methods, particularly with high rates of use of air-entraining agents that produce an abundance of very small air voids, at high water-cement ratio, and at high slump. In such instances, the microscopically determined air content may exceed that observed in the fresh concrete by several percentage points and the difference may be reflected in a serious and unexpected reduction in compressive and flexural strength of the concrete.

ASTM Recommended Practice C 457 provides guides for minimum area of surface to be traversed and minimum traverse length required to produce a coefficient of variation of 17 per cent or less in the determined air content. Data on precision of the total analysis procedure will be discussed subsequently.

Additional data are required to establish the reproducibility of the microscopical determination of the air-void parameters as established independently in different laboratories. The scanty information that is available gives cause for concern. Data obtained within a laboratory among operators trained under the same supervision are indicated by available data to be satisfactory. For ex-

ample, in linear traverse analysis of the void system in three concretes by three operators,⁽¹⁰⁾ the air content was found to be within 0.3 percentage points of the average value in all of the determinations, and the spacing factor was found to be no more than 0.0004 in. from the average for the two air-entrained concretes and within 0.006 in. from the average for the non-air-entrained concrete, for which the average was 0.027 in.

Reproducibility of data obtained by the modified point-count procedure is comparable.

Water Void Content

In well proportioned concrete, essentially all of the microscopically visible openings in the cement paste matrix and along the boundary of the cement paste matrix against aggregate particles represent air bubbles that were developed within the fresh concrete during mixing and to some extent during placing and that were preserved as casts by the hardening of the cement paste. The small pits and voids that are common against formed surfaces similarly are casts of original air cells that were present in the fresh concrete. The interior surface of these voids is formed by a smooth glaze of cement paste that was supported in the plastic state by the air pressure within the bubble, the surface tension at the air-water interface, and the rigidity of any adsorbed film of surface active substance that was concentrated at the periphery of the bubble. Unless so supported, the cement paste adjacent to the bubble will collapse into the opening. Consequently, isolated, regularly shaped, and sharply bounded segregations of water cannot exist within the cement paste matrix of plastic concrete.

On the other hand, in concrete in which pronounced bleeding and settlement has occurred, it is common to observe openings and channelways that are both irregular in general form and in details of their inner surfaces. Such openings represent locations of small accumulations of water and zones of movement of water in the fresh concrete. The openings are supported by the granular interlocking of adjacent coarse and fine aggregate. They are most common beneath particles of coarse aggregate and along the sides of large particles of aggregate; in the latter case, a visible channelling or grooving is demarked in the aggregate socket by fine aggregate from which the cement paste has been flushed away by the water flows.

In microscopical measurement of the parameters of the air void system in concrete, such openings are usually recorded as "air voids" because it is impractical for the operator to make a detailed study of the character of the opening during a routine traverse, but, more fundamentally, because such openings function as air voids during freezing of the hardened concrete if they are not filled by water. In actuality, because such openings are always sparse in

concrete, their presence or absence usually does not significantly modify the void spacing factor of air-entrained concrete even though the indicated air void content may be increased by one percentage point or more.

Of course, the observation of the presence, frequency, and distribution of the water voids is an important circumstantial indication of the water content and slump of the fresh concrete and provides a basis for estimating the water content of the concrete. Water voids commonly are less frequent in the uppermost one inch of concrete than in the immediately underlying concrete because of the compactive effort applied in finishing of the exposed surfaces. On the other hand, if finishing is completed before termination of bleeding and settlement of the fresh concrete, such voids may occur throughout the upper portion, possibly being concentrated just below the topmost 1/16 to 1/4 inch that has been densified by the finishing operation.

Total Analysis of Hardened Concrete

Microscopical analysis of hardened concrete by linear traverse or point-count procedures can be used to determine quantitatively the volumetric proportion of aggregate in hardened concrete. If the fine and coarse aggregate are lithologically distinguishable, such as the combination of a crushed limestone coarse aggregate and a natural sand, a quantitative determination of both coarse and fine aggregate can be made by these methods.

Also, these methods can be applied to determine the volumetric proportion of cement paste. At a magnification of about 150 diameters under a stereoscopic microscope with strong illumination, the cement paste can be distinguished with satisfactory accuracy from aggregate particles and voids. Although some very fine particles of sand and rock dust are irresolvable at this magnification, experience shows that cement paste content determined microscopically is typically slightly less by several per cent than that which can be calculated from the proportioning of known concrete mixtures, probably because of loss of a portion of the mixing water by bleeding and evaporation before completion of initial settlement of the fresh concrete. Except for such phenomena, the proportional volume of the cement paste can be calculated as the summation of the absolute volumes of the cement and the mixing water. The cement paste is composed of unhydrated residues of cement, hydration products, and a submicroscopical system of capillary and subcapillary openings. Particles of unhydrated cement and occasional crystals of calcium hydroxide are visible at a magnification of 150 diameters; these are reported as a portion of the cement paste during the analysis.

In performing the microscopical analysis, it is usually helpful to wet the finely ground surface by water so as to permit observation of the aggregate and cement paste below the surface and thus to increase the reliability of establishing the precise location of boundaries and the correct identity of each portion of the surface. Particular attention must be given to detection of thin films or layers of cement paste that separate particles of aggregate from the ground surface; if not correctly identified, the indicated proportion of cement paste will be significantly less than the actual value. Wetting of the ground surface tends to obscure sections of small voids; hence, the determination of air content commonly is more reliable if made on a dry surface.

Although the proportions of fine and coarse aggregate occasionally are the specific subject of investigation and always are pertinent to any analysis of hardened concrete, usually the proportion and quality of cement paste are of maximum significance in determining the strength, durability, and other important engineering properties of hardened concrete. As has been mentioned above, the cement paste can be calculated as the sum of the absolute volumes of cement and mixing water. The closeness of this approximation is indicated by the following data that are obtained on small specimens of concrete that were carefully proportioned and analyzed microscopically:

Cement Content, sk. per cu. yd.	Cement Paste Content, percent by volume			
	Non-Air-Entrained Concrete		Air-Entrained Concrete	
	Actual*	Microscopical**	Actual*	Microscopical**
4	24.68	22.51	23.39	19.67
6	28.61	28.29	26.00	25.49
8	32.30	32.35	29.83	28.89

* Computed as the summation of cement and mixing water.

** Microscopical point-count procedure.

The greatest departure among the results is for the 4-sack mixtures. In these concretes, substantial bleeding was observed and is indicated in the hardened concrete by water voids and channels that constitute 1.08 per cent of the volume of the non-air-entrained mixture and 2.37 per cent of the air-entrained mixture. Addition of these volumes to the observed volumes of cement paste raises the indicated cement paste contents to 23.59 and 22.04 per cent, respectively, these values probably being closer approximations of the actual cement paste content following completion of bleeding to the exterior of the concrete. On the average, the microscopically determined cement paste content of the concretes is 97.3 per cent of that computed from the proportions of cement and water in the batch. Comparable data reported by Axon indicated that the microscopical method yields a cement paste content averaging 97.9 per cent of

that computed from the proportions of the batches of concrete on the assumption that the volume of the cement paste is the sum of the volumes of cement and mixing water. These values are consistent with loss of about 4 per cent of the mixing water by bleeding before hardening of the concrete.

The cement paste content of concrete is not a direct and unambiguous measure of the cement content of concrete. Because the density of water is less than one-third that of portland cement, a variation in water content will create a much greater change in cement paste content of the concrete than will an equal change in the weight of cement per cubic yard. Within the range of plastic concrete mixtures exhibiting little bleeding or segregation, water content can be increased substantially if accompanied by air entrainment or if the concrete is retempered as stiffening occurs. Conversely, water content can be decreased 5 to 10 per cent at constant air content as the result of use of a water-reducing admixture. Hence, at constant cement content, the cement paste content can vary rather widely without indirect effects, such as bleeding and segregation of the fresh concrete, and without essential change in the strength, durability, or other engineering properties and performance of the concrete.

Polivka *et al.*⁽⁵⁾ proposed a procedure by which the cement content is calculated from the microscopically-determined cement paste content of hardened concrete without use of any other experimental data. Although the results appear encouraging, the indicated accuracy is believed to be largely fortuitous because of the untenable assumptions employed.

The determination of cement paste content of hardened concrete can provide valuable information concerning failure or other indications of abnormal behavior of concrete in service. Such analysis is especially meaningful if the proportioning of satisfactory and unsound concrete from the same project can be compared. For example, a concrete patio slab containing portland-blast furnace slag cement was affected by sporadic scaling and surface disintegration as a result of natural freezing and thawing. Microscopical point-count analysis of cores taken from representative sections of sound and disintegrating concrete yielded the following results:

Percent by Volume of the Concrete

Constituent	Sound Concrete	Unsound Concrete	
		Upper 1 inch	Lower 2 inches
Aggregate*	59.6	69.0	74.9
Cement paste	27.8	21.8	17.7
Air voids	12.6	9.2	7.4

* 1-inch nominal maximum size.

The unsound concrete displayed abundant evidence of pronounced bleeding and settlement of the fresh concrete. The proportioning of the sound concrete conforms with the recommendations of American Concrete Institute Standard 613 except for the high air content. The cement paste content of the unsound concrete is substantially below that which can be calculated from the requirements of these standards for concrete to be exposed to freezing and thawing action.

As another example, 3 of 5 concrete cores displayed scaling, spalling, and cracking of non-air-entrained portland cement mortar topping placed on a concrete base. Microscopical analysis of the topping indicated the following:

<u>Constituent</u>	<u>Percent by Volume of Mortar</u>	
	<u>Sound Mortar</u>	<u>Unsound Mortar</u>
Sand	56.1-56.5	54.3-60.6
Cement paste	41.4-41.9	37.0-40.3
Air content	2.0- 2.1	2.4- 5.4*

* Includes numerous large voids.

The examination revealed also that the sand in the unsound mortar was very highly micaceous and included abundant weathered and internally fractured particles, in contrast to the virtual absence of mica and the better physical condition of the sand in the sound concrete. It was concluded that the susceptibility of the unsound concrete lay in the higher water-cement ratio and inferior quality of the sand, coupled with lack of air entrainment of the mortar.

Uniformity of results that can be obtained by total microscopical analysis of hardened concrete is illustrated by data from analysis of the top 4 inches of five 4-inch diameter cores drilled from a laboratory-prepared air-entrained slab containing 1½ inch nominal maximum size aggregate:

<u>Constituent</u>	<u>Percent by Volume of Concrete*</u>
Aggregate	69.1-71.7
Cement paste	23.3-24.9
Air voids	4.7- 6.3

* Each result determined on approximately 16 sq. in. of surface.

These results were compared with the analysis of cores obtained from three bridge decks for which the concrete was supposedly similarly proportioned. The results were as follows:

<u>Constituent</u>	<u>Percent by Volume of Concrete</u>
Aggregate	60.6-70.1
Cement paste	22.0-31.8
Air voids	6.3- 9.8

The bridge deck concrete was characterized by low strength, low abrasion resistance, and low resistance to freezing and thawing. The concrete containing the highest proportions of cement paste included small masses of mortar that were clearly distinguishable microscopically from the matrix of the concrete. These features indicated that retempering of the concrete had been employed to reclaim concrete that had stiffened excessively before completion of the delivery, with resulting inordinate increase in water-cement ratio and in the proportional volume of cement paste in the concrete. Consequently, in this instance, although the microscopical examination revealed important information concerning the quality of the cement paste and the usually excessive air content of the bridge deck concrete, the cement paste content itself was no indication of the quality of the concrete inasmuch as its volume was maintained at a high level by the excessive water content.

Supplementing the total analysis of the concrete by determination of the geometrical parameters of the air void system provides information that is of value in determining cause of lack of durability of concrete. The following data relate to a series of cores of nominally similar concrete taken from three residential driveways showing varying degrees of resistance to scaling and spalling during the first winter.

Item	Sample No.—Results of Examination		
	1	2	3
Condition	Sound	Superficial disintegration	Surface completely scaled
Coarse aggregate, % *	32.40	34.82	34.99
Sand, % *	30.60	29.91	33.89
Cement paste, % *	30.00	30.51	25.40
Air voids, % *	7.00	4.76	5.72
Specific surface of voids, in. ⁻¹	680	840	390
Spacing factor, in.	.0063	.0062	.0110

* Per cent by volume of the concrete.

The extensive scaling of Core No. 3 correlates with the very low content of cement paste, indicating excessive water-cement ratio, and presence of a void system made up of quite coarse air voids and characterized by an excessive spacing factor. The concrete of Core No. 2 was generally sound and well proportioned; but the topmost 1/16 to 3/16 inch was very weak, highly carbonated, and highly absorptive as a result of improper curing and lack of protection of the fresh concrete from drying. The disintegration of Core No. 2 is expected to involve only the superficial zone of the pavement.

In order to evaluate the reproducibility of the analysis as made by point-count procedure, a determination was made five times by one operator over a surface 13.5 sq. in. in area prepared on air-entrained concrete containing 1-inch nominal maximum size aggregate and 6 sacks of portland cement per cubic yard. Each analysis included 1475 to 1901 counts uniformly, but randomly spread over the area, the traverse length in each determination being 73 to 95 inches. The results are as follows:

<u>Constituent</u>	<u>Mean, percent by volume</u>	<u>Coefficient of Variation, percent</u>
Coarse aggregate	37.03	0.97
Sand	27.64	3.26
Total aggregate	64.67	1.41
Cement paste	27.87	2.87
Air voids	7.46	3.62

Four similar surfaces of the same concrete were analyzed by the point-count procedure. Figure 1 shows the indicated composition as a function of the cumulative number of counts. The indicated proportions of the constituents were within 10 per cent of the final value after the first 750 counts and within 5 per cent after the first 750 to 4500 counts. The proportional variation of the determined value was least in the indicated cement paste content. The data on precision of microscopical method given above as well as inspection of the prepared surfaces demonstrate that the main cause of the variance is inhomogeneity of the concrete.

DETERMINATION OF MIXING WATER CONTENT BY TESTING OF HARDENED CONCRETE

Because water-cement ratio is one of the most, if not the most important qualities of concrete, many investigators have attempted to make direct determinations of original water content by testing of hardened concrete. With such a determination and an independent determination of the cement content, such as ASTM Method C 85, the original water-cement ratio can be calculated.

However, the determination of original water content of concrete is not an easy matter. A portion of the mixing water emerges from the concrete and no longer constitutes a part of the bulk volume of the concrete. A part of the water reacts with the cement and is combined in the composition of the hydration products. A part of the water is adsorbed on the outer surfaces of the hydration products or along internal surfaces of crystalline hydration products such as the 001 intra-crystalline surface of the tobermoroid phase of the cement paste. In addition, a part of the volume of mixing water is represented by capillary and sub-capillary openings within

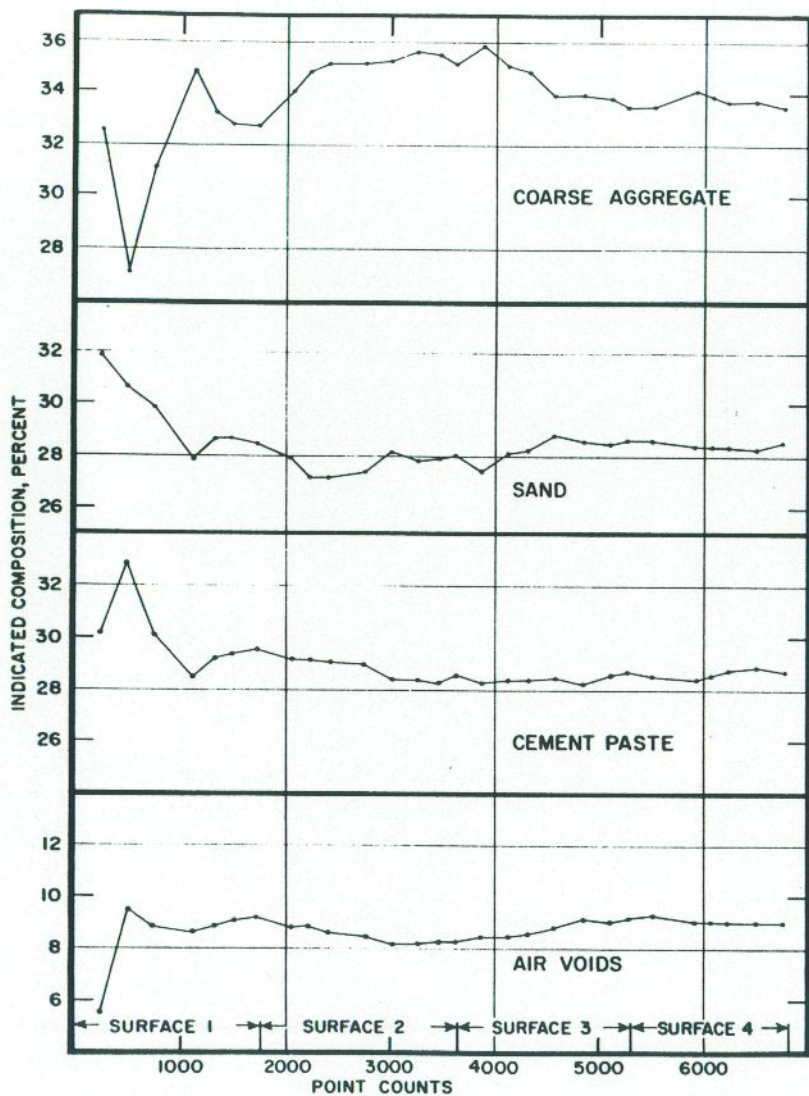


FIGURE 1.

Variation of indicated composition of hardened concrete during point-count analysis over four surfaces totaling 54 square inches.

the cement paste. Moreover, a part of the original mixing water that originally was combined as hydroxyl in hydration products of the cementitious compounds, such as in calcium hydroxide, is released from the concrete by carbonation, that is, interaction of the hydroxyl with carbon dioxide of the atmosphere, with resulting formation of calcium carbonate and release of a water molecule for each molecule of carbon dioxide taken up. No precise method for determining the total of these quantities of water has as yet been developed. Several approximate methods have been proposed.

For example, in 1954, Blackman⁽¹¹⁾ proposed a method for determining the original water content of concrete, at time of hardening, that involved immersion of a sample in water for 24 hours and subsequent drying at 1,100° F. for two hours. Within the range of water-cement ratio (0.455-0.664 by weight) and aggregates employed in the tests, a good correlation was found between the amount of water lost during the high-temperature drying of the partially saturated samples and the original water content of the fresh concrete. However, in published discussion, Bloem⁽¹²⁾ showed that water taken up by concrete during 24 hours of immersion increases the total water content over that of the fresh concrete, the excess being as high as 6.9 gallons per cubic yard. The excess was found to depend primarily upon the water-cement ratio and the conditions under which the concrete was cured. It is well known that concrete is not saturated after 24 hours of curing in moist air because of the uptake of water by the cement during hydration; consequently, such concrete can absorb additional water upon immersion. As a result, this method is subject to grave error. Bloem's tests indicate that the determined water content might be expected to exceed the actual by 0.5 to 19 per cent. Blackman's data indicate an expectable error of up to 9 per cent greater or less than the actual water content.

A. W. Brown⁽¹³⁾ published a method that is essentially as follows: The sample is dried at 105° C. and is then saturated under vacuum in carbon tetrachloride. After the amount of absorbed carbon tetrachloride is determined, the sample is again dried to remove the organic liquid. Combined water is determined by ignition and a correction of the indicated water content is established by chemical analysis for carbon dioxide that resulted from carbonation of the cement paste by atmospheric carbon dioxide. The original water content of the concrete is calculated as the sum of the weight of water equivalent to the absorbed carbon tetrachloride and water combined in hydration products. In the tests published by Brown the water content of the concrete was determined within an accuracy of about 4 per cent by this method. The tests were applied to non-air-entrained concrete containing dense aggregates. The indicated errors would be increased by use of porous aggregates and air entrainment inasmuch as the additional voids would be in part

indicated as original water content. Moreover, the procedure includes the same defect as does Blackman's method, namely, the equating of the absorbed volume of liquid with the amount of mixing water in excess of the water combined in the hydration products.

In 1962, Axon⁽¹⁴⁾ published an entirely physical method for the determination of the composition of concrete, including the aggregate, cement, and mixing water. The proportions of coarse aggregate and fine aggregate (separately if distinguishable), cement paste, and air voids are determined microscopically in accordance with the procedures described in ASTM Recommended Practice C 457. The volume of the cement paste is taken to be the actual volume of the cement and mixing water following cessation of bleeding of the fresh concrete. The original water content is determined by vacuum saturation of the dried concrete in water and use of a "maturity factor" that is an estimated value expressing the proportion of cement that will have been hydrated under the conditions to which the concrete was or is presumed to have been exposed.

In Axon's application of the procedure to seven concrete mixtures of known composition, the maximum error was 5 per cent of the water content, the determined values typically being lower than the actual. The cement content is determined by subtracting the proportional volume of combined water and submicroscopical pore volume in the cement paste from the proportional volume of cement paste in the concrete. In Axon's determinations the maximum error in indicated cement content is about 11 per cent and that in water-cement ratio is about 7 per cent. In analysis of 24 cores from one bridge deck, the average determined water-cement ratio was 97.3 per cent of the actual, and the coefficient of variation among the experimental data was 7.4 per cent. The average determined cement content was less than one per cent higher than the actual, and the coefficient of variation of the results was 6.4 per cent. Samples of the coarse and fine aggregates must be available for determination of their absorptivity. Also, the specific gravity of the cement should be known. The microscopical analysis is based upon a traverse length of at least 200 inches spread over about 230 sq. in.

The recency of publication has prevented proper evaluation of the method by others. The validity of the microscopical procedure for total analysis of hardened concrete is confirmed. The novel feature of Axon's procedure applied only to the partitioning of the cement paste between original cement content and mixing water content. Major problems are the value of the "maturity factor" to be applied under given conditions of exposure, with cements of individual characteristics, and with the possible presence of accelerating or retarding admixtures.

The Axon procedure was applied to a series of three non-air-entrained and three air-entrained concretes for which the batch weights were carefully controlled. The indicated cement contents were consistently high, ranging from 109 to 123 per cent of the known value. The indicated water content was consistently low, ranging from 86 to 93 per cent of the known value (disregarding loss of water by bleeding). Since this trend of results would occur if water absorbed during the soaking period following drying was less than that required to saturate the concrete, the concrete was subjected to 5000 psi hydrostatic pressure while immersed in water in the chamber of a high-pressure air meter identical with that described by Erlin⁽¹⁵⁾. Additional water absorbed amounted to 0.3 to 0.7 per cent by weight of the concrete. With use of these values of absorption, corrected for the additional absorption by the aggregate that was similarly treated, the indicated contents of cement and water would be closer to the actual.

On the other hand, the value taken by Axon for the nonevaporable water content of completely hydrated Type I portland cement should be decreased by about 11 per cent because his method employs oven drying rather than a desiccant as was done by Powers and Brownyard⁽¹⁶⁾. Also, this change may dictate changes in the value of several parameters selected from their data. Consequently, there is little point in attempting to introduce detailed and somewhat arbitrary adjustments to cause the results to accord more closely with the known proportioning of the concretes. Such an effort should be based upon carefully designed experiments that include several cements as well as close control of all details of preparation of the concrete, including effects of carbonation of the cement paste.

CONCLUSIONS

Diagnosing failure or unsatisfactory performance of concrete requires coordination of observation in the field, careful sampling, and appropriate application in the laboratory of petrographic examination, chemical analysis, and physical tests. Although somewhat subjective, petrographic examination is usually very helpful in determining the cause of unsatisfactory performance of concrete and aids in selection of particular chemical and physical tests that will provide essential quantitative information.

The process of diagnosing unsatisfactory behavior of concrete in service is an attempt to correlate the manifestations of unsatisfactory performance with one or more deleterious processes and with the nature and identity of any defects in the concrete.

Several chemical and physical methods for partial analysis of hardened concrete are available. Microscopical procedures alone permit quantitative determination of the proportions of coarse

and fine aggregate, cement paste, and air voids in hardened concrete, and the relative size and distribution of the air voids can be measured. The most powerful methods combine microscopical analysis and chemical or physical methods.

With adequate sampling, the microscopical analysis of hardened concrete can be conducted at a high level of accuracy and precision. The linear traverse or point-count procedures should indicate the proportions of aggregate or cement paste, respectively, within about 1.5 percentage points. The accuracy of determination of the proportions of coarse aggregate or fine aggregate individually depends in large measure on their distinctiveness lithologically or otherwise. Air content should be readily determinable within 15 per cent of the actual value if the air content is 3 per cent or more and somewhat greater precision should be obtained in the determination of the air-void spacing factor. The coefficient of variation in determination of coarse aggregate, fine aggregate, cement paste, and air-void content ranged from about 1.0 to 3.6 per cent in one series of analyses by one operator.

Determination of the proportions of cement and water used in batching of the concrete presents the greatest technical problems. Available procedures are subject to errors that probably are on the order of 15 per cent of the actual value under ordinary conditions and may be much greater. Various investigators report differing accuracy of various methods, the variance probably depending upon the sampling procedures, details of technique, the nature of the concrete and concrete-making materials, and the correction factors that were applied to the analytical results.

Research to develop more accurate procedures of analysis of hardened concrete to establish the original proportioning of cement and water should be encouraged. Of greatest urgency is the need for reliable determination of original water-cement ratio. At present, the errors inherent in the available methods for determining original water content and cement content preclude dependable calculation of water-cement ratio from the analytical data. In this regard, Axon's method is especially promising. The results of this method might be improved by development of better factors for estimating the volume of water that is combined with the cement, application of a standard accelerated curing to the sample of concrete so as to minimize the effect of the varying degree of hydration of the cement at time of sampling, and use of an organic liquid in lieu of water in the determination of porosity so as to shorten the required soaking period and to avoid effects of hydration of the cement during the test period, and possibly use of a high hydrostatic pressure during the soaking period to assure thorough saturation of the concrete.

And so we see Dr. Bates was right! Failure and abnormal performance of concrete originate in all areas of production and

control of concrete and concrete-making materials. Imperfect knowledge is a restriction that will be progressively relaxed by continued research and creative conception. Irresponsible attitudes are the more deplorable because they are avoidable; and yet they are destructive of both the public good and those who give vent to them. Stanton Walker's long record of service provides for us a valued guide to further development of concrete, the most challenging part of the construction industry.

REFERENCES

- (1) Mielenz, R. C., "Petrography Applied to Portland-Cement Concrete," *Reviews in Engineering Geology*, Geol. Soc., Am., vol. 1, pp. 1-38, 1962.
- (2) American Society for Testing and Materials, ASTM Standards, Parts 9 and 10, 1964.
- (3) Kriege, H. F., "Cement Content of Hardened Concrete," *Am. Soc. Testing and Mat., Spec. Techn. Publ. No. 169*, pp. 221-227, 1955.
- (4) Ford, C. L., "A Study of Methods for the Determination of the Portland Cement Content of Hardened Concrete," *ASTM Bulletin*, No. 181, pp. 47-52, 1952.
- (5) Polivka, M., Kelly, J. W., and Best, C. H., "A Physical Method for Determining the Composition of Hardened Concrete," *Am. Soc. Testing and Mat., Spec. Techn. Publ. No. 205*, pp. 135-152, 1958.
- (6) Yaltkaya, E., Urkan, S., Sentürk, S., Köksal, K., and Enüstan, B. V., "Nondestructive Estimation of Cement Content of Finished Concrete (Abstract)," *Am. Soc. Testing and Mat., Int. Conf. on Materials*, Philadelphia, Pa., Feb. 3-6, 1964.
- (7) Swenson, R. G., and Thorvaldson, T., "Detection of Lignosulfonate Retarder in Cement Suspensions and Pastes," *Am. Soc. Testing and Mat., Spec. Techn. Publ. No. 266*, pp. 159-169, 1960.
- (8) Verbeck, G. J., "The Camera Lucida Method for Measuring Air Voids in Hardened Concrete," *Proc., Am. Concrete Inst.*, vol. 43, pp. 1025-1039, 1947.
- (9) Brown, L. S., and Pierson, C. U., "Linear Traverse Technique for Measurement of Air in Hardened Concrete," *Proc., Am. Concrete Inst.*, vol. 47, pp. 117-124, 1950.
- (10) Mielenz, R. C., Wolkodoff, V. F., Backstrom, J. E., and Burrows, R. W., "Origin, Evolution, and Effects of the Air Void System in Concrete," *Proc., Am. Concrete Inst.*, vol. 55, Part 1, pp. 95-121, Part 2, pp. 261-272, Part 3, pp. 359-376, Part 4, pp. 507-517, 1958.
- (11) Blackman, J. S., "Method for Estimating Water Content of Concrete at the Time of Hardening," *Proc., Am. Concrete Inst.*, vol. 50, pp. 533-541, 1954.
- (12) Bloem, D. L., Discussion of Reference 11, *Proc., Am. Concrete Inst.*, vol. 50, pp. 544-1—544-4, 1954.
- (13) Brown, A. W., "A Tentative Method for the Determination of the Original Water-Cement Ratio of Hardened Concrete," *Jour. Applied Chem.*, vol. 7, pp. 565-572, 1957.
- (14) Axon, E. O., "A Method of Estimating the Original Mix Composition of Hardened Concrete Using Physical Tests," *Proc., Am. Soc. Testing and Mat.*, vol. 62, pp. 1068-1080, 1962.
- (15) Frlin, Bernard, "Air Content of Hardened Concrete by a High-Pressure Method," *Jour. PCA Res. and Dev. Labs.*, vol. 4, pp. 24-29, 1962.
- (16) Powers, F. C., and Brownyard, T. L., "Studies of the Physical Properties of Hardened Portland Cement Paste. Part 2. Studies of Water Fixation," *Proc., Am. Concrete Inst.*, vol. 43, pp. 249-336, 1947.



Plate 1. Scaling of a trowelled surface of a concrete floor in a furniture warehouse.



Plate 2. Cross-section of the concrete floor shown in Plate 1. Note the poorly bonded layer of sand-cement mortar applied to the surface and not integrated into the surface of the base concrete. The construction specifications called for a monolithic floor slab. Magnification X 9.



Plate 3. Extensive carbonation of the near-surface portion of base concrete of a floor placed in enclosures where unvented combustion heaters were employed. As a result of the weakened condition of the surface more than 30,000 sq. ft. of concrete topping became disbonded and required replacement. Magnification X 1.



Plate 4. Sealing of finished surface of bridge deck concrete resulting from finishing and application of a membrane curing compound before completion of bleeding. Accumulation of bleeding water beneath the surface of the concrete resulted in immediate spalling of the topmost 1/16-1/8 inch.

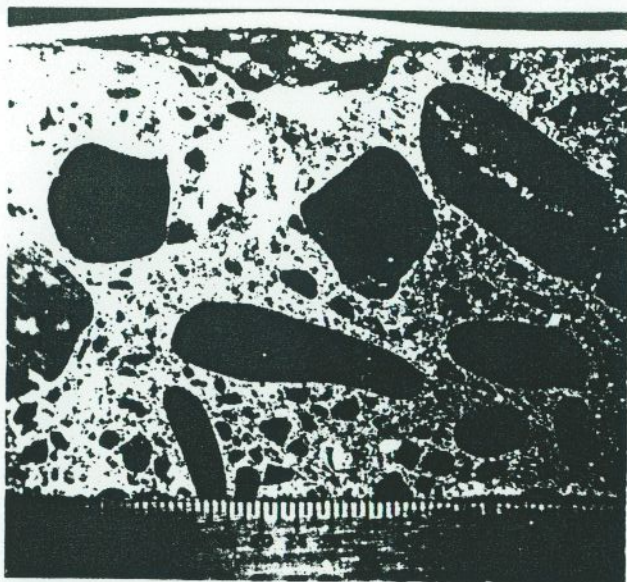


Plate 5. Bulging of vinyl tile as a result of formation of a popout in the surface of a concrete floor. The popout developed above a particle of artificial glass as a consequence of alkali-silica reaction. Magnification X 1½.



Plate 6. Cross-section of lining of a flume structure that displayed spalling of finished surfaces in limited areas. A weakly bonded layer of mortar at the top demonstrates poor finishing procedures whereby the surface was brought to grade by a mortar slurry that was not integrated with the underlying concrete. Fissures (arrows) demark bleeding channels; note that the channels are obliterated by the finishing operations. White masses of gypsum in the dolomite coarse aggregate had produced no deleterious effects. Magnification X 2.

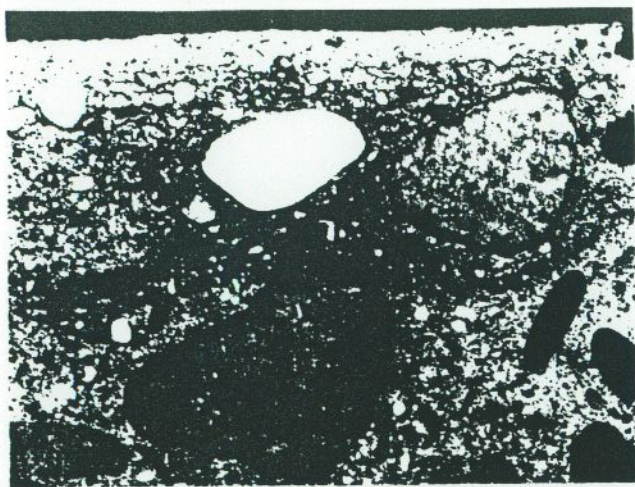


Plate 7. Cross-section of a concrete patio slab displaying intimate cracking in the upper portion as a result of freezing and thawing. The concrete was susceptible to such destruction because of excessive water content and water-cement ratio in spite of high air content. Note settlement of mortar beneath particles of gravel in the upper portion of the section. Magnification X 1.

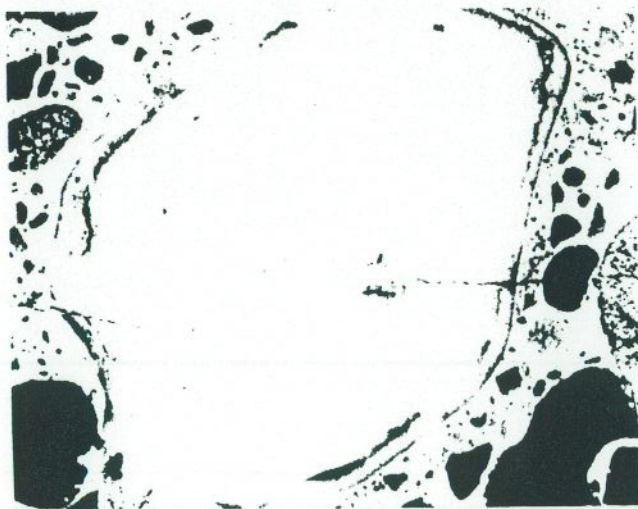


Plate 8. Cracking of concrete produced by expansion of a pebble of highly porous chert as a result of freezing while saturated or nearly so. The colored rim on the pebble is the result of natural weathering of the gravel. Magnification X 5.

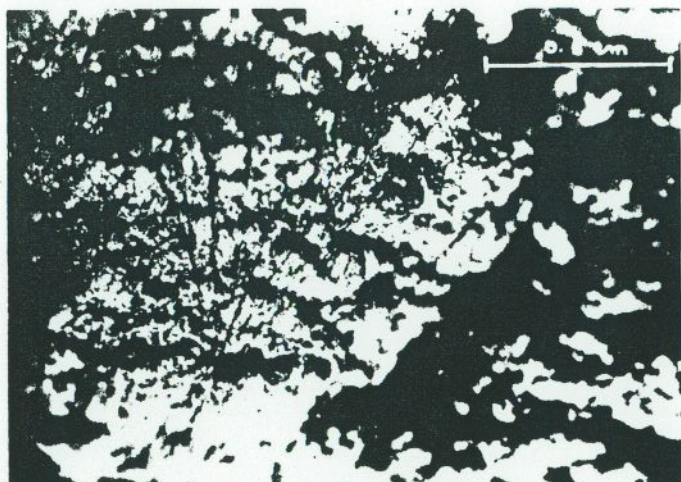


Plate 9. Imprints of ice crystals in mortar of a concrete block wall. The mortar was weak, fractured, and largely disbonded from the block. Magnification X 5.

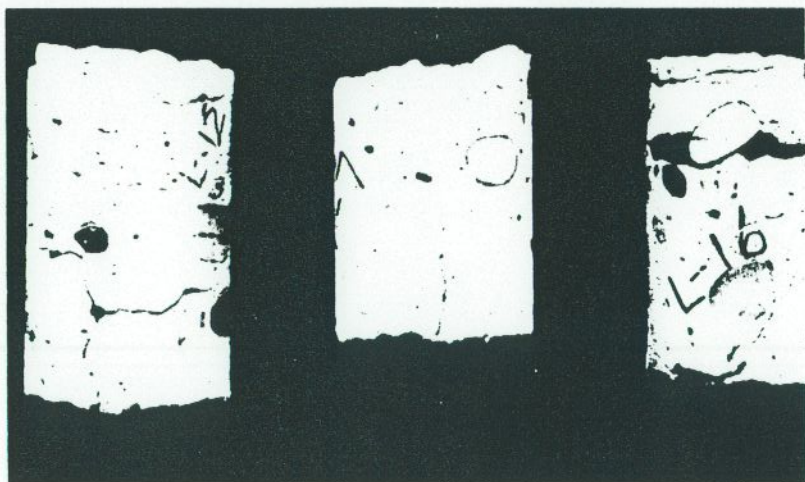


Plate 10. Fracturing of concrete of pavement as a result of early freezing following setting. Note the predominant and repeated horizontal fractures and subordinate vertically-trending fractures.

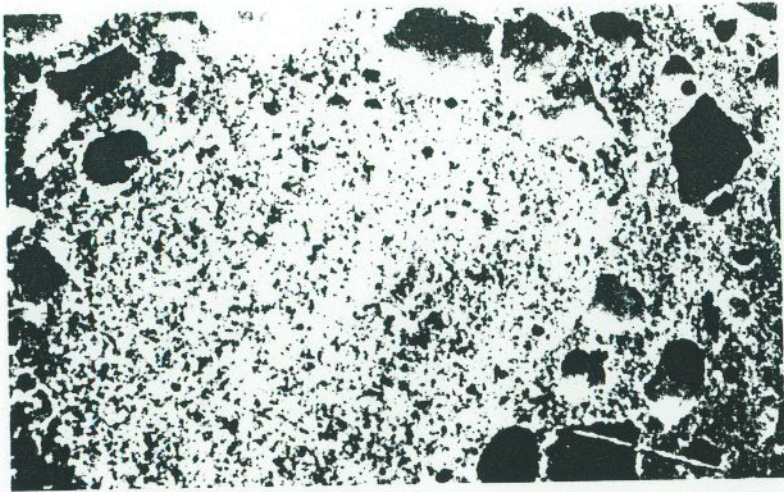


Plate 11. Lump of cement in concrete as a result of aeration of the cement before use. Magnification X 25.

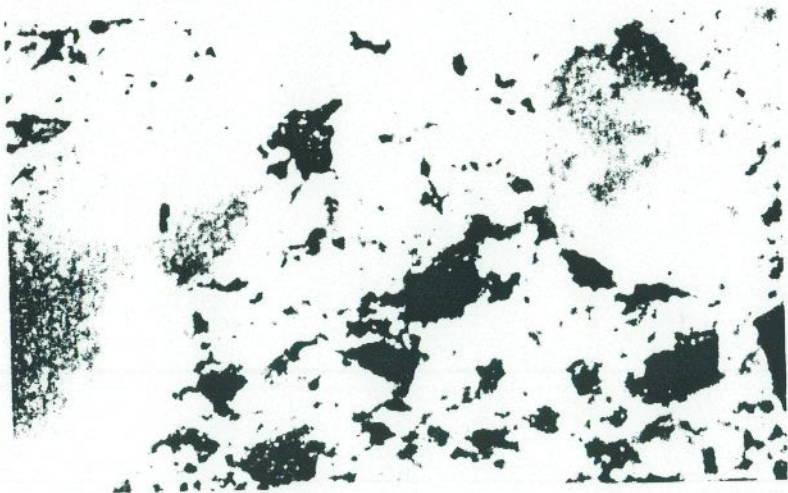


Plate 12. Excessively coarse portland cement whose inefficiency as a bonding medium resulted in inadequate strength of the concrete. Magnification X 40.

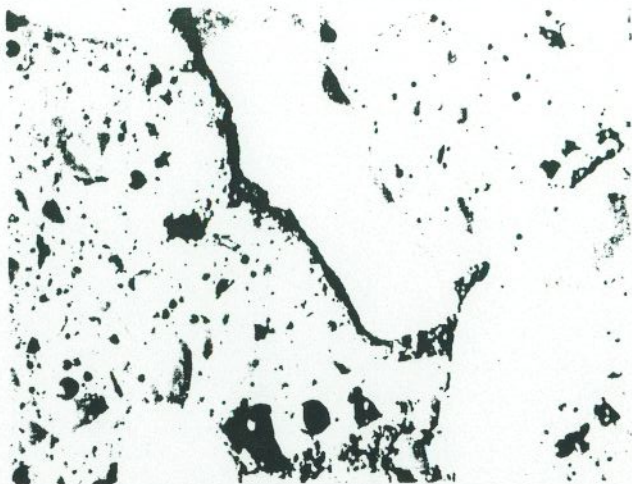


Plate 13. Water void beneath a particle of coarse aggregate in concrete of high water-cement ratio. Magnification X 2.



Plate 14. Excessive air content in concrete from highway pavement (air content = 30 percent). The pavement was rejected and removed. Magnification X 2.

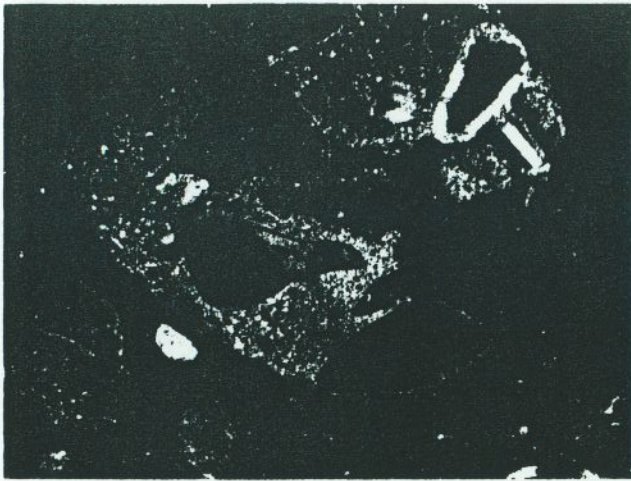


Plate 15. Non-uniformity of concrete resulting from inadequate time of mixing. Note areas rich in cement paste and gravel in contrast to those of lean mortar. The sample is from pavement typified by variable and usually low strength. Magnification X 1½.

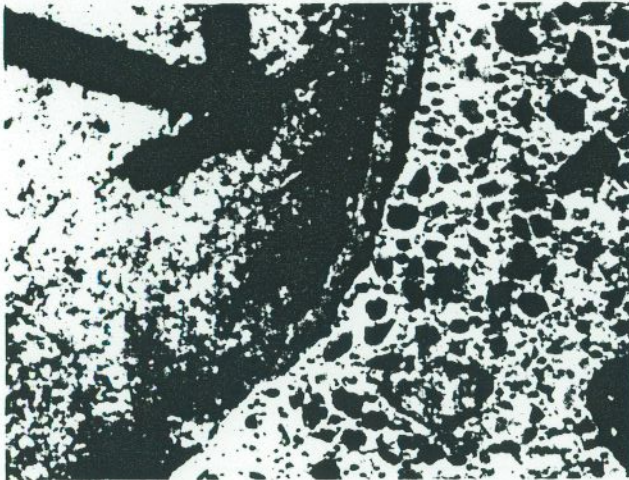


Plate 16. Partial coating of dense mortar on aggregate resulting from incomplete mixing of the concrete following rettempering to recover slump. The concrete also includes random lumps of compact mortar. The concrete is from a bridge deck that was rejected because of low strength. Magnification X 7.

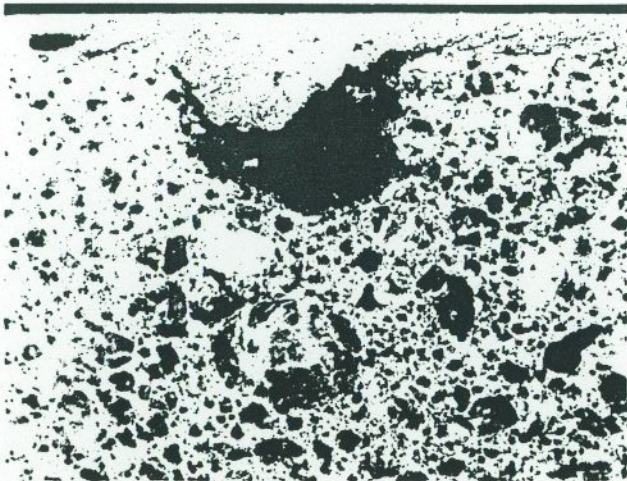


Plate 17. Sand-filled depression in the top surface of a concrete core that had been capped for compression testing. Such features explain some spurious indications of low strength. Magnification X 1½.

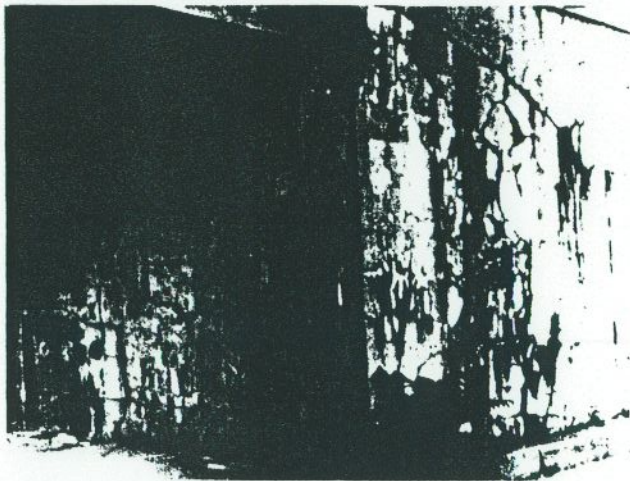


Plate 18. Advanced distress resulting from alkali-aggregate reaction in an abutment of an overpass structure. Note typical pattern cracking and exudations. The concrete was 19 years old at the time the photograph was taken.

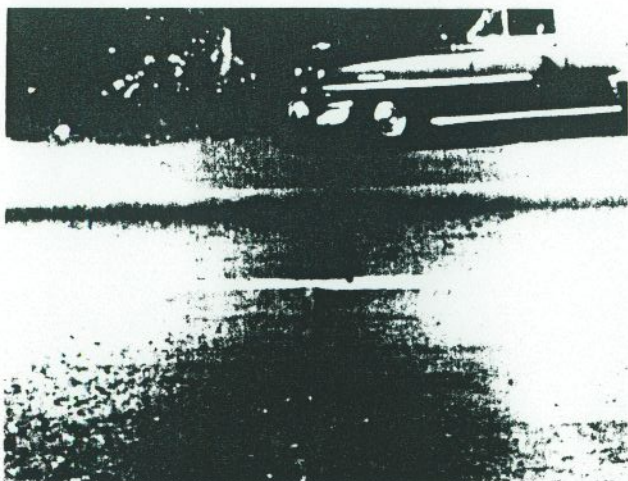


Plate 19. Six-inch offset in construction joint of concrete pavement resulting from progressive expansion as a result of alkali-aggregate reaction. The pavement was in satisfactory condition after 28 years of heavy use.

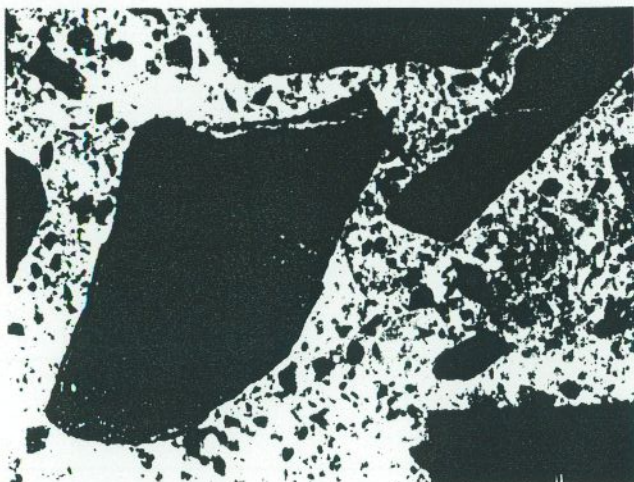


Plate 20. Photomicrograph of concrete affected by alkali-silica reaction. Note the body of white alkali silica gel in an air void. Fractures produced by expansive forces in the aggregate tend to form immediately below the outer surface of the particle. Magnification X 6½.



Plate 21. Particle of chalcidonic chert that has been wholly converted to wax-like calcium-alkalic silica gel by alkali-aggregate reaction. The reaction was accomplished without apparent fracturing of the surrounding matrix. The concentric cracks are the result of drying shrinkage of the gel following preparation of the ground surface. Magnification X 30.