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The Nature of Concrete

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THE NATURE OF CONCRETE

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The term concrete can be construed to include a considerable variety of products made from portland cement or other cementing media, but in this publication the term concrete usually refers to a material which was at first a plastic mixture (or mixture that became plastic as a result of manipulation, especially vibration) of portland cement, water, air, and mineral aggregate. Therefore, this discussion of the nature of concrete will have the scope indicated by that description.

A writer's concept of the nature of concrete can hardly be revealed in a few words, but his treatment of certain topics and his definitions are indicative. Here are some examples: in 1878 Trautwine, in the 11th edition of his *Pocket Book for Civil Engineers*, said "Cement concrete, or beton, is ... cement mortar mixed with gravel or broken stone, brick, oyster shells, etc., or with all together." He described mortar as sand containing a volume of cement equal to the volume of voids in the sand.[2] In 1907, L. C. Sabin in a book on concrete said, "Concrete is simply a class of masonry in which the stones are small and of irregular shape. The strength of concrete depends largely on the strength of the mortar; in fact, this dependence will be much closer than in the case of other classes of masonry, since it may be stated as a general rule, the larger and more perfectly cut are the stone, the less will the strength of the masonry depend on the strength of the mortar." Feret in 1896 considered water and air to be definite components of mortar (and presumably also of concrete), but it is not clear that he thought of cement paste as an entity. Zielenski, once head of the Hungarian Association for Testing Materials, in 1910 called concrete a conglomerate body; he considered the conglomerate to be composed of mortar and coarse aggregate, and the mortar to be composed of paste and sand, with or without air voids. Taylor and Thompson, authors of perhaps the best of early books on concrete, in the 1912 edition said, "Concrete is an artificial stone made by mixing cement, or some similar material which after mixing with water will set or harden so as to adhere to inert material, and an aggregate composed of hard, inert, materials of varying size, such as a combination of sand or broken stone screenings, with gravel, broken stone, cinders, broken brick, or other coarse material." D. A. Abrams, in the first bulletin from the Structural Materials Research Laboratory, Lewis Inst., Chicago, Ill. (1918) emphasized the significance of the ratio of water to cement in concrete, and he abandoned the notion that concrete is a mixture of mortar and coarse aggregate, pointing out that the whole aggregate, fine and coarse combined, should be considered as one, even though fine and coarse aggre-

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[2] He said also, "Nearly all the scientific principles which constitute the foundation of civil engineering are susceptible of complete and satisfactory explanation to any person who *really* possesses only so much elementary knowledge of arithmetic and natural philosophy as is *supposed* to be taught to boys of 12 or 14 in our public schools."

gates are proportioned separately. F. R. McMillan in his book, *Basic Principles of Concrete Making* (1929) said, "Expressed in the simplest terms, concrete is a mass of aggregates held together by a hardened paste of portland cement and water ... the paste is the active element." In their textbook on concrete, Troxell and Davis (1956) wrote, "Concrete is a composite material which consists essentially of a binding medium within which are embedded particles or fragments of a relatively inert mineral filler. In portland cement concrete the binder or matrix, either in the plastic or in the hardened state, is a combination of portland cement and water." This definition was adopted by the American Concrete Inst. (ACI) Committee 116 on Nomenclature in 1964. The Encyclopedia Britannica, 1963 edition, says, "Concrete is a building material consisting of a mixture in which a paste of portland cement and water binds inert aggregates into a rock-like mass as the paste hardens through chemical reaction of cement with water."

Although it is possible to discern an evolution of concepts in the above definition and descriptions, the early concept of concrete as a mixture of mortar and coarse aggregate tends to persist, despite Abrams' contention that the total aggregate functions as a unit. The idea lingers with us, perhaps, because it has simplicity and plausibility and partly because it is not altogether unrealistic, especially when there is a gap between the largest size in the sand and the smallest size in the coarse aggregate. However, gap gradings are not common, and in any case the correctness of Abrams' conclusion can hardly be questioned.

Even the latest definitions provide but a superficial idea of the nature of concrete. They give no hint as to how and why the originally plastic mass becomes hard and strong and, indeed, say nothing

as to how and why the mixture had plasticity in the first place. Moreover, they give no adequate basis for understanding such aspects of concrete as volume change characteristics, and stress-strain-time phenomena. We must, therefore, go far beyond a superficial definition or description to attain today's understanding of the nature of concrete. To do the subject full justice would be a book-length project; I cannot do more than touch on a few fundamental topics.

GROSS STRUCTURE OF CONCRETE

When we inquire into the nature of concrete we find it necessary to regard concrete not as an entity—a substance—but as a structure having component parts, as has already been indicated. The predominant component of concrete is an aggregation of mineral particles, called the aggregate, and this aggregation requires a certain minimum of space per unit weight of material. The volume of space occupied by a properly compacted fresh concrete mixture is slightly greater than would be the compacted volume of the aggregate it contains, and the difference is significant: it shows that the individual rock[3] particles in concrete need not be in contact with each other. There is clear evidence that the rock particles in concrete are, in fact, not in contact with each other: freshly mixed concrete could not be plastic if the solid particles were not dispersed to some degree; inspection of broken sections of hardened concrete show that not only are the rock particles in a dispersed state while the mixture is fresh, but also they remain dispersed, although generally not exactly to the same degree that prevails immediately after mixing, owing to settlement under the force of gravity before setting occurs.

[3] Throughout this discussion, the term rock refers to the particulate mineral matter that makes up the aggregate, regardless of the size or shape of the particles.

Rock particles in plastic concrete are dispersed in a matrix composed of paste and air bubbles;[4] the paste is composed of portland cement and water. The degree of dispersion actually depends upon the consistency of the paste and the volume of air; the stiffer the consistency and the higher the air content the greater the mean clear distance between aggregate particles. In practical terms, this means that the degree of dispersion of rock particles is greater the lower the water-cement ratio of the paste, and the higher the air content; in any case, the volume of concrete seldom if ever exceeds the compacted volume of the aggregate by more than 10 per cent, and usually it does not exceed it by more than 3 per cent when no air-entraining agent is used.

Without an air-entraining agent, concrete placed by a standardized procedure contains a characteristic amount of air in the form of bubbles, the amount being a function of certain variable factors. The main factors are the consistency of the paste and the gradation of the aggregate. At a given paste consistency, and with a standardized mixing procedure, air content depends mainly on those features of aggregate grading that control the mean size of the voids in the aggregate, voids being here defined as the space occupied by paste and air. The mean size and the size range of the air bubbles in concrete are also significant structural features, particularly with respect to the ability of concrete to withstand the effects of freezing. These characteristics also are subject to systematic variation as will be discussed later.

The foregoing statement as to the effect of aggregate grading on air content is applicable principally to the leaner types of mixtures. In richer mixtures, water-cement ratio less than about 0.5 by weight or $5\frac{1}{2}$ gal per sack, aggregate char-

[4] Voids due to incomplete filling of mold or form are not considered here, only the voids that are normal components of the mixture.

acteristics have little effect. Throughout the range of the most frequently used mixtures, air content and void characteristics are strongly influenced by water-cement ratio, the air content and average air void size increasing with increase of water-cement ratio under given conditions.

When a suitable air-entraining agent is used, the air content can be raised to almost any desired level. At an air content higher than that normally present in a given mixture, the mean size of air bubbles is controlled by the characteristics of the air-entraining agent used and, in the leaner range of mixtures, by the same factors that control the normal air voids. Specifically, if the normal air content of a given mixture is relatively high and the mean size of the voids relatively large (the two usually go together), raising the air content by means of a given approved air-entraining agent will result in a system of voids having a relatively large mean size, as compared with the mean size when the amount of air normally present is smaller, and the original mean size also smaller. This means that with a given air-entraining agent used in different mixtures a wide range in average void size may be observed.

In short, the gross structure of concrete appears to be that of an aggregation of rock particles slightly dispersed in a matrix of paste and air bubbles, the proportion and size characteristics of air bubbles being subject to systematic variation just as is the proportion of aggregate.

A conclusion arising directly from consideration of the gross structure of concrete is that the firmness or mechanical stability of concrete cannot be attributed to mechanical stability of the aggregation of rock particles; it is clearly due to the mechanical stability of the matrix and to the mechanical stability of individual particles of rock. Also, it is clear

that the stability of the matrix is due to that of hardened cement paste.

INTERPARTICLE FORCES IN FRESHLY MIXED CONCRETE

We have already seen that plasticity of freshly mixed concrete is possible because the rock particles of the aggregate are slightly separated from one another by matrix material; otherwise, any deformation would necessarily be dilatant rather than plastic. The matrix, itself, is plastic because the cement particles and air bubbles are dispersed in water and especially because the interparticle forces tend to hold particles together while at the same time preventing actual point to point contact. Such a state is due to the coexistence of forces of attraction and repulsion between cement particles. Attraction is due to relatively long range intermolecular forces known as van der Waals forces, about which more later; the forces of repulsion are, in this case, due to electrostatic repulsion and to a "disjoining pressure" (Deryagin)[5] maintained by adsorbed water molecules covering the surfaces of the grains. Electrostatic repulsion is due to what is called a Gouy diffuse layer of ions, in this case negative ions, the negative ions being held near each cement particle by positive ions selectively adsorbed from the surrounding aqueous solution.

Owing to the existence of opposing interparticle forces, a pair of cement grains has a minimum of potential energy with respect to those forces when the particles are separated from each other

    [5] In previous publications I have used terms such as *film pressure, swelling pressure,* or *spreading pressure,* to indicate the force developed by adsorbed films of water in spaces too narrow to accommodate the normal thickness of the films. Several years ago Deryagin, a surface physicist of the Soviet Union, introduced the term *disjoining pressure* and another, *disjoining action;* when thinking of the tendency of water to disperse a coherent system of particles, Deryagin's term seems most apt.

by a certain small distance, the distance amounting to perhaps ten water molecule diameters, more or less; hence, cement particles tend to assume positions with respect to each other corresponding to minimum potential energy with respect to balance of internal forces, and this is an essential condition for the plastic state.

When particles are in positions of minimum potential energy with respect to the forces acting between them, they are said to be in "potential troughs," and any mechanical displacement of particles with respect to each other requires a certain amount of work to "lift" the particles out of their potential troughs. Thus, we see that interparticle forces give freshly mixed paste in the quiescent state, a structure having a low degree of firmness or shearing strength. When shearing stress exceeding shearing strength is applied and maintained, a paste is caused to flow continuously if its solid content is considerably smaller than that at normal consistency, which is the case for pastes used in concrete. The shearing strength (yield value) and the resistance to continuous shearing stress (the mobility or structural viscosity) is often used as a measure of paste consistency, but such a measure pertains only to paste in the fluid state maintained by a sufficiently high shearing stress.

Consistency of freshly mixed paste can be made softer by diminishing the depth of the potential troughs, and this can be done by using an appropriate surface-active material able to increase interparticle repulsion; indeed, repulsion can be raised to such a degree as to destroy plasticity, changing paste from a plastic to a fluid material. In some concrete mixtures, the water content of the pastes is so high that the paste has very little plasticity to begin with; even though the interparticle forces discussed above exist, the particle concentration is so low that interparticle forces are rela-

tively ineffective. The paste in a properly constituted freshly mixed concrete has an optimum consistency, neither too soft nor too firm (stiff); under no circumstances should it be completely fluid.

CHEMICAL NATURE OF HYDRATED CEMENT

The chemical compounds found in hydrated cement are complex; most of them are impure in the sense that they contain elements not ordinarily given in their formulas, and they do not have exactly the same composition when formed under different conditions, especially with respect to temperature and original cement concentration. For our present purpose it will suffice to mention a few outstanding characteristics.

All the components of hydrated cement are basic; the hydroxyl-ion concentration is always at least as high as that of a saturated solution of calcium hydroxide, and it is usually considerably higher because of the presence of alkali hydroxides. Any of the compounds can be decomposed by carbonic acid and, therefore, by ordinary rain water. That concrete is not generally destroyed this way is explainable mostly in terms of physical factors: under ordinary conditions of exposure the quantity of acid in contact with concrete during a given time is small relative to the quantities of basic material available, and the permeability of concrete to water is so low that the action of weak acids is only superficial. Even contact with soft-water streams usually causes decomposition at a negligible rate. In cities where rain falls through industry-polluted air and becomes distinctly acid, acid action is evidenced by surface etching. But, whenever a continuous supply of strong acid is encountered, concrete must be protected or it will be destroyed.

Hydrated cement is able to react also with carbon dioxide gas in the presence

of water vapor, but the effect is not destructive; actually such reaction may increase chemical stability.

The reactions between the anhydrous components of portland cement and water are remarkable in that they involve a doubling of the volume of space required by solid material while the apparent volume of the system remains constant. There is one exception: the formation of calcium sulfo-aluminate by reactions involving gypsum and tricalcium aluminate tends to cause volume expansion, and when the sulfate ion concentration is too high, expansion can be destructive. Normally, the amount of gypsum needed to control the setting of cement gives only tolerable expansion, but when an unlimited supply of sulfate ion is present in the environment, concrete may be destroyed by it. Practically, such destruction is avoidable by using a cement of low tricalcium aluminate content.

Chemical Aspects of Mineral Aggregates:

The petrographers and mineralogists contributing to this publication have much to say on this subject; I shall mention only some chemical characteristics that are of special interest because of the structural and chemical characteristics of the paste component of concrete.

Rocks used for concrete aggregates are generally materials that have survived geologic ages and are thus those that have demonstrated some degree of chemical and physical stability. Some are chemically basic; some are acidic. Limestone is, of course, basic and vulnerable to acid attack, but when used as concrete aggregate it is less vulnerable than the hydrated cement paste which envelopes it. There are at least two other kinds of undesirable chemical attack on certain minerals that seem to be the result of conditions peculiar to the interior of con-

crete; one kind involves siliceous rocks; the other, certain dolomites.

Some kinds of siliceous rocks, opal being an outstanding example, may be decomposed by the caustic solutions found in concrete. Under some conditions this reaction is accompanied by destructive expansion, and under other conditions, no expansion. The conditions mentioned involve chemico-physical factors too complex to be described here, as may be ascertained by referring to the literature on the alkali-silica reactions in concrete. A principal factor determining the physical effect of such reactions is the special and selective hindrance to the diffusion of various ions through the structure of cement paste; another is the quantity and specific surface area of the reactive form of silica.

Also, some dolomites react with the caustic aqueous solution in concrete and expand destructively; the reaction involves decomposition of the dolomite and the formation of magnesium hydroxide (brucite); it is called dedolomitization.

Structure of Hardened Cement Paste:

We have already seen that freshly mixed cement paste is a dispersion of cement particles in water and that it has a certain structure owing to the forces of attraction and repulsion among the cement particles. This structure is the starting pattern of the structure that subsequently develops from the materials produced by reactions between the components of cement and water. These reaction products are collectively that which we have already called hydrated cement; now we shall stress the physical aspects of hydrated cement.

Although hardened cement paste looks the way we might expect an amorphous continuum to look, we know that it actually comprises a hierarchy of aggregations of matter. Moreover, we know that cement paste contains submicro-

scopic voids, its void content usually being upwards of 40 per cent, although a lower void content is possible. Since, in general, we have learned to think of matter as intrinsically granular, we are inclined to regard the pore space as having the character of interstices in a granular aggregation. By dispersing the structure and examining the fragments by electron microscopy, we have seen particles and have been impressed by their smallness and irregularity of shape. These particles, not all of the same kind chemically, may be regarded as the primary particles of paste structure, even though atoms and molecules are the primary and secondary aggregations of matter in general.

The term gel particle refers to particles having dimensions in the submicroscopic range of sizes called colloidal; in this particular case colloidal bodies can be defined as molecular or ionic aggregations having a very high specific surface area, such as is possible only in the submicroscopic range. The colloids observed in cement paste are mostly quasicrystalline, lack of normal crystallinity being due to the extremely small size and imperfect atomic or molecular organization of the solid material. The high specific surface area is due mostly to the thinness of the particles, one of the three dimensions, and perhaps two, being greater than the limit usually stipulated for the colloidal state; these particles are usually only three or four molecules thick.

Along with the colloidal material in hardened cement paste is crystalline calcium hydroxide having relatively low specific surface area. The amount of calcium hydroxide is different for cements having different chemical compositions, but it is usually between 20 and 30 per cent of the weight of the dry hydrated cement. Calcium hydroxide crystals are usually surrounded by and intergrown with colloidal material, and thus they

constitute an integral part of the solid structure.

The most abundant colloidal constituent of hydrated cement is an impure calcium silicate hydrate of somewhat indefinite stoichiometry. It has characteristics resembling those of a natural mineral called tobermorite and has thus come to be called *tobermorite gel*. (The term gel designates a rigid aggregation of colloidal material.) There are also amounts of calcium aluminate hydrate and calcium alumino ferrite hydrate; the physical states of these materials are not known exactly, but it appears that they are colloidal but with a lower order of specific surface area than those of tobermorite gel.

An outstanding characteristic of the colloidal matter in hydrated cement paste is that its specific surface area is virtually the same in all pastes made of the same cement regardless of differences in paste density, and among pastes made with different portland cements it is not much influenced by differences in chemical composition. This observation is one of the cornerstones of our concept of paste structure.

The colloidal matter together with calcium hydroxide appear as a continuous solid structure apparently occupying the whole volume of any specimen of hardened cement paste. As already indicated the structure is porous; normally the solid matter occupies 45 to 60 per cent of the apparent volume, and the highest possible solid content (exclusive of unhydrated cement if any) has been found to be about 72 per cent or perhaps a little more of the total volume occupied by hydrated material. In other words, a specimen of hydrated cement paste may have a porosity of not less than about 28 per cent, and it usually has a porosity between 40 and 55 per cent; the porosity will have a higher range if the paste is not fully mature, which means if com-

plete curing has been deliberately or inadvertently omitted. The apparent volume of a specimen of paste, expressed as a volume per unit quantity of cement, is determined by the net volume of mixing water per unit volume of cement. The net volume of mixing water is that which remains within the specimen at the end of the period of settlement (bleeding) which is normally from 1 to 2 hr after mixing.

The solid content of any freshly mixed paste is a little over 62 per cent of what the solid content will be after chemical reactions have converted all the cement to the hydration products described above. As already mentioned, the increase of solid volume takes place without appreciable change of over-all volume,[6] regardless of how high the cement content may be or how little water per unit of cement. One cubic centimeter of cement, solid volume, produces about 1.6 cc of hydrated cement. On this basis we might expect that the hydration products will require 0.6 cc of space in addition to the space originally occupied by 1 cc of cement, or 0.19 cc of space per gram of cement; this amounts to saying that if the water-cement ratio is 0.19 by weight, there will be ample room within the specimen for all hydration products that can be derived from one gram of cement, and the material would become a voidless solid. But experimentally it was found that void space cannot be eliminated. This experimental observation is another cornerstone on which our concept of paste structure rests.

As just indicated, it was found that under no circumstance can completely mature paste be made entirely solid; the highest possible solid content is about 72 per cent, and the rest of the unit volume remains full of water or is void if all the

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[6] The microscopic changes that may occur later as the result of drying and wetting are properly ignored here.

water in such space is caused to evaporate. The densest possible hydrated cement paste contains a continuous system of pores, as evidenced by its permeability to water. Because of the intrinsic porosity of the structure, which limits the solid content to 72 per cent of the apparent volume, it follows that instead of 1.6 cc/cc of cement, the volume of paste must be at least 1.6/0.72 = 2.2 cc/cc of cement to provide enough space for all the hydration products that can be derived from 1 cc of cement, and this means that the water-cement ratio by weight must be at least 0.38. In any paste containing less than this amount of water-filled space, some of the cement remains anhydrous regardless of the duration of curing, and a residue of the original cement remains a permanent feature of the structure of the paste, the residue appearing in cross sections as scattered remnants of the largest grains.

Of course, when the volume of cement paste is greater than 2.2 cc/cc of cement, as it usually is, there is more than enough space to accommodate the hydration products and thus less than 72 per cent of the space can become filled with solid matter. When there is more space available than the minimum required by the hydration products, the extra space is a feature of the structure of paste.

Various observations lead to the concept that in every paste the hydration products tend to become locally concentrated to the maximum degree possible, even when excess space is available, but at the same time they form a continuous structure having an over-all volume equal to the apparent volume of the paste. One line of evidence supporting this view develops from consideration of the structure of freshly mixed paste. Although cement particles in freshly mixed paste are individually dispersed throughout the volume of mixing water, they

can not be uniformly spaced because of the interparticle forces, already discussed, that hold the particles practically (but not exactly) in point to point contact. This being true, it seems that if we could subdivide a freshly mixed specimen of paste having a certain water-cement ratio into a large number of cubical cells each having an edge length of say 100 μ (about the same as the mean diameter of the largest cement particles but about 100 times as large as the spherical equivalent of a "particle" of tobermorite gel), we would not find the same volumes of cement and water in each cell; we would find some cells almost filled with a single grain, some would contain many small grains, and some might contain few if any grains. In other words, we would find that the over-all water-cement ratio is an average of many different local water-cement ratios some higher and some lower than the average. Since some of the cells must be nearly full of solid material to start with, considering the size of many of the cement grains, and since interparticle attraction tends to hold particles close together, it seems almost certain that the 72 per cent limit of the content of solid hydrated material will be achieved in many cells after all the cement has become hydrated, even though some of the cells cannot become filled to this extent. In other words, it is reasoned that if the hydrated material in a specimen of paste can reach an average density of 72 per cent but no higher, at any sufficiently low water-cement ratio, that same degree of density can be and is produced locally at various places throughout any paste, however high the water-cement ratio. If any of the imagined cells contain excess cement, which presumably is the case wherever the local water-cement ratio is lower than about 0.38 by weight, such cells can get rid of their excess material by diffusion of mate-

rial into adjacent cells lacking cement, so that eventually all the cement can become hydrated if the average water-cement ratio is high enough.[7]

I have used the term *cement gel* to designate hydrated cement paste in its densest form. It should be noted that by this definition cement gel is not synonymous with gel as used above, for example, tobermorite gel. The term cement gel is convenient for designating the predominantly colloidal material found in hydrated cement paste, but it must be kept in mind that the term includes noncolloidal calcium hydroxide and other noncolloidal material, if any, and therefore it does not conform exactly to the term gel, properly defined as a solid composed of colloidal material.

The concept of paste structure described above, which requires us to visualize an uneven distribution of cement gel, entails a corresponding uneven distribution of the sizes of interstitial spaces; surface to surface distances range from zero at chemically bonded points to a maximum distance that is probably greater the greater the capillary porosity of the paste, but which in any case is not known exactly. The order of mean pore size is indicated by the quotient of the volume of pore space by the boundary area of that space, which quotient in hydraulic engineering is called the hydraulic radius. For a porosity of 28 per cent and for solid matter having a specific surface area of 5.2×10^6 cm²/cc of solid

matter, which is about the specific surface area of cement gel, the quotient is 7.5×10^{-8} cm or 7.5 A.[8] The corresponding average distance from solid surface to solid surface is between two and four times the hydraulic radius, depending upon the shape of the interstitial spaces; in the present case where many of the spaces are believed to be slit-like, about 18 A seem to be a reasonable estimate. When the porosity exceeds 28 per cent, which is to say when the paste contains spaces other than gel pores, the mean pore size is, of course, greater than the mean size of gel pores.

We can now describe hardened paste as a solid composed of cement gel, remnants of cement grains, if any, and space not filled with cement gel, if any. Any space not filled with cement gel or grain remnants is regarded as interstitial spaces among masses of cement gel and is called capillary space, capillaries, or capillary cavities. The latter term is applied in pastes so dense that the capillaries are discontinuous, the original interstitial space among the cement grains having become segmented into isolated cavities by the growth of cement gel. The pores within cement gel are called gel pores.

Rock Structure:

The structure of concrete is characterized not only by the structure of cement paste but also by the structure of individual pieces of rock making up the aggregate. Some pieces, particularly the smallest, may consist of practically voidless crystals or fragments of crystals; but in most concrete aggregates most of the particles have granular structure and are

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[7] Theoretically, if a 2-in. cube, for example, of fresh paste containing excess cement is joined to one with a deficiency of cement, and if after hardening both are kept saturated with water, the excess cement in one cube could, after the density of hydrated material had reached 72 per cent, diffuse into the excess space in the other; but this conclusion would be hard to prove because the process would probably require geological ages for completion. However, diffusion for a distance of a few microns can occur in a normal curing period, as has been verified by microscopic observations.

[8] To acquire an idea of the magnitude of an angstrom unit, try the following: if one could place two marks one angstrom apart on a piece of superrubber 1 in. long, and then if one could stretch the rubber until it could encompass the earth, the two marks would have become a little over 6 in. apart.

porous, and most are permeable to fluids. The pores in permeable rock are usually larger than those in cement paste; also rocks are less porous than paste, as a rule. A rock having a porosity of say one per cent, may have a coefficient of permeability to water equal to that of a specimen of hardened paste having a porosity of 50 per cent; thus, we know that the pores in rocks are usually larger than those in hydrated cement paste; in other words, rocks have a relatively coarse texture. A few kinds of rock do have fine texture, and unless they are also practically nonporous they do not make satisfactory concrete aggregate; certain argillaceous limestones are examples of unsuitable fine textured rocks; certain cherts also.

Some rocks contain pores that reduce their apparent specific gravity but do not affect their permeability. Among these are vesicular rocks and artificially expanded shales in which isolated voids were formed by expansion of trapped gas. Such rocks are useful when concrete of low unit weight is desired.

States of Water in Concrete:

The solid matter in mature concrete may contain water molecules or ions derived from water, as indicated by the formulas for the compounds in hydrated cement, and by those for some minerals found in concrete aggregate. Of principal interest, however, is the water that remains chemically free, and which is found in gel pores, or in capillary spaces in paste or rock. We shall confine the discussion mostly to chemically free water found in cement paste; it influences the properties of concrete to a very important degree.

It is commonly known that water in a vessel open to the atmosphere will eventually evaporate unless the atmosphere is saturated with water vapor. Cement paste can be regarded as a vessel open to

the atmosphere so far as contained water is concerned, but not all of the water it is capable of holding can evaporate unless the surrounding atmosphere is practically empty of water vapor; if the cement paste was originally saturated, some of the water can evaporate, but a definite fraction of it will be retained, the amount retained being a larger fraction of the total evaporable water the higher the degree of saturation of the ambient atmosphere, that is, the higher the humidity. At low ambient humidities, water molecules are restrained from evaporating by the van der Waals forces of attraction between them and the surfaces of the gel particles, which attraction holds a condensed film of water molecules; in other words, the restrained molecules are held by van der Waals forces.

Because of cement paste the internal surface area is very extensive, a large fraction of the total evaporable water can exist as a thin film spread over solid surface. As has already been pointed out, opposite surfaces are necessarily quite close together. In spaces up to about 18 A wide (see above) adsorption of two molecular layers on each surface is sufficient to fill most of such space, and such will be the condition when the ambient humidity is about 50 per cent. At higher ambient humidities, the pore space may be almost completely full, adsorption being aided by hydrostatic tension maintained by curved meniscuses of the water in capillary spaces. A state of mechanical tensile stress between water molecules in the condensed state restrains evaporation in about the same way that van der Waals attraction restrains evaporation from a thin layer on a solid surface.

Of the total capacity of mature cement paste for evaporable water, from about one third to two thirds of it will be full when the ambient humidity is only 50 per cent. In rocks having porosities upwards of one per cent the relatively large

pores can retain very little water at that humidity, but at humidities upwards of 90 per cent, a considerable fraction of the total capacity of rock for evaporable water may be retained. Of course, different rocks differ considerably in this respect; the fine textured rocks usually retain a comparatively large amount of water at an intermediate humidity.

The failure of water in concrete to evaporate as it normally does shows that it is altered to some degree by the material with which it is in contact. Some of the alteration may be due to dissolved material, particularly the alkalies, but removal of solutes only modifies the situation. The principal forces acting on water and preventing it from evaporating into an unsaturated atmosphere have already been identified as van der Waals forces of attraction and capillary-induced tension. Naturally, such forces are balanced by counterforces, the counterforces corresponding to elastic strains of one kind or another in the solid structure within which the water is held. Such strains correspond to the reversible part of volume changes due to drying and wetting of concrete.

There is good evidence that some of the evaporable water normally held in concrete contributes to its strength, that is, van der Waals attraction between water molecules and between solid material and water molecules seems to contribute to the total cohesive force. However, there is a somewhat greater weakening effect due to swelling.

Strength:

In the above discussion dealing with cohesion and adhesion we necessarily spoke of strength. But there are other aspects of the strength of concrete depending on the nature of its structure, and some of these will be discussed in the following paragraphs.

It would be expected that with a given

aggregate the more cement gel per unit volume of paste and the more paste per unit volume of matrix, which means the lower the air content of the matrix, the greater the strength of the concrete. Strength tests of many kinds of concrete show that such is indeed the case; it was the fact underlying the cement-space ratio law for strength given by Feret (1897), and the less general water-cement ratio law given by Abrams (1918), and earlier by Zielinski (1908). For aggregates composed of strong particles, the upper limit of concrete strength tends to be established by the upper limit of the density of the matrix, that limit usually being established by the means at hand for compacting the mixture. On the other hand, with aggregates composed of relatively weak particles, the upper limit tends to be established by the strengths of the aggregate particles. This does not mean, however, that concrete cannot be stronger than the strength of individual aggregate particles, as is evident when one considers air bubbles as aggregate.

The strength of a given kind of concrete is not a single valued property of the material. Compressive strength, in particular, is a function of the rate at which stress is applied, the function being such that strength appears higher the higher the rate of loading. If a stress less than the strength indicated by an ordinary test procedure, and yet greater than about two thirds of that stress, is maintained without increase, the specimen will eventually fail. There are good reasons to believe that failure is essentially a random (stochastic) process, and therefore the stress existing at time of failure is intrinsically a variable number; in other words, two absolutely identical specimens would not be likely to fail at exactly the same stress, or, under a sustained high stress less than the mean "instantaneous" strength, they are not likely to fail at the same elapsed time

after loading. Thus, it seems that even with a perfect testing machine and with test specimens exactly alike, we would still find variation of test results about the mean value from a large number of identical specimens.

When a concrete cylinder is subjected to a steadily increasing axial stress, as in the ordinary compression test, the observed increase in diameter at low stress is a certain constant fraction (Poisson's ratio) of the longitudinal shortening (compressive strain). There is no tensile stress associated with the lateral strain just mentioned, but after the compressive stress becomes about two thirds of the stress at failure, further increase in compressive stress causes lateral dilation to increase more than can be accounted for by Poisson's ratio, and this extra strain does denote the development of tensile stress. When such stress begins to exceed tensile strength, vibrations due to internal splitting can be detected with suitable instruments. At failure, fractures appear as uneven surfaces having an inclination to the axis somewhat less than 45 deg, or fractures appear as cracks parallel to the axis, or both kinds of fractures appear. Such experimental evidence indicates that the failure of concrete under compression, or when subjected to shear stress, is essentially failure in tension. If failure under compressive stress were limited only by strength in pure shear, the principal strains preceding failure would involve only the sliding of one smooth surface over another, and thus no increase in volume other than that accounted for by Poisson's ratio would be necessary; hence, the observed extra dilation with simultaneous internal cracking shows that tensile stress develops across the incipient fracture surfaces and causes separations at such surfaces.

Current theory of fracture indicates

that during a compression test tensile stress necessarily develops around holes, cracks, or flaws in the material, and thus tensile stress would develop even in a continuum, structureless except for flaws. Without questioning this deduction we can at the same time suggest that tensile stress would arise anyway, simply because of the granular nature of the material. Since the individual particles of which paste or rock are composed are much stronger than the structure, it is impossible for the surface of a fracture in paste to be smooth. Specimens of neat cement show evidence of tension failure in a compression test; they have a strong tendency to split. In concrete made of strong aggregate material and weak paste, the nominal shearing surfaces are likely to follow the contours of rock particles, in which case the cause of tensile stress is obvious; in concrete made with strong pastes, fracture surfaces usually pass through rock particles, but even so the fracture surface is not smooth, and again it is not difficult to account for the development of tensile stress as one rough surface is forced to move away from the other as it tends to slide. These considerations amount to classifying cement paste or concrete as an intrinsically dilatant system, just as compact, uncemented, granular systems are intrinsically dilatant.

CONCLUSION

While discussing the structure of concrete and the internal forces that give it stability, various properties were discussed. It would be possible to elaborate these brief discussions and to add other topics; however, other papers in this publication are concerned with such reviews, and no doubt interpretations in terms of structure will be found in them. Therefore, this paper is concluded without further development of the subject.

Bulletins Published by the
Research Department
Research and Development Laboratories
of the
Portland Cement Association

100. "List of Published Bulletins and Papers of the Research Department," May, 1959 (Also lists earlier research papers of the Portland Cement Association).

101. "Determination of the Apparent Density of Hydraulic Cement in Water Using a Vacuum Pycnometer," by C. L. FORD.
Reprinted from ASTM Bulletin, No. 231, 81-84 (July, 1958).

102. "Long-Time Study of Cement Performance in Concrete—Chapter 11. Report on Condition of Three Test Pavements After 15 Years of Service," by FRANK H. JACKSON.
Reprinted from Journal of the American Concrete Institute (June, 1958); Proceedings, 54, 1017-1032 (1957-1958).

103. "Effect of Mixing and Curing Temperature on Concrete Strength," by PAUL KLIEGER.
Reprinted from Journal of the American Concrete Institute (June, 1958); Proceedings, 54, 1063-1081 (1957-1958).

104. "The Successive Determination of Manganese, Sodium and Potassium Oxide in Cement by Flame Photometry," by C. L. FORD.
Reprinted from ASTM Bulletin, No. 233, 57-63 (October, 1958).

105. "The Surface Energy of Tobermorite," by STEPHEN BRUNAUER, D. L. KANTRO and C. H. WEISE.
Reprinted from Canadian Journal of Chemistry, 37, 714-724 (April, 1959).

106. "The Flow of Water in Hardened Portland Cement Paste," by T. C. POWERS, H. M. MANN and L. E. COPELAND.
Reprinted from Highway Research Board Special Report 40, 308-323 (1958).

107. "The Ball-Mill Hydration of Tricalcium Silicate at Room Temperature," by D. L. KANTRO, STEPHEN BRUNAUER and C. H. WEISE.
Reprinted from Journal of Colloid Science, 14, 363-376 (1959).

108. "Quantitative Determination of the Four Major Phases of Portland Cement by Combined X-Ray and Chemical Analysis," by L. E. COPELAND, STEPHEN BRUNAUER, D. L. KANTRO, EDITH G. SCHULZ and C. H. WEISE.
Reprinted from Analytical Chemistry, 31, 1521-1530 (September, 1959).

109. "Function of New PCA Fire Research Laboratory," by C. C. CARLSON.
Reprinted from the Journal of the PCA Research and Development Laboratories, 1, No. 2, 2-13 (May, 1959).

110. "Capillary Continuity or Discontinuity in Cement Pastes," by T. C. POWERS, L. E. COPELAND and H. M. MANN.
Reprinted from the Journal of the PCA Research and Development Laboratories, 1, No. 2, 38-48 (May, 1959).

111. "Petrography of Cement and Concrete," by L. S. BROWN.
Reprinted from the Journal of the PCA Research and Development Laboratories, 1, No. 3, 23-34 (September, 1959).