Petrography Applied to Portland-Cement Concrete

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ABSTRACT

Portland-cement concrete is a construction material of fundamental importance and unique versatility in the world today. The increasing variety of uses for it and the increasing stringency of engineering requirements and economic limitations have spurred research and the application of widely varying techniques in all aspects of concrete technology. Geological sciences, including petrography, are among the disciplines now being employed in this field with increasing frequency. Geology, as such, is mainly applied in the search for, exploration of, and progressive exploitation of deposits of materials pertaining to concrete, such as raw materials for portland cement; stone, gravel, and sand for aggregate; clays, shales, and other materials for the manufacture of light-weight aggregate; and clays, volcanic ashes and tuffs, and other materials for pozzolans. Petrography finds widespread application in selection, testing, and manufacture or processing of materials for concrete; concrete research; and evaluation of concrete in service, particularly the investigation of causes for distress or failure. Techniques of petrography include visual examination of concrete structures and of samples supplied from the field and laboratory, as well as detailed examination by the stereoscopic microscope, by the petrographic microscope by means of immersion liquids and thin sections, and by the metallographic microscope by means of polished and etched surfaces. In general, optimum results require application of all these techniques. Many of the determinations are qualitative and provide data of value only in supporting conclusions based primarily upon other evidence. Frequently, however, the petrographic observations are quantitative and may be of such nature that they are used unilaterally to support important engineering or forensic decisions. The petrography of concrete is discussed comprehensively and in some detail.

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INTRODUCTION

GENERAL STATEMENT

Portland-cement concrete[1] is the plastic or hardened combination of portland cement, fine aggregate, coarse aggregate, and water, with or without addition of small proportions of one or more admixtures designed to produce special properties. In current engineering practice, the constituents for concrete are selected, and the concrete is proportioned and mixed in accordance with prescribed procedures so that the concrete will be (1) sufficiently plastic and cohesive (workable) to be placed and compacted economically in the structure for which it is manufactured; (2) when hardened, sufficiently strong and durable to perform adequately under the conditions of service imposed during the economic life of the structure; and (3) at a minimum in cost of materials, mixing, placing and finishing operations, and maintenance. These requirements impose stringent demands upon the materials engineer, designer, and architect. It is precisely for this reason that modern concrete technology needs the joint efforts of specialists in many fields, including chemists, physicists, a variety of engineers, and also geologists and petrographers.

In this report, many types of distress of concrete in service are described. This emphasis on partial or complete failure of concrete should not be taken to indicate that portland-cement concrete ordinarily does not meet the demands placed upon it in service and so typically requires undue maintenance or premature replacement. On the contrary, concrete proportioned, mixed, placed, and cured with reasonable care, and containing materials selected under reasonable specifications, can be expected to render economical service in an amazing range of environments. Emphasis is placed on the characteristics of distressed concrete primarily because the engineering petrographer is called upon to examine and evaluate unsound or inadequate concrete with considerably greater frequency than he is called upon to investigate satisfactory concrete. This is not to say that satisfactory concrete cannot be studied profitably in much greater detail than has been accomplished.

SOME PRINCIPLES OF CONCRETE TECHNOLOGY

Of fundamental importance in the proportioning and manufacture of high-quality concrete of adequate strength, maximum volume stability, and satisfactory resistance to deterioration is the use of a minimum proportion of water in the concrete mixture so as to maintain a minimum water content and low water-cement ratio, consistent with an adequate degree of workability of the plastic concrete. The water content required for given consistency of concrete can be reduced by increase in the maximum size of the aggregate; decrease in the ratio of fine aggregate to total aggregate; selection of aggregates of proper grading, particle shape, and surface texture; use of

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[1] The term concrete is applied more generally to similar combinations in which bituminous material or any of several hydraulic cements are used as the binding medium. In this report, the term "concrete" will refer to portland-cement concrete. This report relates specifically to portland-cement concrete for use in general construction, as distinct from concrete products subjected to steam curing, autoclaving, or elimination of a portion of the mixing water.

certain types of admixtures which reduce the proportion of water required for given consistency; and use of air-entraining admixtures to cause development in the concrete of a system of minute air bubbles. The water requirement of concrete is changed only to a minor degree by variation in the quantity of cement per unit volume.

POZZOLANS FOR CONCRETE

During the past 2 decades, interest has been renewed in the use of pozzolans as an admixture for portland-cement concrete. Pozzolans are siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (American Society for Testing Materials, 1958, p. 195). Pozzolanic admixtures are of particular value in hydraulic structures for reduction of heat o hydration, reduction of permeability, improved resistance of the concrete to aggressive action of sulfate-bearing or acidic waters, control of alkali-aggregate reaction, and reduction of cost of concrete of given quality. Except for fly ash, the finely divided flue dust produced by burning of pulverized coal, pozzolans of current interest are produced from geological materials, most important of which are various tuff and volcanic ashes, diatomaceous earth, and several types of clays and shales.

ROLE OF THE GEOLOGIST AND PETROGRAPHER IN CONCRETE TECHNOLOGY

The geologist and the petrographer assist in several ways in making feasible and economical the consistent production of satisfactory concrete. They aid in the selection, production, processing, and testing of aggregates and pozzolans; they contribute to the selection of raw materials and manufacturing procedures for portland cement and the petrographer contributes in important ways to the evaluation of hardened concrete from structures, particularly when it is necessary to determine causes o inadequate service. Petrographers are active also in research on properties, testing and manufacturing procedures for both mineral and synthetic aggregates; portland cement manufacture and its hydration reactions; use of admixtures for concrete and causes of deterioration of concrete. Application of geological sciences in th selection, processing, evaluation, and use of aggregates and pozzolans is described in detail in several fairly recent publications (Mather and Mather, 1950; Mielenz, 1954 Rhoades and Mielenz, 1948; Mielenz, Greene, and Schieltz, 1951; Mielenz, Witte Glantz, 1949; Mather, B., 1948; Knight and Knight, 1948; Swenson and Chaly, 1956 Spencer and Dart, 1957a; 1957b).

PREVIOUS MICROSCOPICAL INVESTIGATIONS OF CONCRETE

Mather (1953) comprehensively reviewed the application of light microscopy to portland-cement concrete, cement, and aggregates. Although the literature of microscopical study as a basis for engineering evaluation of concrete extends bac to 1915 (Johnson) and covers the application of stereoscopic procedures as well a use of thin sections and polished and etched surfaces, no comprehensive treatmen of the constitution and internal structure of concrete and its alteration in place ha been published. The literature deals primarily with detailed statements of th development or application of specific techniques or with description of findings pertinent to specific problems of concrete research or technology. Mather's reports (1953; 1956) are excellent statements on microscopical methods and their application in this field.

OBJECTIVES OF THIS REPORT

This report attempts to cover in some detail what may be called the "petrography of concrete." Of course, concrete is not a rock, but concrete is characterized, as are the various classes of rock, by a circumscribed range of composition, texture, and internal structure; and concrete is subjected to environmental conditions which, in the light of the properties of any particular mass of concrete, modify it both physically and chemically during its history in an engineering structure. Moreover, the various microscopical techniques developed for study of rocks and minerals are applicable directly to the description of concrete and its solid constituents. Hence, there is considerable justification for the extension of the concepts of petrology and petrography to concrete. The writer and his former colleagues employed a similar approach in a study of cement-aggregate reaction in concrete (McConnell *et al.*, 1950).

The present report is broad in scope; it discusses certain aspects of the design and manufacture of concrete, methods of petrographic study in the field and laboratory, the composition and internal structure of concrete, and the most important types of deterioration causing inadequate service of concrete. Each phase is covered only briefly, both because of the limitations of space and because information on some aspects is all too meager. The writer is convinced that petrography will find progressively wider and more diversified application in the investigation of concrete as experience accumulates and techniques are developed.

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PETROGRAPHIC EXAMINATION OF CONCRETE

GENERAL STATEMENT

Petrographic examination of concrete is primarily visible examination and analysis of concrete in structures, specimens, or samples obtained from structures, to determine the composition texture, and internal structure of the material. The methods employed include inspection by the unaided eye, microscopical examination, and thermal or X-ray diffraction analysis. The examination is directed to determining the identity and mineralogic (or compound) composition of the aggregate, cementitious materials, products of deterioration, and other components and to describing the textural and structural relationships existing in the concrete, including the distribution, size, and continuity of voids and fractures.

PURPOSE OF THE PETROGRAPHIC EXAMINATION OF CONCRETE

Concrete is examined petrographically to describe or determine any one or more of the following features or conditions:

1. Description of the concrete
    a. Mix proportions
    b. Internal structure
    c. Cement-aggregate relationships
    d. Deterioration
2. Description of the cement
    a. Composition especially presence of free CaO or MgO in undesirable amounts.
    b. Relative fineness
    c. Identification of certain addition
3. Description of the aggregate
    a. Composition, grading, and quality
    b. Identification of the type, kind, and source or source area of the aggregate
    c. Presence of coatings
    d. Detection of contamination
4. Identification of certain admixtures
    a. Mineral admixtures
    b. Pozzolans
    c. Siliceous aids to workability
5. Evaluation of the microscopic and megascopic void system
    a. Air content of the concrete
    b. Size and spacing of the voids in the cement paste
6. Determination of the cause of inferior quality or failure of concrete
    a. Cement-aggregate reaction
    b. Attack by aggressive waters
    c. Freezing and thawing
    d. Unsound aggregate
    e. Unsound cement, especially excessive free CaO or MgO
    f. Inadequate proportioning, mixing, placing, curing, or protection
    g. Structural failure, abrasion, or cavitation.
7. Determination of the cause of superior quality and performance of the concrete

Many of these determinations are qualitative and may provide data of value only in supporting conclusions based primarily upon other evidence. In other instances, the microscopical observations are quantitative and/or of such a nature that they are used unilaterally to support important engineering or forensic decisions.

COMPOSITION OF CONCRETE

Hardened concrete is composed of coarse aggregate, fine aggregate, cement paste, and air voids. In well-designed and well-placed concrete the aggregate and cement paste are uniformly intermixed and closely knit into a compact texture and internal structure. In poorly proportioned or poorly placed and compacted concrete, the coarse aggregate may be segregated so as to produce a honey-combed mass of high porosity (Pl. 1, fig. 1), or the coarse aggregate may be distributed irregularly in the hardened mass. The proportion of cement paste usually is about 30 per cent by volume in concrete containing aggregate of ½ inch maximum size; the proportion decreases progressively to about 15 per cent as the maximum size of the aggregate is increased to 6 inches. The proportion of coarse aggregate (retained on the $\frac{3}{16}$-inch sieve) ≈5mm varies from about 32 to about 64 per cent by volume, and the proportion of fine aggregate from about 30 to about 18 per cent. Air voids of microscopic or macroscopic size constitute 8–3 per cent by volume of concrete in this range of proportioning.

The coarse or fine aggregate in ordinary concrete may be natural sand or gravel, crushed sand or gravel, crushed rock, blast-furnace slag, or any of several natural or synthetic light-weight aggregates. The composition and quality of aggregate in concrete and many effects of the aggregate upon performance of the concrete in service can be determined petrographically.

Cements used in the manufacture of portland-cement concrete include 5 types of portland cement differing in chemical composition and fineness; portland blast-furnace slag cements containing 25 to 65 per cent by weight of granulated blast-furnace slag; or portland-pozzolan cements containing 15 to 50 per cent by weight of a suitable pozzolan (American Society for Testing Materials, 1958, p. 1, 6, 10, 15). The various cements are manufactured either with or without intergrinding of an air-entraining agent.

The cement paste of hardened concrete includes the hydration products of the cement; unhydrated particles of cement; residues of admixtures or interground constituents of the cement, such as pozzolans or blast-furnace slag; products of cement-aggregate reaction; products of deterioration of the cement or its hydration products (Table 1); and a system of minute capillaries and pores not visible under the optical microscope.

Air voids of microscopic and macroscopic dimensions are present in the cement paste of all concrete (K. Mather, 1956, Fig. 2, p. 75). These voids are different from the capillaries and pores in the paste in order of dimension, origin, and effect on the properties of concrete. The air voids commonly are designated as "entrapped" and "entrained" voids. "Entrapped" voids are present in both air-entrained and nonair-entrained concrete. They are typically large (*i.e.*, greater than 1 mm) and irregular in shape, commonly being molded against adjacent particles of aggregate. "Entrained" voids typically are small, usually between 10 and 1000 microns in diameter (average size being 150–250 microns, but spherical voids as small as 2 microns have been observed), and spherical or nearly so because they are subjected to the hydrostatic pressure of the surrounding cement paste in the plastic concrete.

DETERIORATION OF CONCRETE

GENERAL STATEMENT

Viewed geologically, hardened concrete is metastable both physically and chemically under ordinary conditions of service. Hence, the excellent performance provided by most concrete demonstrates that the permeability and absorptivity are usually sufficiently low to prevent excessively rapid ingress of destructive agents, the most important of which are water, air, acids, and sulfates. In addition to the benefit of

TABLE 1.—*Secondary deposits in concrete*

Compound	Mineral equivalent	Indices of refraction	Form and occurrence	References*
Calcium carbonate ($CaCO_3$)	Calcite	$\omega = 1.658$ $\epsilon = 1.486$	Fine-grained, white or gray masses or coatings in the cement paste, in voids, along fractures, or on exposed surfaces; very common	
	Aragonite	$\alpha = 1.530$ $\beta = 1.680$ $\gamma = 1.685$	Minute, white prisms of needles in voids or fractures in concrete; rare	Mielenz (unpublished data); K. Mather (personal communication)
	Vaterite		Spherulitic, form-birefringent, white encrustations on moist-stored laboratory specimens (vaterite A); also identified in sound concrete from structures by X-ray diffraction (α-vaterite); common	K. Mather (1956, p. 78); N. C. Schieltz (personal communication)
High-sulfate calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$)	Ettringite	$\omega = 1.464–1.469$ $\epsilon = 1.458–1.462$	Fine, white fibers or needles or spherulitic growths in voids, in the cement paste, or in fractures; very common	Lerch *et al* (1929); Idorn (1957, p. 30–32)
Low-sulfate calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$)		$\omega = 1.504$ $\epsilon = 1.488$	White to colorless, minute, hexagonal plates in voids and fractures; very rare	Mielenz (unpublished data); Lerch *et al* (1929)
Calcium aluminate hydrate ($3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$)		$\alpha = 1.517$ $\beta = 1.549$ $\gamma = 1.554$	Micalike, colorless, pseudohexagonal, twinned crystals in voids; very rare	Idorn (1957, p. 28–30)
Hydrous sodium carbonate ($Na_2O \cdot CO_2 \cdot H_2O$)	Thermonatrite	$\alpha = 1.420$ $\beta = 1.506$ $\gamma = 1.524$	Minute inclusions in alkalic silica gel; rare	Idorn (1956, p. 9)

Hydrated aluminum sulfate ($2Al_2O_3 \cdot SO_3 \cdot 15H_2O$)	Paraluminite	$\alpha = 1.462$ $\beta = 1.471$ $\gamma = 1.470$	Occurring in cavities in intensely altered concrete; very rare	Hutton (1945, p. 242–244)
Calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$)	Gypsum	$\alpha = 1.520$ $\beta = 1.523$ $\gamma = 1.530$	White to colorless crystals in voids, in the cement paste, or along the surfaces of aggregate particles in concrete or mortar affected by sulfate or sea-water attack; unusual	
Calcium hydroxide ($Ca(OH)_2$)	Portlandite	$\omega = 1.574$ $\epsilon = 1.545$	White to colorless, hexagonal plates or tablets in the cement paste, in voids, along fractures; ubiquitous in concrete	
Magnesium hydroxide ($Mg(OH)_2$)	Brucite	$\omega = 1.561$ $\epsilon = 1.582$	White to yellow, fine-grained encrustations and fillings in concrete attacked by magnesian solutions or sea water; unusual	Mielenz (unpublished data); Kennedy and Mather (1954, p. 172); Lea and Desch (1956, p. 294–297)
Hydrous silica ($SiO_2 \cdot nH_2O$)	Opal	$\eta = 1.43$	White to colorless, finely divided, amorphous; resulting from intense leaching or carbonation of cement paste; unusual in recognizable proportions	
Alkalic silica gel ($Na_2O \cdot K_2O \cdot CaO \cdot SiO_2$)		$\eta = 1.46–1.53$	White, yellowish, or colorless; viscous, fluid, waxy, rubbery, hard; in voids, fractures, exudations, aggregate; common	McConnell *et al.* (1948, p. 97–100); B. Mather (1951, p. 220-223)
Hydrated iron oxides ($Fe_2O_3 \cdot nH_2O$)	Limonite	Opaque or nearly so	Brown stain in fractures and on surfaces; common	

* The literature and private reports include data on many unidentified secondary compounds in concrete; these are not included in the tabulation. Indices of refraction of common mineralogic types are taken from standard works on mineralogy.

its dense structure, concrete is protected to an important degree by a superficial highly carbonated layer produced by reaction between the calcic hydration products of the cement and atmospheric carbon dioxide. On sound concrete, this layer is usually $\frac{1}{16}$ to $\frac{1}{2}$ inch thick and is composed primarily of calcium carbonate (calcite) and amorphous hydrous silica resulting from the complete hydrolysis of the hydrous calcium silicates of the cement paste. The thickness of the carbonated zone probably depends mainly on the water-cement ratio and the duration and conditions of moist curing of the concrete; it is less for lower water-cement ratio and longer period of moist curing. The carbonated zone is hard, resistant to abrasion and freezing and thawing, and low in permeability. If disrupted, it will reform by carbonation of the newly exposed cement paste. Carbonation appears to be harmful to concrete only if it occurs before the cement paste has hardened.

Nevertheless, concrete frequently cannot withstand the conditions of service to which it is subjected, and failure is not uncommon.

DETERIORATION BY FREEZING AND THAWING

Freezing of plastic concrete.—Procedures stipulated by the American Concrete Institute and many other specifications (American Concrete Institute, 1954) require that fresh concrete be protected from freezing for several days so that it can develop strength sufficient to resist several cycles of freezing and thawing. In spite of such specifications, however, some freshly placed concrete is frozen while plastic or at very early ages.

Freezing of fresh, plastic concrete produces any of several effects depending upon the strength of the concrete and the severity of freezing. Slow, superficial freezing causes development of long, bladed, subradiate crystals of ice which scar the surface of the concrete and leave characteristic imprints. The superficial concrete at these places is weak and easily scaled so that these imprints usually are soon broken away on pavements subjected to traffic. More intense freezing stiffens the superficial concrete to varying depth. Bleeding water passing upward from the underlying plastic concrete accumulates beneath the frozen layer, weakening bond at the base of the frozen layer, and ultimately causing scaling of the surface of the concrete. In this situation, imprints of ice crystals may be visible within the hardened concrete, but absence of such imprints is not conclusive evidence that the concrete was not frozen while plastic.

Slow and prolonged freezing can develop ice lenses throughout the concrete in the freezing zone (McHenry and Brewer, 1945). Such lenses can disrupt the concrete and produce a system of more or less parallel fractures beneath the exposed surface. Concrete pavements frozen before hardening typically are weak and easily broken into slabby pieces parallel with the surface. Horizontal fractures are closely spaced, especially in the uppermost inch. Exposure of fresh concrete in thin members to extreme cold effects a rapid freezing which produces no ill effects except that development of strength is postponed until the concrete is thawed and properly cured at above-freezing temperatures (Shideler, Brewer, and Chamberlin, 1951).

Freezing of hardened concrete.—Freezing of hardened concrete causes (1) development of hydrostatic pressure within the concrete paste or particles of aggregate as a result of the crystallization of ice and the consequent increase in volume occupied by ice and water over that occupied by the water alone prior to freezing (Powers, 1945) and (2) diffusion of water from the gelatinous hydration products to capillary openings and air voids in the cement paste in the frozen concrete (Powers and Helmuth, 1953). If water occupies more than 91.7 per cent of the volume of the capillary channels and pores in the cement paste or in aggregate at the onset of freezing, water must be expelled at a rate commensurate with the development of ice, or an excessive pressure developed in the water may cause the concrete to fail in tension. The diffusion of water from the gel-like phases of the hydration products toward openings in the cement paste takes place in a manner analogous to formation of ice lenses in soil (Taber, 1930). Bodies of ice thus will accumulate in fractures in the concrete and in separations at the periphery of particles of aggregate as well as in capillaries and air voids in the cement paste. Thus, development of fractures by any process, such as alkali-aggregate reaction or excessive drying shrinkage, not only permits penetration of water into the interior of the concrete but also accelerates the destructive action of freezing.

The result of repeated cycles of freezing and thawing of near-saturated concrete is progressive development of internal fractures, expansion, and loss of strength and modulus of elasticity. Presence of an adequate system of air voids in the cement paste may increase by five-fold or more the ability of a given concrete to withstand freezing and thawing, but entrained air offers only minor relief if breakdown of the concrete results primarily from action of unsound aggregate.

Concrete affected by freezing and thawing characteristically develops a system of fractures in a roughly hexagonal pattern ranging from about 1 to 6 inches across. This fracture system results from overall expansion of the concrete. Other fractures are concentrated at and tend to parallel edges and corners and ultimately give rise to general disintegration of the concrete (Pl. 1, figs. 2, 3). The fractures and general deterioration of the concrete are concentrated where the concrete is most frequently wet. On slabs, such as road pavements and sidewalks, scaling of the superficial concrete is common and is greatly accelerated by application of salts (Pl. 1, fig. 4). Scaling is increased under given conditions of exposure if the near-surface concrete is excessively rich in cement and fine sand as a result of bleeding, segregation, or overworking of the surface or addition of neat cement or water during finishing.

Highly porous and absorptive particles of aggregate, such as some cherts, argillaceous limestones and dolomites, ferruginous concretions, and shales, cause popouts or general surface scaling of concrete, depending upon their abundance in the concrete. The identity of the offending particles can be determined by examination of the craters or pits in the surface (Pl. 1, fig. 5).

With progress of deterioration and fracturing of the concrete, the cement paste is leached and carbonated. Calcium hydroxide is progressively converted to the carbonate (usually calcite, although vaterite has been identified in slightly affected concrete) (Table 1), which deposits in the cement paste, in fractures and voids and as encrustations at and adjacent to fractures intersecting the surface of the concrete. In addition, the high-sulfate calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) is deposited in fractures and voids where it produces linings and tufts of extremely minute, white needles (Table 1). The compound is so voluminous as frequently to be thought more abundant than it is in fact, thus suggesting erroneously that the concrete has been attacked by sulfates from an external source.

When very weak, hardened concrete is frozen for extended periods, ice lenses of considerable size and continuity, similar to those formed during slow freezing of plastic concrete or some soils, can cause its complete disruption (Collins, 1944). Because the potentiality for stress development by this process is small, ice lenses produce fracturing and general breakdown of hardened concrete only if the concrete is very low in tensile strength. Such low strength obtains either because the concrete is very young or inadequately cured, or because it is characterized by a very high water–cement ratio. This process probably contributes significantly to scaling of the surface of concrete during freezing. Breakdown of weak, porous, or fractured rocks, and scaling of concrete can be produced in the laboratory by freezing of specimens in a liquid, such as nitrobenzene, which contracts rather than expands on freezing. Under this condition, hydraulic-pressure development in the specimen will not account for its disruption.

DETERIORATION BY ALKALI-AGGREGATE REACTION

Alkalies (sodium and potassium) released during the hydration of portland cement, together with the calcium hydroxide produced by hydrolysis of the hydrous calcium silicate hydration products, can develop in concrete a highly caustic solution capable of chemically attacking susceptible siliceous rocks and minerals in aggregate. The rock and mineral types participating in this reaction to a degree sufficient to cause distress of concrete include the silica minerals opal, chalcedony, cryptocrystalline quartz, tridymite, and cristobalite; glassy to cryptocrystalline rhyolites, dacites, latites, and andesites, and their tuffs; and at least certain phyllites. Any rock containing a significant proportion of these substances is potentially deleteriously reactive. At least certain artificial siliceous glasses also are alkali reactive in concrete.

Experience indicates that the alkali-aggregate reaction is deleterious to concrete in the field only if the cement contains more than about 0.6 per cent by weight of these alkalies, expressed as equivalents of sodium oxide (percentage of Na_2O plus 0.658 times the percentage of K_2O). A deleterious degree of reactivity also can be prevented by use of adequate proportions of certain types of pozzolans even if a high-alkali cement is employed. Adverse reactions may be avoided if the concrete is dry, such as in ordinary interior construction. Also, a deleterious degree of alkali-aggregate reaction will not occur if the reactive forms of siliceous material are sufficiently abundant in the concrete to consume the available alkalies in production of alkali-silica combinations of very low alkali to silica ratio, so that they lack the capacity to develop swelling or osmotic pressure by absorption of water.

Alkali-aggregate reaction proceeds rapidly or slowly depending upon many factors, primarily the reactivity of the aggregate particles, their abundance in the concrete, and their size; the alkali content of the cement; and the availability of water. Distress may develop very rapidly in a concrete structure—that is, in 1–2 years—or it may be evident only after 10 or 20 years. The particles are attacked peripherally with production of "reaction rims" of varying thickness which appear dark in reflected light but are clarified in transmitted light (Pl. 2, figs. 1, 2, 3). These rims commonly are softened and are separated easily from the interior of the particle. Care must be taken to differentiate such rims from rims produced by weathering of the sand and gravel in the deposit.

Alkalic silica gels of varying composition are produced by the action of the caustic alkalic solution on the susceptible siliceous phases. These absorb water, and the resulting osmotic or swelling pressure may become sufficient to distend and ultimately to fracture the surrounding concrete. The resulting fractures extend outwardly from the site of the pressure development, transecting both the paste and innocuous aggregate particles (Pl. 2, figs. 4, 5, 6; Pl. 3, fig. 1). However, it is typically very difficult to relate any specific fracture to a particular particle because of the proximity of numerous reacting particles in the concrete. Following fracturing, continued uptake of water by the alkalic silica reaction products causes their migration along fractures. They commonly accumulate in voids or they may emerge at the surface of the structure.

The alkalic silica gel is typically colorless or white; opaque, translucent, or clear; and rubbery, waxy, viscous, or watery when fresh (McConnell *et al.*, 1950, Pls. 2, 3; B. Mather, 1951, p. 220–223). When dried, the gel is white, hard, and brittle. It occurs in the attacked particles, in voids, and in fractures, and as exudations on surfaces (Pl. 3, fig. 2; Pl. 4, fig. 1). Several layers of gel of varying properties commonly can be seen in individual voids or fractures. Under the microscope, the gels are usually anisotropic as a result of strain on drying. The index of refraction ranges from about 1.46 to about 1.53. The silica content is in the range 50 to 85 per cent (moisture-free basis). The content of CaO may exceed 21 per cent. Rhombohedra of calcite are sometimes visible within the gel, but the main portion of the calcium indicated by analysis is present as a component of a sodium potassium calcium silicate gel of variable composition.

The gel typically is accompanied by deposits of needlelike calcium sulfoaluminate occurring in subradiate tufts (Pl. 3, figs. 3, 4, 5). This compound is incidental to the alkali-aggregate reaction but demonstrates general deterioration of the cement paste.

Progress of alkali-aggregate reaction in concrete results in expansion and cracking, with accompanying decrease in strength, elasticity, and durability. Two kinds of fracture systems are recognizable: (1) those forming as a consequence of the irregular and variable extension of the concrete, and (2) those representing lines of structural failure where the distension of individual members is resolved into compressive, tensile, shearing, or torsional stresses of great magnitude. Cracks related directly to the expansion of the concrete develop an irregular pattern cracking (Pl. 5, fig. 1; Pl. 6, fig. 1). These cracks are evident at the surface and may be as wide as 1.5 inches where the internal expansion is very great; invariably they extend into the concrete only for short distances, and are lost in a maze of ramifying fractures of microscopic dimensions. These fractures frequently are delineated by secondary deposits of alkalic silica gel and/or calcium carbonate.

It is difficult to evaluate the significance of alkali-aggregate reaction as a cause of distress in a given concrete structure if the evident distress is minor. In some instances, the essential role of alkali-aggregate reaction is the production of internal cracking which, although insufficient in itself to produce distress in the structure, opens the interior of the concrete to penetration by water and consequent increased damage as a result of freezing and thawing or attack by aggressive waters. Conversely, evidence of alkali-aggregate reaction may be meager in a given sample of concrete even though the structure from which the sample was taken is severely affected by expansion and cracking caused by this reaction. In particular, alkali-aggregate reaction may be poorly developed in the superficial concrete, say to a depth of 3 inches, because of the dry condition ordinarily prevailing to that depth, whereas the reaction may be proceeding vigorously in the interior of the structure.

Under unusual circumstances, alkalies participating in alkali-aggregate reaction can be derived from sources other than the cement. These include (1) release of alkalies from aggregates as a result of water-soluble salts of sodium or potassium or cation exchange reactions in which sodium or potassium in zeolites or clays is exchanged for calcium; (2) highly alkaline mixing water, such as sea water; and (3) alkaline waters that penetrate the concrete after hardening. Alkalies so contributed participate in alkali-aggregate reaction because the sodium and potassium thus entering the solutions permeating the cement paste increase the alkalinity (pH) well above that developed by calcium hydroxide alone.

PLATE 1.—SURFACE DEFECTS AND DETERIORATION OF CONCRETE

FIGURE 1.—Honeycomb structure in concrete. × *ca* 1/40

FIGURE 2.—Pattern cracking and disintegration of concrete as a result of freezing and thawing

FIGURE 3.—Disintegration of concrete by freezing and thawing concentrated in a zone of frequent wetting

FIGURE 4.—Scaling of concrete pavement by freezing and thawing, probably aggravated by application of de-icing salts

FIGURE 5.—Popout produced by a particle of highly porous chert in the near-surface concrete. × *ca* 1/8

PLATE 2.—PHOTOMICROGRAPHS OF FEATURES RELATED TO ALKALI-AGGREGATE REACTION IN CONCRETE AND MORTAR

FIGURE 1.—Darkened reaction rim produced on a particle of phyllite by alkali-aggregate reaction. × 10

FIGURE 2.—Darkened reaction rim produced on a particle of rhyolite by alkali-aggregate reaction. × 10

FIGURE 3.—Clarified reaction rim produced by alkali-aggregate reaction on a grain of andesite Plane light; × 25

FIGURE 4.—Microfractures originating at particles of opal embedded in portland cement paste of high alkali content. Plane light; × 27

FIGURE 5.—Microfractures in chalcedonic and quartzose chert embedded in concrete affected by alkali-aggregate reaction. The microfractures are filled by alkalic silica gel. × 25

FIGURE 6.—Microfractures resulting from alkali-aggregate reaction involving a chalcedonic dolomite. Note that the fractures are parallel to and just beneath the exterior surface of the particles The fractures are filled by alkali silica gel and calcium sulfoaluminate. The arrow indicates a voi filled by alkalic silica gel. × 2¾

FIGURE 1

FIGURE 2

FIGURE 3

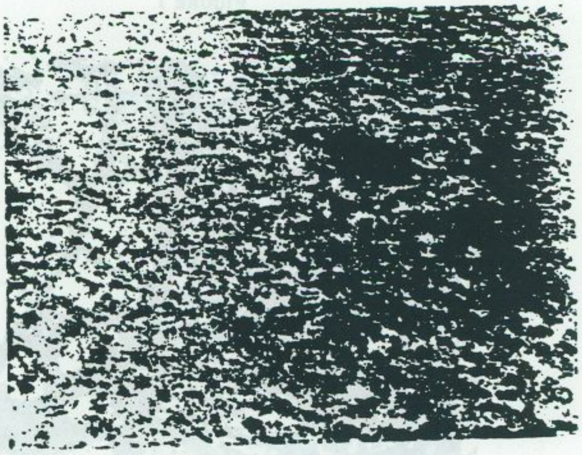

FIGURE 4

FIGURE 5

SURFACE DEFECTS AND DETERIORATION OF CONCRETE

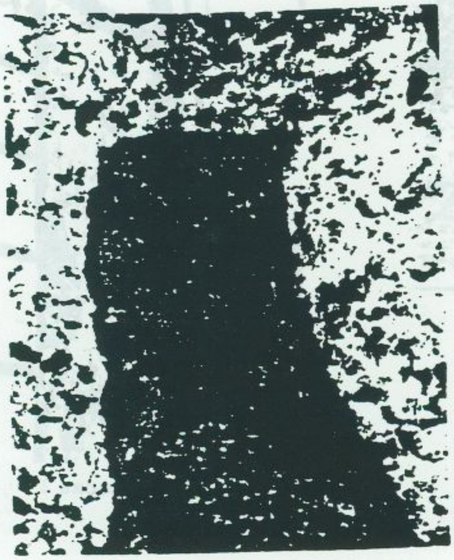

Figure 1

Figure 2

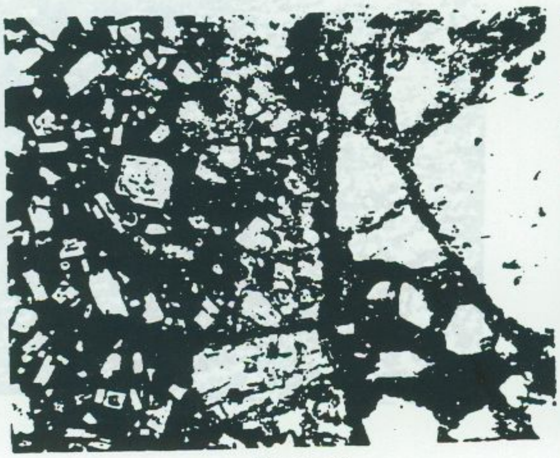

Figure 3

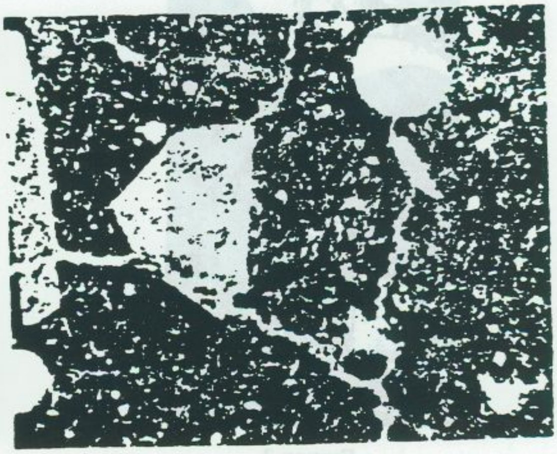

Figure 4

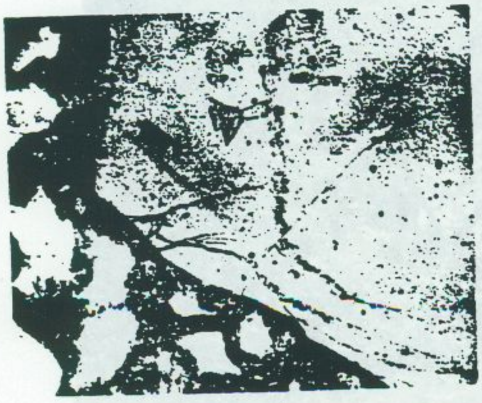

Figure 5

Figure 6

PHOTOMICROGRAPHS OF FEATURES RELATED TO ALKALI-AGGREGATE REACTION IN CONCRETE AND MORTAR

FIGURE 1

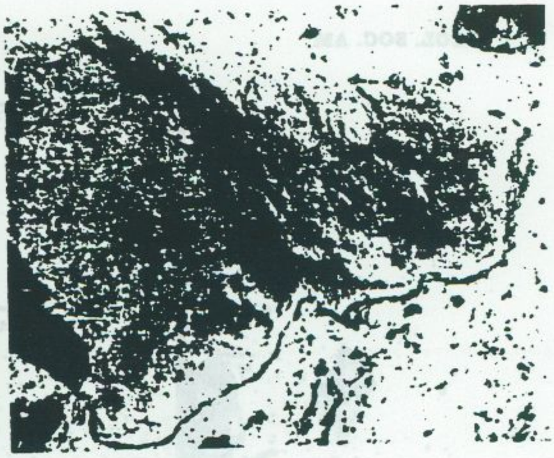

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

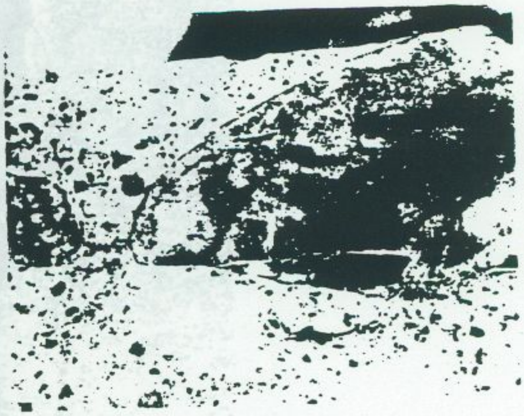

FIGURE 6

PHOTOMICROGRAPHS OF FEATURES RELATED TO DETERIORATION OF CONCRETE

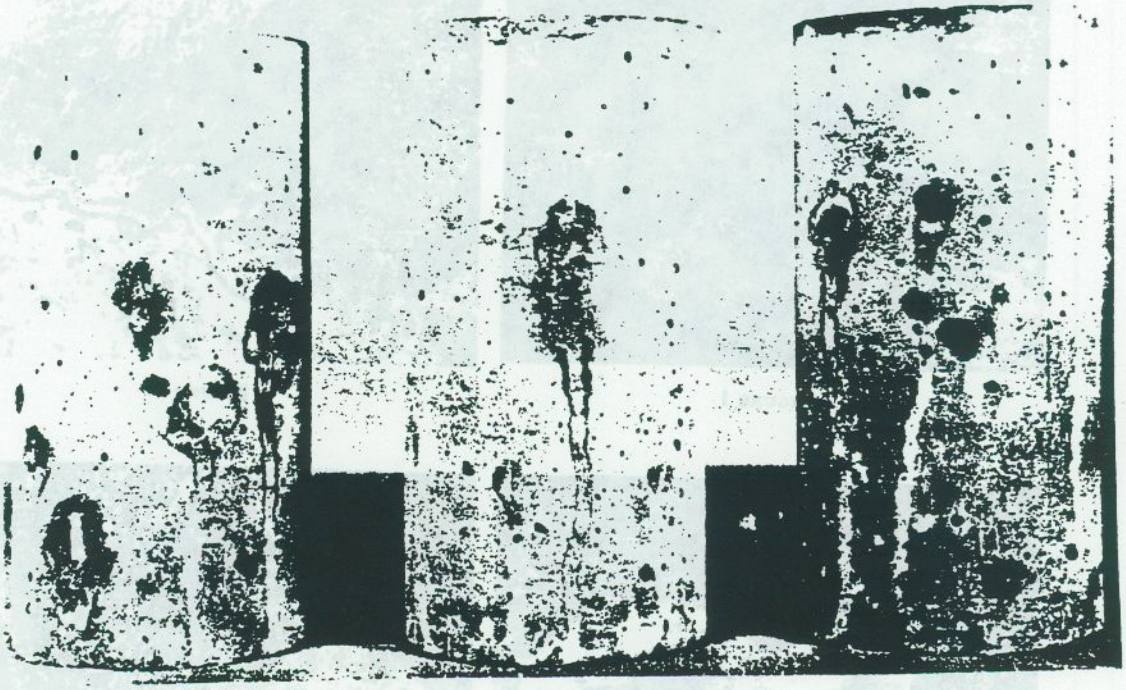

FIGURE 1

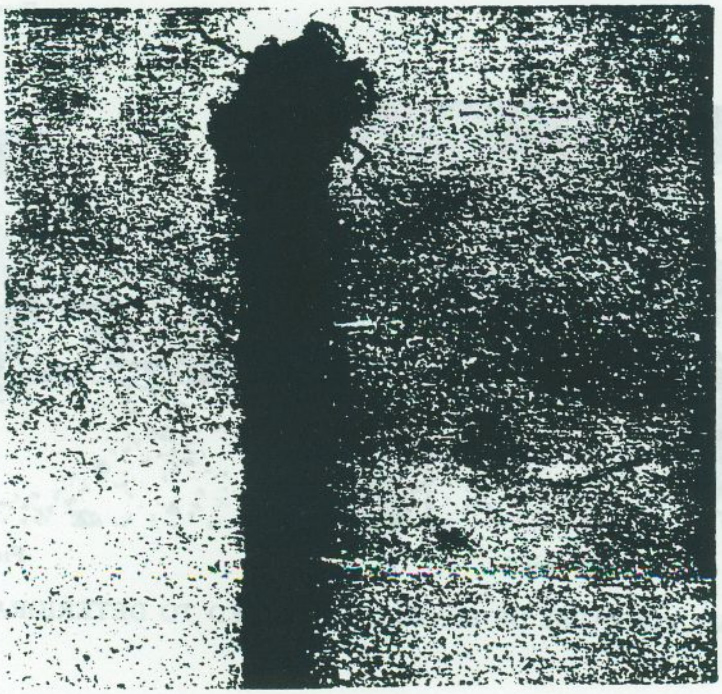

FIGURE 2

EXUDATIONS ON CONCRETE

$$\left\{\begin{matrix} Na_2SO_4 \\ CaSO_4 \end{matrix}\right\} + \left\{\begin{matrix} + \\ 3CaO.Al_2O_3 Ca(OH)_2 \cdot 12H_2O \end{matrix}\right\} \Rightarrow \left\{\begin{matrix} + \\ 3CaO.Al_2O_3 3CaSO_4 \cdot 31H_2O \end{matrix}\right\} + \left\{\begin{matrix} NaOH \\ Ca(OH)_2 \end{matrix}\right\} *$$

Water-soluble Sulfates

calcium aluminate hydrate gel

Ettringite

DETERIORATION BY SULFATE ATTACK

Water carrying dissolved sulfates, or moist sulfate-bearing soils in contact with concrete, can be very destructive. According to the Bureau of Reclamation (1955, p. 12), sulfate attack is "considerable" or "severe" for concrete containing Type I portland cement if soil in contact with the concrete contains more than 0.20 per cent by weight of water-soluble sulfate (as SO_4), or if water in contact with the concrete contains sulfate in concentrations over 1000 ppm. The rate of attack is minimized if Type II or (preferably) Type V cement is used because of the limitation of alumina (C_3A) content of these cements. Imperviousness and low absorptivity are prerequisites to adequate sulfate resistance in any portland-cement concrete.

The deterioration is due to reaction of the sulfate with hydration products constituting the cement paste and the production of calcium sulfoaluminate and calcium sulfate dihydrate (gypsum) or, under extreme conditions, hydrated alumina, $Mg(OH)_2$, and hydrous silica gel (Lea and Desch, 1956, p. 294–297) (Table 1). In its intermediate stages, the reaction with alkaline soils and waters produces great expansion in the cement paste with resulting progressive distension, warping, and fracturing of the concrete. The cement paste tends to expand away from the periphery of aggregate particles, and the resulting opening commonly becomes partially filled by secondary deposits. In its later stages, the cement paste is decomposed completely and becomes soft and friable, and some rock types in the aggregate may be altered as well. Commonly, the outer hull of highly carbonated mortar remains as a shell until finally disrupted by expansion and breakdown of the underlying concrete (Pl. 5, fig. 3). Such severe attack is common in arid areas in parts of western United States and where alkali sulfate waters are employed in industrial installations, such as cooling towers, where dissolved salts are progressively concentrated by evapora-

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PLATE 3.—PHOTOMICROGRAPHS OF FEATURES RELATED TO DETERIORATION OF CONCRETE

FIGURE 1.—Microfractures transecting mortar and quartzite aggregate in concrete affected by alkali-aggregate reaction. × 3½

FIGURE 2.—Alkalic silica gel and high-sulfate calcium sulfoaluminate accumulated in a fracture in a particle of phyllite involved in alkali-aggregate reaction. × 4

FIGURE 3.—Acicular crystals of high-sulfate calcium sulfoaluminate accumulated in a void in concrete. × 6

FIGURE 4.—Tufts of high-sulfate calcium sulfoaluminate in a void in concrete. × 8

FIGURE 5.—Acicular high-sulfate calcium sulfoaluminate in fracture resulting from alkali-aggregate reaction. × 142

FIGURE 6.—Air void in concrete containing a deposit of unidentified, white, acicular crystals, possibly a hydrous calcium silicate. × 2¼

PLATE 4.—EXUDATIONS ON CONCRETE

FIGURE 1.—Alkalic silica gel exuding from concrete affected by alkali-aggregate reaction. × ¼

FIGURE 2.—Surface of retaining wall displaying staining and surface pitting produced by oxidation and hydration of pyrite in a particle of coarse aggregate. Superficial deposits in the stained areas are composed of hydrated ferric oxides, commonly in association with the high-sulfate calcium sulfoaluminate. Note the radial fractures extending from the pit. × *ca* ¼

tion of a portion of the water. The main deterioration may occur either above or below the ground level (Tuthill, 1955).

Solutions of calcium sulfate are less aggressive than are sodium sulfate solutions, and solutions of magnesium sulfate are much more aggressive than are other sulfates. Calcium sulfate produces calcium sulfoaluminate by reaction with calcium aluminate hydrates in the cement paste. Sodium sulfate produces gypsum ($CaSO_4 \cdot 2H_2O$) by reaction with calcium hydroxide, or calcium sulfoaluminate by reaction with calcium aluminate hydrate. Magnesium sulfate reacts with calcium silicate hydrates as well as with calcium hydroxide and calcium aluminate hydrate to produce magnesium hydroxide as the end product. Chemical attack by sea water forms similar end products (Lea and Desch, 1956, p. 296–297; Kennedy and Mather, 1954). However, the degree of expansion and disintegration of the concrete is usually less rapid.

To prove the occurrence of sulfate attack on concrete, the petrographic examination should be supplemented by chemical analysis to determine whether more acid-soluble sulfate is present than was contained in the original cement. Such sulfates will be up to several-fold that derived from the normal calcium sulfate content of the cement. However, in some situations, the excess sulfate may be leached from the concrete and so not be as high as might be suggested by the extent of deterioration. Where attack by magnesium sulfate solutions or sea water is indicated, analysis for acid-soluble magnesium is helpful in evaluating the progress of the chemical reactions.

A form of sulfate attack on the cement paste can originate within the concrete by release of sulfates from the aggregate. Soluble sulfates, such as mirabilite, gypsum, or epsomite, occurring as coatings or inherent constituents of the aggregate particle, can cause expansion and deterioration of the cement paste, to the extent that they are dissolved while enclosed in the concrete. Also, decomposition of alunite or jarosite or oxidation and hydration of pyrite, marcasite, or pyrrhotite (Hagerman and Roosaar, 1955) can cause similar effects. Pyrite or marcasite in soft and porous particles in aggregate is a common cause of popouts and surface staining of concrete in some areas (Pl. 4, fig. 2). In dense, impermeable rocks, pyrite causes no distress of concrete over many years of service. Lea and Desch (1956, p. 493) indicate that "reactive" and "nonreactive" types of pyrite can be distinguished by testing of the aggregate particles in lime water; the reactive types quickly produce a blue-green precipitate of ferrous hydroxide which progressively is oxidized to brown ferric hydroxide.

MISCELLANEOUS CAUSES OF DETERIORATION

General statement.—Concrete fails in service when it is strained beyond its yield point by either internal or external forces. Freezing and thawing of water and alkali-aggregate reaction are two very important sources of internal forces leading to deterioration of concrete by both internal breakdown and development of structural failure by external forces originating in restraint of the affected concrete members. Other causes of distress are indicated below.

Failure of concrete under stress.—Overstressing of the concrete by superimposed loads, impact, abrasion, or cavitation may cause failure either because the proportioning of the concrete was not appropriate to the conditions of service or because the concrete, although properly designed, was not correctly proportioned, mixed, placed, and cured. Concrete so affected usually can be identified by examination of the structure to detect such phenomena as undue deflection of members, shear failure (Pl. 5, fig. 2), flexural failure, cracking over reinforcement, or attrition of areas of traffic on pavements or concentrated water flow in hydraulic structures. When such failure is of long duration, marked evidence of deterioration will be found in the cement paste because of penetration of the concrete by water along fractures and planes of shear. The deterioration will be marked by carbonation in the cement paste and accumulation of deposits of various calcic compounds in voids, along fractures, and on exposed surfaces. Such indications of deterioration should not be interpreted as originating in cement-aggregate reaction or the effects of aggressive waters. Examination of the concrete should be directed to a determination of any divergences in the composition and quality of the concrete from the specifications under which the construction was carried out.

Drying shrinkage.—Drying shrinkage can cause severe cracking of concrete if the water or entrained-air content of the concrete was excessive or if the aggregate possesses certain properties (Carlson, 1938; Stutterheim, 1954). Aggregate contributes in two general ways to drying shrinkage: (1) if the aggregate contains a high proportion of argillaceous or organic material which itself participates in shrinkage on drying, or (2) if the aggregate is weak and compressible, such as are some highly porous, micaceous, and clayey sandstones which cannot restrain the normal drying shrinkage of the cement paste. A first objective in the investigation of drying shrinkage is to establish that the concrete has contracted rather than expanded. Superficial effects, such as the pattern cracking of the surface of the concrete (Stutterheim, 1954, Fig. 3, p. 3) are similar in concrete that has expanded. However, expansion will be indicated by partial or complete closing of expansion or construction joints and abutting of adjacent members (Pl. 5, fig. 2). Drying shrinkage usually will not be accompanied by opening of joints because the volume change will be accommodated by opening of internal cracks.

If the aggregate is at fault, its properties may be recognized by petrographic examination. If excessive drying shrinkage results from inordinate water content of the concrete, the cause may lie either in excessive water-cement ratio at normal cement content or normal water-cement ratio at a cement content that is excessive for the particular design of the concrete. Excessive air content can be established quantitatively by microscopical methods.

Acidic waters.—Acidic natural waters, such as "pure" waters in streams flowing from fields of snow and ice, as in the high mountains and in the far north, with the value of pH in the range 5.7 to 7.0, aggressively attack portland-cement concrete by dissolution of calcium hydroxide and calcium carbonate (Tremper, 1931; Tuthill, 1955). Similar action occurs in natural waters made acidic by organic acids produced by decaying vegetation. Such action extracts also the calcium of the hydrated silicates and aluminates, initially causing disintegration of superficial mortar and exposing the coarse aggregate (Tuthill, 1955, Fig. 1, p. 189) but ultimately producing a friable mass composed mainly of hydrous silica and ferric oxides, together with the aggregate. In intermediate stages of deterioration, aluminum hydroxide and low-lime silicate hydrates are present. A more aggressive action may occur in concrete i contact with certain industrial waters or sewage (Tuthill, 1955, Fig. 2, p. 190–194).

Carbonation of plastic concrete.—Carbonation of the surface of plastic concret such as by use of unvented, oil-burning heaters to provide protection of the concre from adversely low temperatures, can prevent development of adequate resistan to abrasion and lay the basis for excessive wear and dusting of floors (Kauer ar Freeman, 1955). This action is indicated by the presence of a zone of intense carbon tion to a depth of ⅛ inch or more on newly placed concrete. Unlike carbonatic developing after the normal structure of the cement paste has been formed by th hydration process, carbonation occurring prior to hardening of the concrete preven formation of a firm, abrasion-resistant surface.

Reactions of sand-gravel aggregates in the Great Plains area of the United States.—Properties of aggregate not dependent upon alkali-aggregate reaction can be ver important locally. One of the most important reactions of this type involves th highly feldspathic, granitic sand-gravel aggregates of the Republican, Platte, Lou and Kansas rivers in Kansas and Nebraska and also occurring in northweste Missouri and western Iowa. The cracking and expansion of concrete and mort associated with the action can be produced by heating and cooling and simultaneo wetting and drying (Mielenz, 1953). Extensive studies by Conrow (1952) demonstra that the critical conditions of curing and storage conducive to development adverse expansion are (1) a period of hydration (the action is increased by mo storage in excess of 28 days) and (2) a hydration period during which the temperatu is raised above 75° F., followed by (3) water storage at about 70°–75° F. If the cc crete or mortar contains a cement-aggregate combination susceptible to this actic rapid expansion, cracking, and general deterioration take place during the storage water at constant temperature. The rate and magnitude of expansion are increas by introduction of a period of drying during the curing period. This action has cc tributed to rapid and costly deterioration of concrete in pavements, bridges, a other structures in the indicated area and probably will be found to occur elsewh as a major or subsidiary cause of distress in exposed concrete.

The deterioration shows no clear-cut relationship to alkali content of the ceme Great expansion has been obtained in the laboratory on specimens containing ceme whose alkali content is less than 0.2 per cent (Mielenz, 1953), as Na_2O. In the fie alkali-aggregate reaction commonly occurs contemporaneously, although larg independently, if alkali-reactive rock types are present in the aggregate and if cement is high in alkali content. One outstanding feature of this type of deteriorat is separation of the cement paste from the periphery of particles of coarse aggreg and the development in such openings of deposits of calcium hydroxide, with

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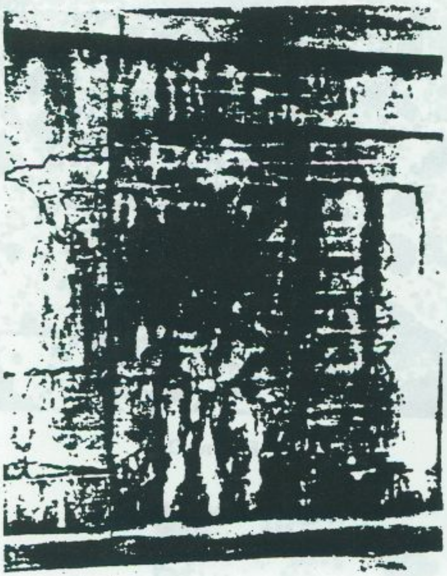
PLATE 5.—DETERIORATION OF CONCRETE IN STRUCTURES

FIGURE 1.—**Pattern cracking caused by expansion resulting from alkali-aggregate reaction concrete of an overpass structure**

FIGURE 2.—**Shear failure in a concrete curbing caused by expansion of adjacent concrete mem**

FIGURE 3—**Concrete disintegrating as a result of sulfate attack. Concrete below the ground l was intact, whereas the exposed concrete is severely affected. Deposits of salts were visible in superficial portion of the exposed concrete**



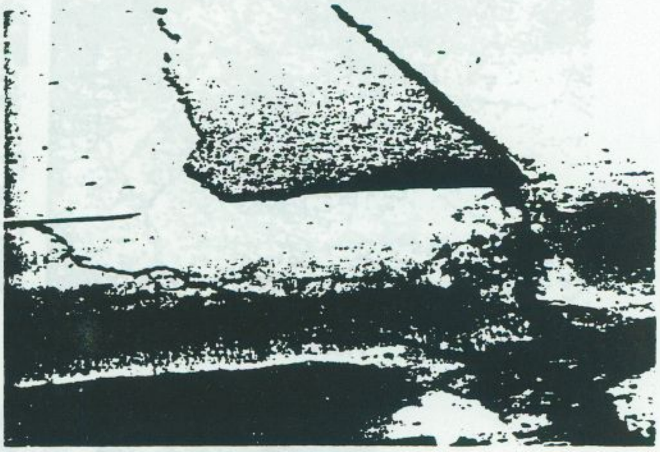


FIGURE 2

FIGURE 1

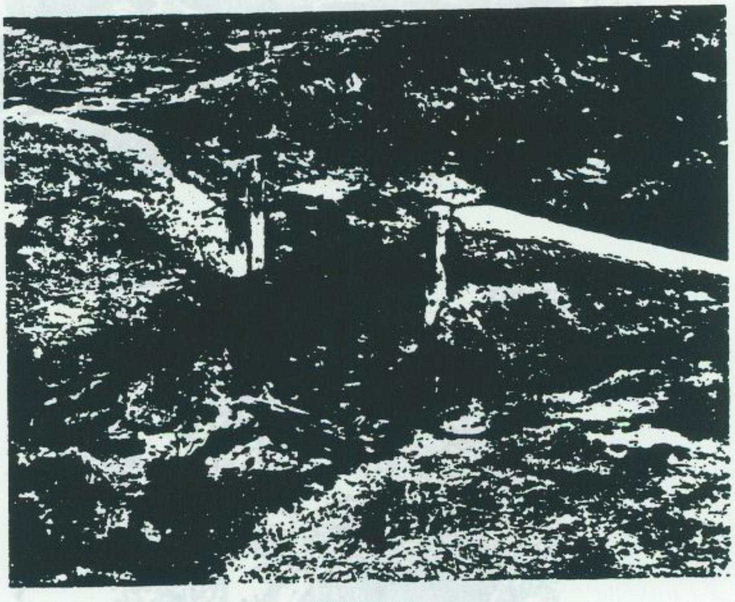


FIGURE 3

DETERIORATION OF CONCRETE IN STRUCTURES

Figure 1

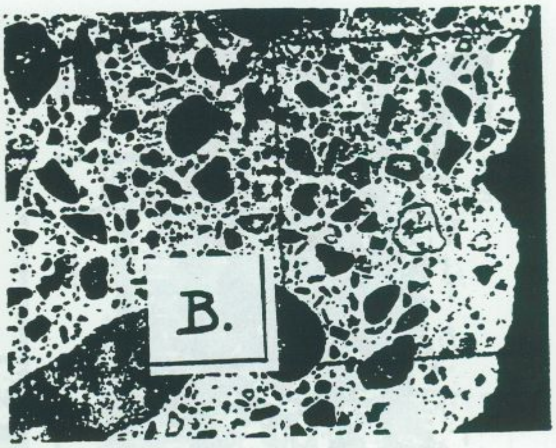


Figure 2

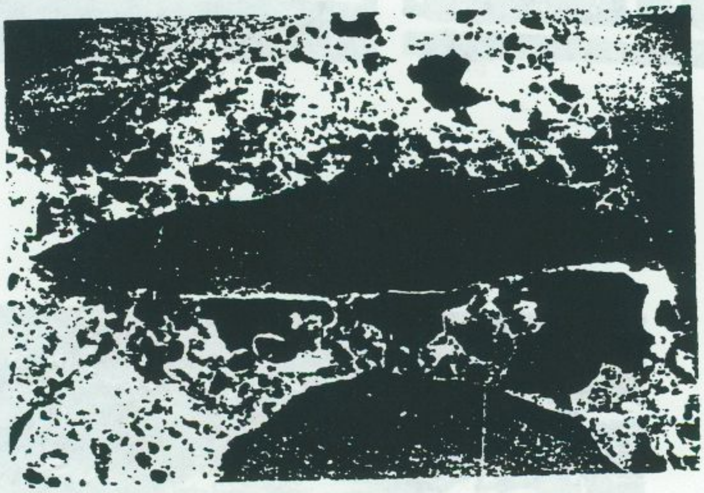


Figure 3

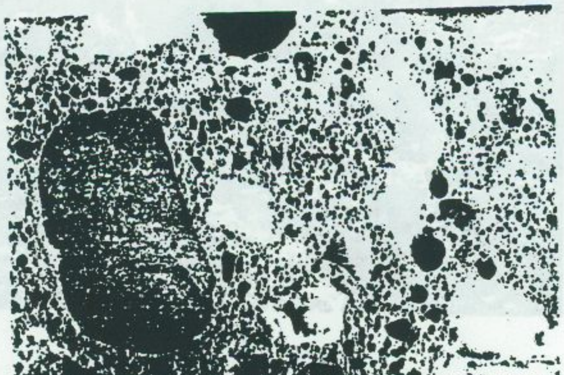


Figure 4

FEATURES OF CONCRETE AT LOW MAGNIFICATION without accompanying calcium carbonate, calcium sulfoaluminate, or alkali silica gel.

unlike sulfate attack

Differential thermal volume change.—Differential thermal expansion or contraction of aggregate and cement paste apparently is locally significant if the aggregate possesses an extremely low coefficient of thermal expansion or if the thermal coefficient of expansion of the aggregate varies greatly in different crystallographic directions, such as in calcite. Adverse experience with a marble aggregate is described by by Pearson (1941). Thermal properties of aggregate are much discussed as a source of distress in concrete, but no instances in which such properties are significant have been demonstrated unequivocally.

Oxidation, hydration, or carbonation of aggregate.—Certain types of chemical activity of aggregates are locally significant. They include oxidation and hydration of the iron sulfides pyrite, marcasite, and pyrrhotite (Pl. 4. fig. 2), resulting in release of sulfuric acid and hydrated iron oxides (limonite). Oxidation and hydration of ferrous and ferric oxides in clay-ironstone particles cause expansion which may create popouts and initiate deterioration of the surface of concrete. Carbonation together with hydration can be significant in aggregates produced from industrial wastes if CaO or MgO is present; these can be transformed to calcium or magnesium hydroxides or carbonates. Artinite ($MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$) has been identified as a product of hydration of MgO in a dead-burned dolomite occurring as a contaminant in concrete (Rhoades and Mielenz, 1948, p. 39). Loughlin (Pearson and Loughlin, 1923) concluded that disintegration of certain installations of cast stone and stucco in the vicinity of Los Angeles, California, was caused by the dehydration and rehydration of the zeolite laumontite with accompanying volume change during wetting and drying. The zeolite is a constituent of an altered facies of anorthosite. The process involves the reversible transformation of original laumontite to leonhardite (Rhoades and Mielenz, 1948, p. 40), which may be watched microscopically.

EXAMINATION OF STRUCTURES

INSPECTION

The technique of examination of concrete in the field varies widely depending upon the size and complexity of the structure and the purpose of the examination. Some reasons for examination of concrete structures are: routine survey of condition of structure as a part of maintenance; examination of structures containing specific aggregates, cements, cement-aggregate combinations, or admixtures so as to estab-

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PLATE 6.—FEATURES OF CONCRETE AT LOW MAGNIFICATION

FIGURE 1.—Typical pattern cracking on concrete seriously affected by alkali-aggregate reaction. Similar cracking can result from expansion resulting from any of several processes. × 1/3

FIGURE 2.—Sawed and finely ground surface of concrete revealing reaction rims on particles of aggregate. Area of interest located on such surfaces may be marked and later prepared as thin sections or polished and etched surfaces. × 1 1/3

FIGURE 3.—Sawed and ground surface in concrete affected by cement-aggregate reaction involving dolomitic limestone. Note the disappearance of the reaction rim at the intersection of the boundary of the particle and air voids in the mortar. × 5

FIGURE 4.—Typical air-void system in air-entrained concrete. × 2 1/4

lish the suitability of these materials for use in proposed new construction; and examination to evaluate the progress and to determine the cause of evident distress in a structure.

Any serious study of a concrete structure should be preceded by a review of all available construction records, particularly concrete-control reports and test data and specifications on the aggregates and cements. It is helpful to examine petrographically samples of aggregates from the sources of supply for aggregates used in the existing construction.

Visual examination should be directed to complete, quantitative description of the severity and distribution of structural failure or distress of the concrete, such as cracking, deterioration, deflection of members, opening or closing of joints, shear or flexural failure, rusting of reinforcement, formation of secondary deposits, and the relationship of these to environmental conditions in the structure and the general quality and composition of the concrete as placed.

FIELD TESTS

The visual inspection in the field usually will be only a part of a more comprehensive investigation being directed by engineers or architects. Various means may be applied to evaluate the stability of the structure, the physical properties of the concrete, and the degree of distress, such as setting of reference points in the concrete to permit measurement of progressive expansion, or use of a soniscope (Leslie and Cheesman, 1950) to determine the strength and elasticity of the concrete in place. Taking of samples of the concrete for testing and petrographic examination in the laboratory commonly will be a part of such a study. Description of the condition of the structure should be supplemented by photographs depicting the distress and locating points of sampling or drilling.

TAKING OF SAMPLES

Samples should be taken so that they represent the true nature of the concrete in the structure. Samples obtained by coring are preferable to those obtained by other means because drilling disturbs the concrete to a minimum and permits probing of the structure to any desired depth. If coring equipment is not available, sampling usually is restricted to portions of the concrete removed as a part of repairs or rebuilding, or to near-surface concrete that can be broken free by sledges or air hammers.

Caution must be used in evaluating results of laboratory study of near-surface samples because they ordinarily will differ greatly from the concrete at depth in development of cracking, weathering, and adverse chemical reactions.

The cores should be identified and oriented by painted marks on the core itself and should be packed both for protection from damage and to minimize drying. Complete data on the location of the core hole, the direction of drilling, and the depth from which the core was recovered should be transmitted to the laboratory.

MEGASCOPIC EXAMINATION OF CONCRETE IN THE LABORATORY

LOGGING OF SAMPLES

Core and groups of samples of concrete received at the laboratory should be examined visually and described (logged) so that all general features and variations of composition and structure are recorded. This description should include: (1) superficial effects, such as pattern cracking, scaling, popouts, staining, carbonation, general deterioration, secondary deposits, evident variation in the composition or grading of the aggregate, segregation, changes in color of the cement, variation in the composition or grading of the aggregate, segregation, changes in color of the cement, variation in distribution of voids or "honey-combining", and related phenomena. Photographs of the core and samples always are helpful in supplementing the notes and referencing the location of portions of the concrete subjected to various laboratory tests.

CORRELATIVE TESTS

Ordinarily at this time, representative sections of the core or portions of the samples will be selected for such physical and chemical tests as evaluation of strength, elasticity, permeability, unit weight, cement content, and expansion in storage. The samples should be correlated with the notes and photographs made during general inspection of the samples as well as with data on the location and orientation of the portions of the core or samples. The residue of the samples and cut ends from sawed sections usually are adequate for petrographic examination.

VISUAL EXAMINATION

Representative portions of the core and samples are examined visually and under the stereoscopic microscope, generally at magnification from 8 to 100 diameters. The examination is directed to a complete description of the compositional and structural features on original exposed surfaces, on fracture surfaces, in voids, within aggregate particles, and on fresh surfaces through the cement paste. During this examination, the following features are studied:

Composition and condition of the aggregate
Cement-aggregate reactions
Deterioration of aggregate particles in place
Hardness and density of the cement paste
Tenacity of the cement-aggregate bond
Occurrence of segregation or bleeding
Depth and extent of carbonation
Distribution and occurrence of fractures
Occurrence and identity of secondary deposits
Characteristics of the voids in the mortar
Miscellaneous features of the concrete.

As a part of this examination, interesting portions of the concrete, secondary deposits, or particles of aggregate are separated for more detailed microscopical study or chemical or X-ray diffraction analysis. If justified, detailed petrographic analysis of the coarse aggregate can be made by breaking down a representative portion of the concrete. The particles of coarse aggregate are recovered, identified, and described. The fine aggregate is best studied in thin sections of the concrete.

EXAMINATION OF GROUND SURFACES

As a part of the stereoscopic microscope study, it is helpful to prepare sawed and finely ground surfaces. Such surfaces transect aggregate-cement interfaces and so

① Paste = Dark gray, hard, vitreous & amorphous in appearance
② Paste/Aggregate Bond = tight, adheres firmly
③ Large Voids = Sparse, mostly empty (may have few Ca(OH)$_2$ xtals)
④ Aggregate Socket = Dark gray, free of secondary deposit
⑤ Fractures = Go through the aggregates
⑥ Depth of Carbonation = Shallow (1-2 mm)

adequately cured concrete with high w/c ratio
= Light gray, weak & soft, less vitreous (dull) & granular inap
= paste separated from aggregate with openings
= Frequent, filled with secondary deposits of Ca(OH)$_2$
= Light gray or white due to secondary deposits
= Go around the aggregates
= Deep (>3 mm)

RIMS AROUND AGGREGATES

permit detailed study of relationships at this critical juncture. In particular, microfractures, reaction rims, separations at the interface, and secondary deposits are most easily discerned (Pl. 2, fig. 6; Pl. 3, fig. 1). Also, specific areas may be selected for thin sectioning or preparation of polished and etched surfaces (Pl. 6, fig. 2). The characteristics of the void system can be evaluated quantitatively on such surfaces.

An important problem at this stage of the petrographic examination is the determination of whether rims on the aggregate developed before or after preparation of the concrete. Rims formed in the concrete may be identified positively if such rims terminate when the aggregate-cement paste interface intersects an air void in the mortar (Pl. 6, fig. 3). Of course, rims existing on the aggregate prior to manufacture of the concrete will persist in the aggregate particle adjacent to such voids. Particles of crushed stone are not completely rimmed when the aggregate is manufactured, so that occurrence of persistent rims on such particles in concrete demonstrates cement–aggregate reaction. For natural aggregates, weathering rims are common and sometimes are distinguished with difficulty except by the relation of the rims to adjacent voids or by the development of visible cement-aggregate reaction products in spacial relation to particles of specific lithologic types. Reaction rims commonly are perceptibly softer than the interior of the particles, and such rims commonly break away as a thin hull from the interior and cling to the pebble socket when the concrete is broken. Without these direct observations, the secondary or primary origin of rims on aggregate particles enclosed in concrete can be discerned only by detailed comparison of these with rims exhibited by new samples of aggregate from the deposit or plant which supplied the aggregate for the structure.

EXAMINATION OF FRACTURED SURFACES

Sound, well-cured concrete of low water–cement ratio and several years old is tough and dense. Internal fractures are sparse. Intense carbonation extends inwardly from the surface in a somewhat irregular, superficial zone usually less than an eighth of an inch thick. Premature drying of exposed concrete leads to mild carbonation well below the surface. The fracture surfaces through the cement paste are gray, and the freshly fractured cement paste is somewhat vitreous and amorphous in appearance. Close inspection reveals black or dark-brown, vitreous, angular coarse particles of the cement embedded in the paste and still largely unhydrated. The cement paste adheres firmly to the particles of aggregate. Large voids in the mortar are sparse. Many of the particles of fine and coarse aggregate are broken across when the concrete is fractured in the laboratory; even tough and hard particles break rather frequently. The aggregate sockets in the fracture surfaces appear gray and are free from secondary deposits. Voids are empty; the inner surface is smooth and glazed; or the voids contain occasional, thin tabular, white or colorless crystals of calcium hydroxide. At this stage, evidence of alkali-aggregate reaction rims on aggregate or meager deposits of alkalic silica gel may be visible. In very old, satisfactory concrete, such rims will be no cause for concern and indeed could account for some of the toughness of the concrete.

With increase in water–cement ratio, decrease in compaction, inadequate curing or protection from freezing, or initiation of deterioration of the concrete for any of many reasons, the quality of the cement paste and the firmness of the cement-aggregate bond are decreased. The cement paste is weaker, softer, lighter in color, and less vitreous in luster and possibly somewhat granular in appearance, in contrast to equivalent concrete of high quality. Large voids are frequent, especially at the bottom of particles of coarse aggregate (Pl. 6, fig. 3). Also, the cement paste commonly is separated from the aggregate particles. These openings and air voids may be partially filled by secondary deposits of calcium hydroxide, calcium sulfoaluminate (Pl. 3, figs. 3, 4, 5), or other substances (Table 1). Such separations are best developed at the base of particles of coarse aggregate because of settlement in the interstitial paste while the concrete is plastic.

When concrete of inferior quality, or concrete affected by incipient deterioration, is broken, the fracture surface tends to pass around particles of aggregate, along the cement-aggregate contact. The socket so revealed usually is very light gray or white because of the secondary deposits. On finely ground surfaces, careful and detailed examination reveals fine ramifying microfractures in the cement paste. They are most evident at undesirably high or very low water–cement ratio (very high cement content), the former because of excessive loss of water on drying, the latter because excessive shrinkage cannot be controlled by the aggregate when the paste content is very high. At this stage, visible evidence of alkali-aggregate reaction may be slight or pronounced depending upon many factors, even if alkali–aggregate reaction is the main cause of the inferior quality of the concrete.

With development of advanced deterioration, a system of more or less continuous fractures transects the mortar and coarse aggregate (Pl. 2, figs. 4, 5, 6; Pl. 3, fig. 1). These reduce flexural strength of the concrete and permit penetration of the cement paste by water, carbon dioxide, and aggressive solutions. As these fractures are widened, they become lined by secondary deposits and at their intersection with the surface of the concrete may become the scene of considerable deposition of calcium carbonate or, if alkali-aggregate reaction is in progress, of alkalic-silica gel (Pl. 3 fig. 2; Pl. 4, fig. 1; Pl. 5, fig. 1). Rusting of reinforcing steel becomes significant in exposed portions of structures at this stage. When the concrete is broken for inspection, the newly exposed surfaces frequently form along these fractures; hence, superficial appearance of the concrete may suggest much greater deterioration of the mortar than actually has occurred. At this stage, voids in the cement paste and aggregate may contain abundant calcium carbonate, calcium sulfoaluminate, alkalic-silica gel, or other secondary substances (Pl. 3, fig. 6).

Alkalic-silica gel produced by alkali–aggregate reaction may be copious or meager in concrete seriously affected by expansion and cracking from this cause. In other words, there is no direct relationship between the abundance of this gel and its capacity to cause distension and fracturing of concrete by osmotic or swelling pressure as a result of imbibition of water. The pressure-producing capacity depends upon many factors, including the ratio of alkalies to silica and to calcium in the gel, the water content of the gel, availability of water to the gel, the porosity of the aggregate and cement paste, the permeability of the concrete, the tensile strength of the mortar, and the superimposed load on the concrete at any particular place and time. Affected concrete removed from a structure and stored in a moist atmosphere or in water

commonly will exude amazing quantities of fluid, alkalic-silica gel, and reacted p
ticles of aggregate may be displaced at exposed surfaces by expansion of underly
bodies of such gel. Siliceous limestones and dolomites and cherts containing chalc
ony and/or microcrystalline to cryptocrystalline quartz frequently produce mea
quantities of alkalic-silica gel even though significant distress is evident in the c
crete. Conversely, opaline rocks and acidic to intermediate volcanic rocks (ma
glass to cryptocrystalline rhyolites and andesites) commonly produce copious
when combined with high-alkali cements.

EVALUATION OF THE VOID SYSTEM IN CONCRETE

GENERAL STATEMENT

An important part of the microscopical examination of concrete is a determina
of the volume of voids of microscopic or megascopic dimensions included in
cement paste. In nonair-entrained concrete, the voids are primarily large (usually m
than 1 mm in diameter). In well-compacted nonair-entrained concrete, these v
constitute approximately the following proportions of concrete (Bureau of Recla
tion, 1955, p. 120):

Maximum size of aggregate (Inches)	*Approximate content of entrapped air voids* (Per cent by volume)
3/8	3.0
3/4	2.0
1½	1.0
3	0.3
6	0.2

In properly compacted air-entrained concrete, the voids are mainly spheric
ellipsoidal and very small (Pl. 6, fig. 4). The following proportions of air voic
usually desirable to develop proper workability of the fresh concrete and resis
of the hardened concrete to freezing and thawing (Bureau of Reclamation, 195
120):

Maximum size of aggregate (Inches)	*Approximate content of entrapped air voids* (Per cent by volume)
3/8	8
3/4	6
1½	4.5
3	3.5
6	3

The examination may be directed to (1) determination of the content of air
so as to ascertain (for example) whether the concrete is air-entrained as specifi
the cause of very low strength or very low unit weight, or (2) determination
average size and spacing of the air voids in the cements paste so as to ascertain w
the cement paste is adequately protected from effects of freezing and thawing.

These parameters of the air-void system are determined by microscopical trav
on finely ground surfaces of the hardened concrete by the Rosiwal (linear trave
the modified point-count method. Techniques, calculations, theory, and methc

POINT-COUNT METHOD

The necessary experimental data may be obtained also by the point-count method (Chayes and Fairbairn, 1951). In this procedure

$$A = \frac{p_v}{p_t}$$

where p_v is the number of counts falling on voids, and p_t is the total number of count made in the traverse. The number of voids per inch of traverse is obtained as is don in the linear-traverse methods. Hence, since

$$\bar{l} = \frac{A}{n}$$

then the parameters of the void system can be calculated in the same manner as i accomplished following the linear-traverse examination.

Ordinarily, the number of points counted in the point-count method should approximate 2000, and the length of traverse in both the point-count and linear-travers methods should exceed 100 inches. Such minimal limits will provide adequate statistical data on the void system and will accommodate the variability inherent i well-placed, uniform concrete.

Particularly for slabs and pavements subjected to weathering, the quality of th void system in the topmost quarter inch of the concrete should be evaluated separatel from that of the concrete in the slab or pavement as a whole. Inferior air-entrainin agents cannot retain an adequate void system in the near-surface concrete, especial at high water–cement ratio, whereas an adequate void system may exist in the co crete well below the surface. Since the near surface is subjected to the most vigoro and most frequent freezing and thawing, it is essential that the void system in th near-surface zone of the concrete produce an adequate spacing factor, probably 0.0 inch or less.

Microscopical measurement of the void system can be performed routinely trained technicians. However, a petrographer or microscopist should supervise d velopment of techniques and procedures in any given laboratory and training the technician.

DETERMINATION OF THE CONTENT OF CEMENT PASTE, CEMENT AND AGGREGATE IN CONCRETE

The point-count or linear-traverse method also may be used on fine-ground sla of concrete to determine the proportion of cement paste (Kelly, Polivka, and Be 1958). The slabs are prepared as described above for determination of air content a void spacing, and the traverse methods are employed similarly except that the ceme paste is distinguished from all other phases of concrete—namely, the aggregate a voids. The surface should be viewed at a magnification of 100 × or more, so as facilitate distinction of minute portions of aggregate from the cement paste. T writer originally thought that the indicated paste content necessarily would be hig than the actual value because a portion of the fine aggregate always will be below limit of resolution of the stereoscopic microscope, hence would be combined with cement paste during the traverse. However, surprisingly, the value determined experimentally consistently is lower than the actual by several percentile. This disparity probably results because the aggregate, being harder and more abrasion resistant than the paste, is preserved over a proportionately large surface area of the fine-ground slab.

For example, a mortar specimen was prepared by batching a small portion of cement and natural sand in the ratio 1:2.25 by weight, and sufficient water was added to develop a plastic but nonbleeding mixture. The entire quantity of mortar then was cast as a large portion of a 2-inch cube. When the specimen had cured sufficiently to permit preparation of finely ground surfaces, five thin slabs were sawed and ground. The paste content was determined by point-count traversing of five surfaces, using a total of approximately 5000 counts. The indicated paste content was 39.1 per cent by volume, whereas the paste content determined from the volumes of the cement and water added to the mixture was 42.9 per cent.

With proper control of surface preparation of the slabs and proper use of the traverse methods, it is possible that this procedure will be developed as a reliable method for determining the general level of paste content of concrete.

From the determined cement-paste content of the concrete, the approximate cement content of the concrete can be calculated if the water–cement ratio is known. If the water–cement ratio is not known, the order of magnitude of the cement content can be determined by assumption of a value for this ratio. Unless undue bleeding of water or settlement of the cement paste is indicated by examination of representative specimens of the concrete, the volume of the cement paste (sum of the volume of hydration products, unhydrated cement, uncombined water, and submicroscopical voids) may be taken to represent the sum of the volume of the mixing water and the volume of the cement without significant error.

Letting V_c represent the fractional volume of the concrete originally composed of dry cement; V_p the fractional volume of the concrete composed of cement paste; W the water-cement ratio by weight; and d_c the specific gravity of the cement, then

$$V_c = V_p/(1 + d_c W) \quad \text{and}$$

$$\text{cement factor, sacks per cubic yard of concrete} = 27 \times 62.4 d_c V_c/94.$$

Since d_c may be assumed to have the value 3.15 without significant error (Bureau of Reclamation, 1955, p. 118), the cement factor (number of 94-pound sacks of cement per cubic yard of concrete) can be calculated as follows:

$$\text{Cement factor, sacks per cubic yard of concrete} = 56.35 V_p/(1 + 3.15W)$$

If the paste content and air-void content of the concrete are determined experimentally as indicated, then the proportional volume of the aggregate is readily calculable by difference.

DETAILED MICROSCOPIC EXAMINATION OF CONCRETE

GENERAL STATEMENT

Specimens for detailed petrographic examination are selected during the megascopic examination. These specimens may represent typical portions of the cement paste, examples of cement–aggregate reaction, unusual secondary deposits in voids or fractures, or other features. The microexamination usually is a combination of several techniques, such as use of immersion oils, thin sections, or polished and etched surfaces.

IMMERSION METHOD

Immersion oils afford a valuable preliminary or supplementary procedure in the examination of concrete. They are employed by most petrographers as required to obtain optical data on minerals, compounds, or other phases of all types so as to permit identification or thorough description. In addition, use of immersion methods permits examination of textural and structural arrangements in exceedingly finely divided or amorphous materials with a rapidity and in a degree of detail not possible by exclusive use of thin sections or polished surfaces.

In the examination of concrete, immersion oils are employed especially for identification and description of secondary deposits; for description of the cement paste, including such features as degree of hydration, degree of carbonation, leaching, or other alteration of the cement paste; for identification of rocks and minerals in the aggregate; and for identification of mineral additions or admixtures in the cement paste, such as pozzolans, blast-furnace slag, or diluents in chemical admixtures.

THIN-SECTION MICROSCOPY

General statement.—Petrographic thin sections are of especial value in detailed examination of the cement paste, cement–aggregate relationships, description of the fine aggregate, and description of the progress of deterioration and distress in th concrete.

Preparation of specimens.—Preparation of thin sections of concrete requires specia skill and the application of careful techniques, primarily because of the juxtapositio in typical specimens of hard particles of aggregate and the relatively soft cemen paste and because the cement paste is prone to drying shrinkage and other modific tions with application of heat sufficient for use of common binding media.

Because of these difficulties and because it is not feasible to prepare sections of a portions of even relatively small samples, thin-section study must be accompanied thorough examination under the stereoscopic microscope and by use of immersio methods under the petrographic microscope.

Use of an epoxy resin as a bonding agent[2] to fix prepared specimens of concrete the glass slide and also to impregnate fragile specimens in preparation for grindi and mounting has permitted routine preparation of excellent thin sections of concre with thickness preferably in the range 10 to 15 microns. At this thickness, the ceme paste transmits light readily and displays abundant textural and structural deta At greater thickness, the cement paste appears murky and lacks details of structu At lesser thickness, the details of texture within the paste progressively become fain and less easily discerned. Use of the epoxy resin and hardener avoids the heat required by most other mounting media and the consequent dehydration and shri

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[2] Bonding agent R-313 and hardener, Carl H. Biggs Co., 2255 Barry Ave., Los Angeles, California.

age of the hydration products. Canada balsam or certain thermoplastic resins may be used to cement the cover glass. One must familiarize himself with the microscopical appearance of the impregnating and mounting media so that these will not be identified as components of the concrete.

Sequence of examination.—In a microscopical examination of thin sections of concrete it is helpful to follow a prescribed routine. For example, the following sequence of observations ordinarily is made by the writer:

- Fine aggregate
  - Composition
  - Cement–aggregate reaction
  - Alteration in place
- Coarse aggregate
  - As for fine aggregate
- Cement paste
  - Unhydrated clinker particles
    - Maximum and average size
    - Frequency
    - Composition
    - Evidence of associated cracking
  - Hydration products
    - Texture and microstructure
      - Admixtures and additions
      - Calcium hydroxide
      - Alteration of the hydration products
  - Microfractures
    - Extent, width, continuity
    - Origin and relationships
    - Secondary deposits
- Voids
  - Frequency
  - Size
  - Special relationships
  - Secondary deposits

Characteristics of the cement paste.—The cement paste viewed in thin section is a complex of partially hydrated clinker particles, hydration products, and products of decomposition of the cement paste and of cement–aggregate reaction. Partially hydrated clinker particles may be as large as several tenths of a millimeter but usually are much smaller. The smallest particles of the cement hydrate rapidly, and the proportion of partially hydrated particles in the cement paste decreases greatly during the first week of moist storage, and progressively at a substantial rate with moist storage during the first month. Hydration is greatly accelerated by microfracturing of the cement paste, as by severe freezing and thawing, and is virtually stopped by drying of the concrete.

The grains of clinker are composed of rounded, colorless to brown, usually complexly twinned grains of beta-dicalcium silicate; subhedral, colorless crystals of tricalcium silicate; minute yellow to brown, pleochroic, highly birefringent granules of calcium aluminum ferrites such as brownmillerite; and an opaque to colorless, tran-

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sparent interstitial phase. Partially or completely hydrated, rounded particles of calcium oxide occasionally are visible; the resulting calcium hydroxide typically extends radially from the grain of CaO.

Hydration of clinker proceeds more or less uniformly inwardly adjacent to the various phases of the clinker, with formation of easily visible, isotropic to vaguely birefringent, colorless hydration products. The grains become embayed at their ✓ periphery as crystals of the calcium silicates are hydrated more rapidly than is the interstitial matter of the clinker, but the interior of the larger grains may resist hydration for decades of ordinary exposure. Complete hydration of the clinker produces pseudomorphs that are perceptible in detailed textural pattern in the cement paste; even an image of the twinning of beta-dicalcium silicate is preserved.

$Ca(OH)_2$

Calcium hydroxide is the most readily discerned hydration product of portland cement. It occurs in scattered, irregular crystals; as narrow bands in the cement paste or along paste–aggregate contacts, especially at the lower surface of particles of coarse aggregate where a separation developed by settlement of the adajcent cement paste; and in voids and fractures through the concrete (K. Mather, 1956, Figs. 1–4, p. 61–64).

PASTE CARBONATION

Deterioration of the cement paste.—Deterioration of the cement paste is marked by introduction of secondary deposits, most common of which are calcium carbonate and the high-sulfate form of calcium sulfoaluminate. Carbonation is indicated in thin section by progressively increasing proportions of highly birefringent, extremely minute granules of calcite in the cement paste, especially adjacent to fractures. The early stages of carbonation do not produce calcite in proportion to the amount of carbon dioxide taken up by a unit of hydration products. Apparently, a substantial portion of such uptake is akin to adsorption inasmuch as much of the carbon dioxide is lost progressively during heating of the paste in a temperature range well below the decomposition temperature for calcite. With introduction of calcite, the mass index of refraction of the cement paste is raised progressively. The carbonation proceeds mainly by alteration of minute crystals of calcium hydroxide and decomposition of the calcium silicate and aluminate hydrates. Large crystals of calcium hydroxide frequently persist within very highly carbonated cement paste. Carbonation leads to rapid decomposition of the large granules of unhydrated clinker, which have resisted normal hydration.

HIGH SULFATE FORM OF CALCIUM SULFOALUMINATE

Secondary deposits of the high-sulfate form of calcium sulfoaluminate are a virtually ubiquitous indicator of deterioration of cement paste, as a result of either physical or chemical disintegration of the concrete. The low-sulfate form of calcium sulfoaluminate was identified microscopically by the writer in a highly carbonated, porous, and weak concrete from a structure in Vancouver, British Columbia (Table 1). The cause for its development in lieu of the high-sulfate form is not known. Prior to fracturing of the cement paste, microscopically visible accumulations are formed in air voids in the paste or in near-surface voids in the aggregate. When fractures are developed in the concrete, needles of the high-sulfate form of calcium sulfoaluminate occur as linings and partial fillings. In advanced stages of deterioration, the compound produces also irregular patches within the cement paste.

Secondary healing of the cement paste.—Well-prepared portland-cement paste possesses a marked capacity for internal adjustment to strain, presumably by dissolution and reprecipitation of hydration products, plastic flow or "creep", and supply of hydration products by continued hydration of large particles of cement clinker. Internal healing is indicated indirectly by several characteristic properties of concrete, such as recovery of modulus of elasticity and compressive and flexural strength of specimens during moist storage after freezing and thawing or failure in loading tests (Lauer and Slate, 1956). Microscopically, this feature is most clearly recognized by termination of fractures occurring in reacted pieces of aggregate or small particles of clinker at the periphery of the particle against the cement paste. In instances of severe expansion of the concrete, secondary fractures in the aggregate pass uninterruptedly into and through the cement paste and commonly can be traced across several aggregate particles. Conversely, where the cement–aggregate reaction is relatively mild and long-continued, fractures transecting particles of aggregate commonly cannot be observed in the cement paste, or possibly a trace of the fracture is indicated by narrow deposits of calcium hydroxide or gelatinous hydration products. Brown (1955, Fig. 16) has illustrated an analogous example in which a fracture produced by hydration of CaO in a coarse particle of cement terminated at the edge of the clinker particle.

Cement–aggregate relationships.—The boundary relationships of aggregate particles against the cement paste are of special interest because indications of cement–aggregate reactions are concentrated there. On the other hand, detailed examination of this boundary at high magnification frequently suggests corrosion when indeed no corrosion effects of microscopic dimensions exist. This appearance is common because of original irregularities in the surface of some aggregate particles and because the slope of the boundary within the thickness of the thin section commonly produces an appearance suggestive of progressive change of the particle of aggregate at its periphery (McConnell *et al.*, 1950, Pl. 4). Hence, great caution should be applied in evaluating development of cement–aggregate reaction from the physical aspects of the boundary.

Nevertheless, cement–aggregate reaction actually takes place in several situations, as when alkali-reactive rock types are combined with high-alkali cements; when certain types of organic substances in limestones and dolomites are leached from the rock, producing staining of adjacent mortar; when blast-furnace slag produces a green coloration in adjacent cement paste evidently as a result of reduction of ferric compounds in clinker granules or hydration products by release of soluble sulfides; or when decomposition or dissolution of sulfates in particles of aggregate releases soluble sulfate ions and ferric oxides. Some dolomites appear to have been attacked peripherally by adjacent cement paste, and such a conclusion is supported by identification of secondary aragonite in voids and fractures in the concrete, but no secondary magnesium compounds have been identified positively in association with such effects.

POLISHED-SURFACE MICROSCOPY

General statement.—Polished and etched surfaces are used by several petrographers in the study of mortar and concrete and are preferred by some because of the ease and speed with which they are prepared, the definitive microchemical tests that can be applied in the study of both unhydrated cement particles and the hydration products, and the large area of surface that can be produced. The writer prefers thin sections for the study of the aggregate, cement–aggregate relationships, and hydration products, but polished and etched surfaces for study of the incompletely hydrated grains of cement.

Specimen preparation.—A satisfactory procedure for polishing and etching surfaces on concrete is as follows: Obtain a fragment of the interior portion of the concrete under investigation, preferably by sawing; a piece or fragment on which a surface about half a square inch in area can be prepared is satisfactory. Dry the specimen at about 50° C. to constant weight to remove free water. Grind a surface, preferably as selected by prior examination of the concrete under the stereoscopic microscope, on a cast-iron lap using Sizes 220 and FFF silicon carbide in absolute alcohol. Continue the grinding successively with Sizes 303 and 305 emery on a cast-iron lap with absolute alcohol as the lubricant. Wash the specimen carefully in absolute alcohol between the several stages of grinding to remove the residues of the silicon carbide or emery. Polish the surface on a bronze lap covered by a linen cloth (such as may be recovered by washing the starch from tracing cloth) using precipitated tin oxide and absolute alcohol; perform the initial polishing at 1050 rpm. and complete at 550 rpm. Clean the tin oxide from the specimen in absolute alcohol on an 8-inch, bronze lap covered by silk velveteen. Store the specimen at 50° C. until the etching is to be performed.

Etch the polished surface by immersing the specimen, polished surface down, in a 1 per cent aqueous solution of nitric acid for about 2 seconds (*see* below), followed by washing in absolute alcohol and blotting with lens tissue. If desired, the characteristics of the interstitial phases of the clinker particles can be discerned by methods described by Insley and Frechette (1955, p. 180, 190–191).

Control of the etching procedure commonly is difficult because the etchant is absorbed in porous particles of aggregate or within especially absorptive portions of the cement paste and then is fed back to the surface after the etching period is supposedly terminated. This difficulty can be minimized by appropriate variation of etching time or by preliminary immersion of the specimen in absolute alcohol to saturate the concrete and thus to reduce the penetration of the etchant into the interior.

Examination of polished and etched surfaces.—In the above procedure, the incompletely hydrated particles of cement polish readily and, when properly etched, reveal the constitution of the cement. Quantitative measurement of the proportion of partially hydrated clinker granules or the calcium hydroxide in the cement paste, or of the phase constitution of the unhydrated portions of the cement can be made by linear-traverse procedure, such as is described by Insley and Frechette (1955, p. 181–182) for portland-cement clinker. Crystals of tricalcium silicate, dicalcium silicate, calcium oxide, and magnesium oxide can be identified, and the nature of the interstitial phase can be described in detail. Tricalcium silicate is moderately etched so that the outlines of the crystals are sharply delineated; the surface of the crystals appears blue in reflected light because of the accumulation of a film of hydration products. The grains of beta-dicalcium silicate are etched sufficiently to delineate the crystals and to reveal the complex, characteristic twinning; these crystals appear brown. Calcium oxide produces rounded, shallow pits, commonly iridescent within, without pronounced outline, usually in clusters in the interstitial phase or within crystals of tricalcium silicate. Magnesium oxide is prominent as minute, angular, dark-rimmed granules in the interstitial phase of the cement.

Abundant detail is evident in the hydration products as a result of the etching procedure. In particular, masses and individual crystals of calcium hydroxide are readily evident because of the brilliant iridescence developed in this compound by this procedure. The method described by Brownmiller (1943, p. 194–195) for discerning calcium hydroxide by water etching is satisfactory for neat cement pastes but is not suitable for use in the study of concrete. It is not possible yet to differentiate the various silicate, aluminate, or sulfoaluminate phases microscopically in sound portland-cement pastes.

CONCLUSIONS

The principles and methods of petrography are applicable to research on concrete and concrete-making materials and to the investigation of these materials for engineering purposes. Petrographic examination can with benefit be directed to thorough description of the composition and structure of concrete; description of the cement, aggregate, or mineral admixtures; evaluation of the air-void system in the cement paste; or determination of the cause of inferior qualities or inadequate performance. Petrographic examination of concrete involves visual examination of structures or specimens in the field or laboratory, adequate use of the stereoscopic microscope, and detailed examination by the petrographic and metallographic microscopes.

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ADDENDUM

The paper transmitted originally in January 1958 has not been revised as a part of final review prior to publication except for completion of referencing of papers then in press and citation of the current *ASTM Book of Standards*.

During the past 3 years substantial progress has been made in the application of petrography to study of concrete, and numerous substantial contributions have become available in the literature. Most notable is the co-ordinated series of reports on study of concrete structures in Denmark under the sponsorship of the Committee on Alkali Reactions in Concrete, Danish National Institute of Building Research and the Academy of Technical Sciences, one of which was referred to in the original paper (Idorn, 1956). Of greatest interest to the petrographer concerned with concrete are the papers by Idorn (1958a; 1958b), Jeppesen (1958), and Poulsen (1958) on detailed examination of concrete in the field and laboratory and those by Jensen *et al.* (1957), Gry and Sondergaard (1958), Jones (1959), and Sondergaard (1959) on petrographic investigations of concrete aggregates, with particular emphasis on flint and its performance in concrete.

Extensively illustrated reports by Poulsen and Idorn (1957) and by Miesenhelder (1960) described numerous examples of failure of concrete as a result of freezing and thawing.

Several additional studies of alkali-aggregate reaction of interest to petrographers have been published (Plum *et al.*, 1958; Woolf, 1958; Mielenz, 1958; Halstead and Chaiken, 1958). A paper by Bredsdorff *et al.* (1960) provides a summary of the current state of knowledge on all types of cement-aggregate reactions in concrete. Project Committee B-2 of the Highway Research Board (Highway Research Board, 1958) has prepared a brief summary statement on the nature and identification of chemical reactions of aggregates in concrete, dealing mainly with alkali-aggregate reaction and reactions of sand-gravel aggregates in the Great Plains area of the United States.

Additional investigations of phenomena associated with the latter reactions are summarized by Lerch (1959) and by Mather and Mielenz (1960).

The deleterious reactivity of ferrous sulfides, pyrite and pyrrhotite, in shales occurring in the Oslo region of Norway is described by Moum and Rosenqvist (1959), and the relation of reactivity of pyrite in concrete to chemical composition of the mineral has been examined by Midgley (1958). Their findings are new and merit special study. In the Norwegian experience, the deterioration of concrete is caused primarily by oxidation and hydration of pyrrhotite, although pyrite in the shale is known to contribute. Midgley's findings are of great value in petrographic evaluation of concrete aggregates containing pyrite or pyrrhotite inasmuch as he has established a simple chemical test procedure whereby ferrous sulfides susceptible of oxidation while enclosed in concrete are distinguishable from ferrous sulfides not susceptible to such reactions under ordinary conditions. Application of this test by the present author to a variety of pyritiferous igneous and sedimentary rocks clearly indicates widely differing rate of oxidation of pyrite when specimens are immersed in calcium hydroxide solution in accordance with the recommended procedure so as to simulate the condition prevailing within moist concrete.

Wakeman and associates (1958) published a comprehensive discussion on deterioration of concrete in marine environments, including new observations on the mechanism and on the results of such exposure as well as extensive review of literature on this subject.

Papers published during the past 3½ years are defining a new type of cement-aggregate reaction involving argillaceous dolomitic limestones and calcitic dolomites. This reaction is clearly separable from the alkali-silica reaction commonly designated as alkali-aggregate reaction. The phenomenon was described originally by Swenson (1957) and by him and his former coworkers at the National Research Council of Canada in unpublished reports. More recently, Swenson and Gillott (1961) have summarized their laboratory investigations. Their studies were initiated in 1955. A somewhat similar cement-aggregate reaction has been shown to occur in concrete when certain dolomitic rocks occurring in the Cedar Valley formation in Iowa are used as aggregate (Lemish, Rush, and Hiltrop, 1958; Bisque and Lemish, 1958; Bisque and Lemish, 1960; Hiltrop and Lemish, 1960; Harwood and Lemish, 1960). However, the effects of the cement-aggregate reaction on the concrete are considerably less severe in the experience described by Lemish and his coworkers than in that recounted by Swenson and coworkers.

In the experience at Kingston, Ontario, described by Swenson (1957), the phenomena involve an argillaceous dolomitic limestone used as coarse aggregate in combination with cements of high alkali content. Abnormal expansion and cracking of concrete occurred in sidewalks, curbs, floors, walls, and other structures. In instances of severe distress, deterioration is evident within 2–3 months following placing of the concrete. Progress of the distress is marked by development of distinct reaction rims on particles of the aggregate (Pl. 6, fig. 3) and by formation of abundant microfractures in the cement paste, but alkalic silica gel, such as always is associated with alkali-aggregate reaction, is absent or very scanty.

Laboratory investigations have shown that progress of the deleterious effects requires that the cement be of high alkali content. Excessive expansion was not

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