

THE CHEMISTRY OF CONCRETE

The chemical reactions that occur when water is added to portland cement in the mixing of concrete continue for months. Recent studies have elucidated the process

by Stephen Brunauer and L. E. Copeland

The most widely used construction material is concrete, commonly made by mixing portland cement with sand, crushed rock and water. Last year in the U.S. 63 million tons of portland cement were converted into 500 million tons of concrete, five times the consumption by weight of steel. In many countries the ratio of concrete consumption to steel consumption exceeds 10 to one. The total world consumption of concrete last year is estimated at three billion tons, or one ton for every living human being. Man consumes no other material except water in such tremendous quantities.

For all its familiarity and antiquity, concrete has presented the chemist and the engineer with many puzzles. The setting and hardening of concrete involve a number of complex and simultaneous chemical reactions and the process continues for a remarkably long time. It has been particularly difficult to correlate the observable physical properties of hardened cement paste with the principal engineering properties desired in concrete: strength and dimensional stability. Major advances in correlating these two sets of properties have been made only in the past two decades.

The remote ancestor of modern concrete is mortar made from lime (calcium oxide). The remains of primitive kilns indicate that lime was made from limestone (calcium carbonate) as far back as 5,000 years ago. The Egyptians used lime plaster extensively in building pyramids; samples of this plaster more than 4,500 years old are still in good condition. The first cement, a hydraulic lime that would set under water, was invented by the Romans. It consisted of a mixture of lime paste and volcanic ash.

A great many types of cement were developed over the succeeding centuries, but the next major advance was not made until 1824. That year an English bricklayer, Joseph Aspdin, patented a new cementing material he had produced by burning limestone and clay together in his kitchen stove. He named his product Portland cement because its color resembled that of a stone quarried on the Isle of Portland, a peninsula on the English coast. Because of its strength and stability portland cement eventually replaced the older types of concrete.

Although present-day portland cements are a vast improvement on Aspdin's product, they are still made from the same basic ingredients: a lime-containing material (such as limestone, shell or chalk) and a claylike material (such as shale, slate or clay itself). Before being fed into a kiln the raw materials are carefully proportioned to supply the desired amount of lime, silica, aluminum oxide and iron oxide; then they are ground to facilitate burning. In the kiln, at temperatures around 2,700 degrees Fahrenheit, the raw materials react chemically to form hard, walnut-sized pieces of a new material referred to as clinker. The clinker is discharged from the kiln and cooled; a few per cent of gypsum is added to control the rate of setting and the mixture is ground to a fine powder. This powder is portland cement.

When portland cement is mixed with about half its own weight of water, the result is a plastic, mudlike mixture called cement paste. In the course of a few hours the paste sets. "Initial set" is said to occur when a weighted needle dropped on the paste does not penetrate completely. "Final set" is

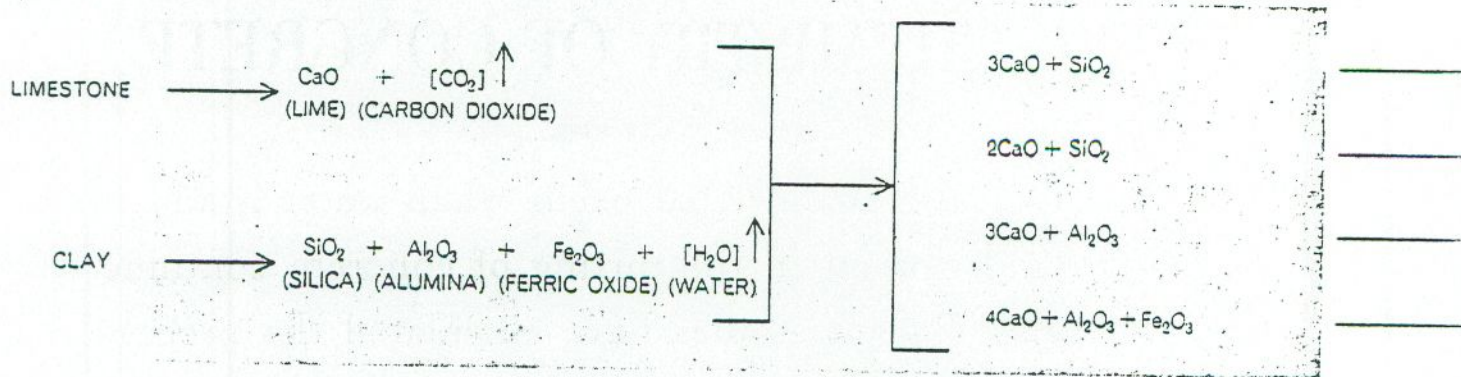
reached when the needle does not penetrate the paste at all.

The setting of cement paste is neither the beginning nor the end of the hardening process. Portland cement starts to react with water immediately on contact, and the presence of the reaction products manifests itself in an immediate increase in the viscosity of the paste. As the hydration process continues the compounds that collectively make up cement disappear and are replaced by their hydration products. After the final set the hardening process continues for months and to some extent even for years. It is a common misconception that drying is the cause of the hardening process. Just the opposite is true: without water there is no reaction and no hardening.

Concrete is the artificial rock created when portland cement paste is mixed with fine aggregate (sand) and coarse aggregate (gravel or crushed stone). The cement paste must completely coat every particle of aggregate and it must also completely fill all spaces between the aggregate particles [*see top illustration on opposite page*].

The chemistry of concrete is essentially the chemistry of the reaction between portland cement and water. (Ordinarily the aggregates are inert. If they should happen to react unfavorably with the cement, ways can usually be found to control such reactions.) In any chemical reaction the main features of interest are the changes in matter, the changes in energy and the speed of the reaction.

These three aspects of a reaction have great practical importance for the user of portland cement. Knowledge of the substances formed when portland cement reacts is important because the cement itself is not a cementing material;



REACTION IN KILN is the first step toward the production of portland cement. Limestone and clay are burned in a kiln in a proportion dependent on the amount of calcium oxide in the limestone and the amount of silicon dioxide, aluminum dioxide and

its hydration products have the cementing action. Knowledge of the amount of heat released when concrete sets is important because the heat is sometimes a help and sometimes a hindrance. The heat is useful in winter for keeping the water in the cement paste from freezing. The heat is harmful in massive structures such as dams because it may produce stresses. To help solve this problem a low-heat portland cement, known as Type IV, was developed.

Knowledge of reaction speed is important because it determines the time of setting and hardening. The initial reaction must be slow enough to enable the concrete to be poured into place. On the other hand, after the concrete has been placed rapid hardening is often desirable. In manufacturing concrete blocks, for instance, the number of molds needed to sustain a given output can be reduced if blocks can be removed from their molds quickly. For such purposes a special portland cement that attains high strength in a shorter time was developed. It is called Type III, or "high early strength" cement.

The chemist represents changes in matter by means of a chemical equation. The amounts and compositions of the reactants appear on the left side of the equation, and the amounts and compositions of the substances produced appear on the right. In the reaction under consideration portland cement and water should be on the left. But how does one represent portland cement?

Actually there is no way to represent portland cement by a chemical formula. It is a mixture of many compounds. Four of these make up more than 90 per cent of cement by weight. They are tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$), dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) and tetracalcium

aluminoferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$). Since each of the compounds contains dissolved impurities in appreciable quantities, the formulas in parentheses are not accurate. In addition to the major compounds, several others play important roles in the hydration process. Only one of these, gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), will be considered here.

Different portland cements contain the four major "phases," or compounds, in different proportions. (The chemist prefers to use the word "phase" because "compound" usually designates a pure substance with a definite formula.) The relative amounts of the four phases depend on the selection and proportioning of the raw materials. For example, if the raw materials do not contain iron, the iron-containing phase (tetracalcium aluminoferrite) is missing from the cement and the cement will be a "white cement." Ordinary portland cement is gray because of the iron-containing phase in it.

The amounts of the elements (calcium, silicon, aluminum, iron and so on) in a portland cement can be determined by chemical analysis, but the amounts of the compounds cannot. The four major compounds have quite different properties; it is important, therefore, to know how much of each is present in a portland cement. Some 35 years ago R. H. Bogue, who was working on a Portland Cement Association Fellowship at the National Bureau of Standards, proposed a method by which one can calculate the amounts of the compounds in a cement if the amounts of the elements are known from chemical analysis. Although these calculations are based on the assumption that certain ideal conditions exist in the kiln and during the cooling of the clinker, which in practice do not exist, the calculated values have been of great importance to the cement and concrete

industry. More recent work has shown that Bogue's "potential" compound values are seldom very far from the correct values.

In a microscope of high magnification the grains of the individual cement compounds can be identified [see bottom illustration on page 80]. By a laborious process one can also determine the amounts of the compounds with the microscope. The smallest grains, however, elude visual determination. For a quantitative determination of the major phases one must turn to the technique of X-ray diffraction.

When an X-ray beam is directed at a crystalline compound, the layers of atoms in the crystals diffract the X rays and produce a characteristic pattern. The top illustration on page 84 shows part of the X-ray diffraction pattern of tricalcium silicate. The diffraction peaks appear in definite positions. The middle illustration on the same page shows the corresponding part of the diffraction pattern of a typical portland cement. The peaks of tricalcium silicate appear in the same positions in the portland cement. Naturally the cement produces other peaks as well, since it contains compounds in addition to tricalcium silicate.

The value of X-ray diffraction for studying complex mixtures such as portland cement is that it provides a quantitative measure of each compound present. This is because the areas under the peaks arising from a compound are proportional to the amount of the compound in the mixture. To study the rate at which a given compound in portland cement disappears during hydration one has only to make X-ray diffraction patterns of the cement paste at various intervals after water has been added. (In actual practice the sample must be thoroughly pulverized before analysis; this does not affect the results.)

→ 3CaO·SiO ₂	TRICALCIUM SILICATE	TRICALCIUM SILICATE	53	47	58	26
→ 2CaO·SiO ₂	DICALCIUM SILICATE	DICALCIUM SILICATE	24	32	16	54
→ 3CaO·Al ₂ O ₃	TRICALCIUM ALUMINATE	TRICALCIUM ALUMINATE	8	3	8	2
→ 4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	TETRACALCIUM ALUMINOFERRITE	TETRACALCIUM ALUMINOFERRITE	8	12	8	12
		TOTAL	93	94	90	94

ferric oxide in the clay. Burning yields four major cement compounds, shown at right.

PROPORTIONS OF MAJOR COMPOUNDS in the four basic types of portland cement are shown in average percentages obtained by X-ray diffraction analysis of several cements.

The X-ray pattern of a partially hydrated portland cement is shown on the next page directly under the pattern of the nonhydrated sample. In these two patterns one can see that a double peak contributed by the two calcium silicates is only about half as high in the hydrated sample as in the nonhydrated one. This means that hydration has partially transformed the calcium silicates into new compounds that are represented by other peaks.

Even though one cannot write a chemical formula for portland cement, X-ray diffraction is able to provide a detailed knowledge of the reaction products as well as of the reactants. The illustration on page 85 shows the diffraction pattern of a completely hydrated portland cement. The peaks cor-

responding to the four major compounds in cement have disappeared and their places are taken by peaks produced by a number of new compounds.

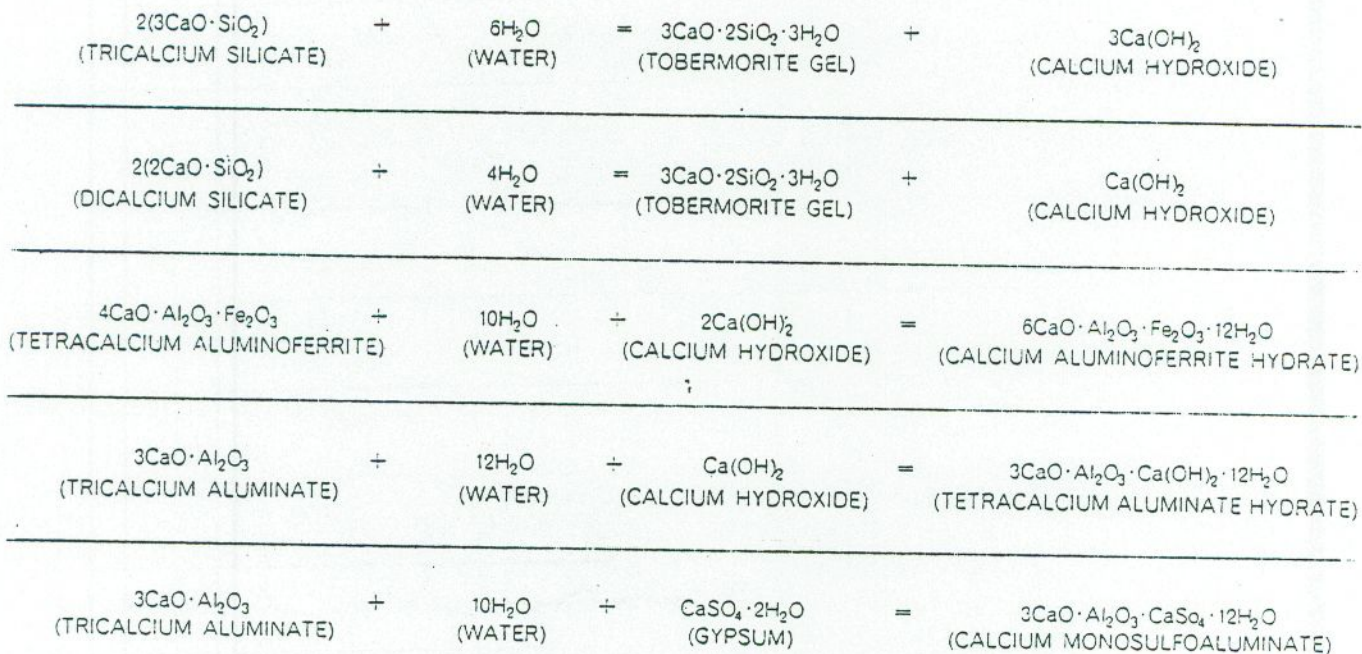
The two calcium silicates, which constitute about 75 per cent of portland cement by weight, react with water to form two new compounds: calcium hydroxide and a calcium silicate hydrate called tobermorite gel. (The reasons for calling it a gel will be explained below.) Calcium hydroxide makes up about 25 per cent by weight of a fully hydrated cement, and the tobermorite gel makes up about 50 per cent.

Other peaks represent calcium aluminoferrite hydrate, which resembles a class of natural minerals called hydrogamets. It is formed by the reaction between tetracalcium aluminoferrite and

water. The reaction between tricalcium aluminate, water and calcium hydroxide yields tetracalcium aluminate hydrate. And the reaction between tricalcium aluminate, water and gypsum produces a calcium sulfoaluminate [see bottom illustration on this page].

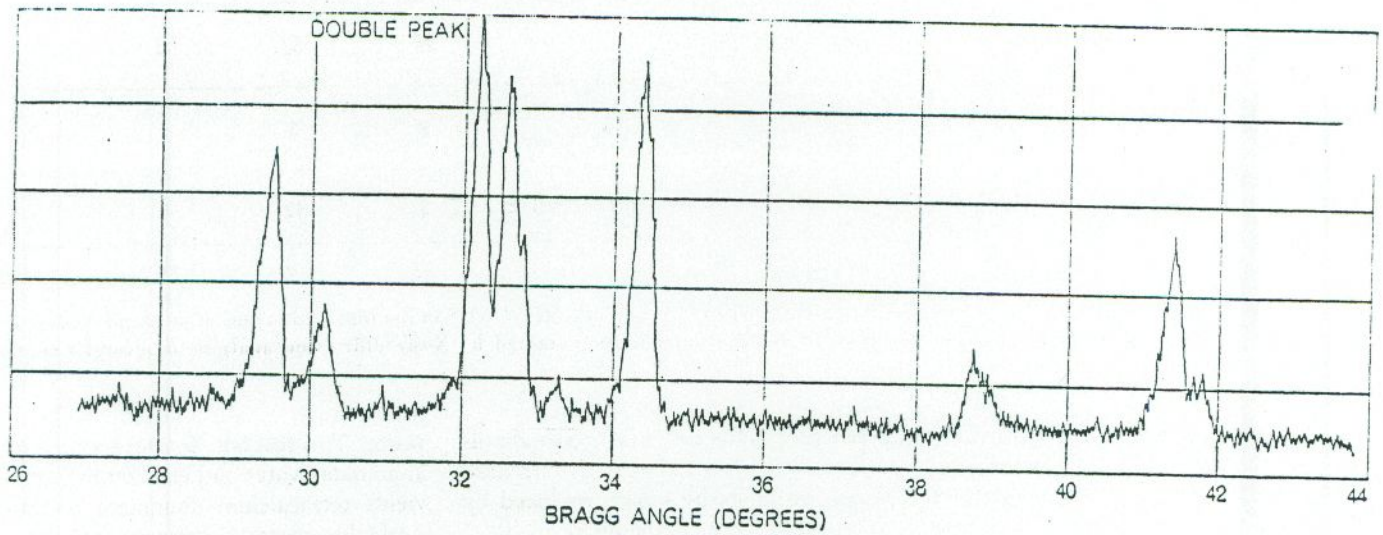
Each of these compounds plays some role in the life of concrete, but they do not play equal roles. By far the most important is tobermorite gel, which is the main cementing component of concrete. The engineering properties of concrete—setting and hardening, strength, dimensional stability and so on—depend primarily on tobermorite gel. It is the heart of concrete and we shall discuss it in some detail.

First, however, we shall describe the energy changes that take place when



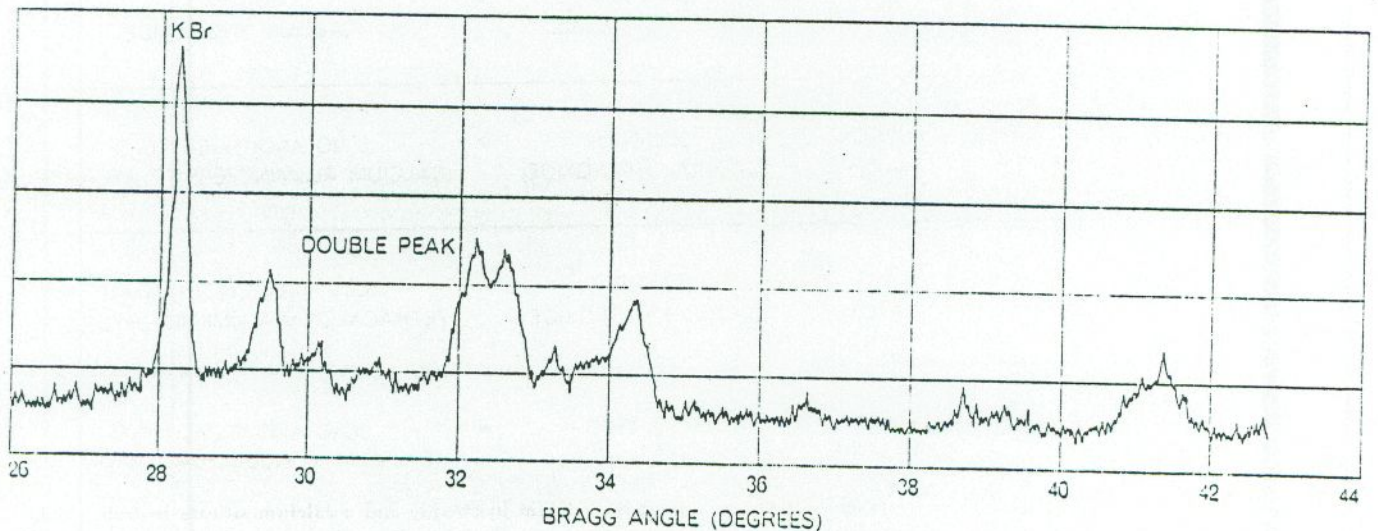
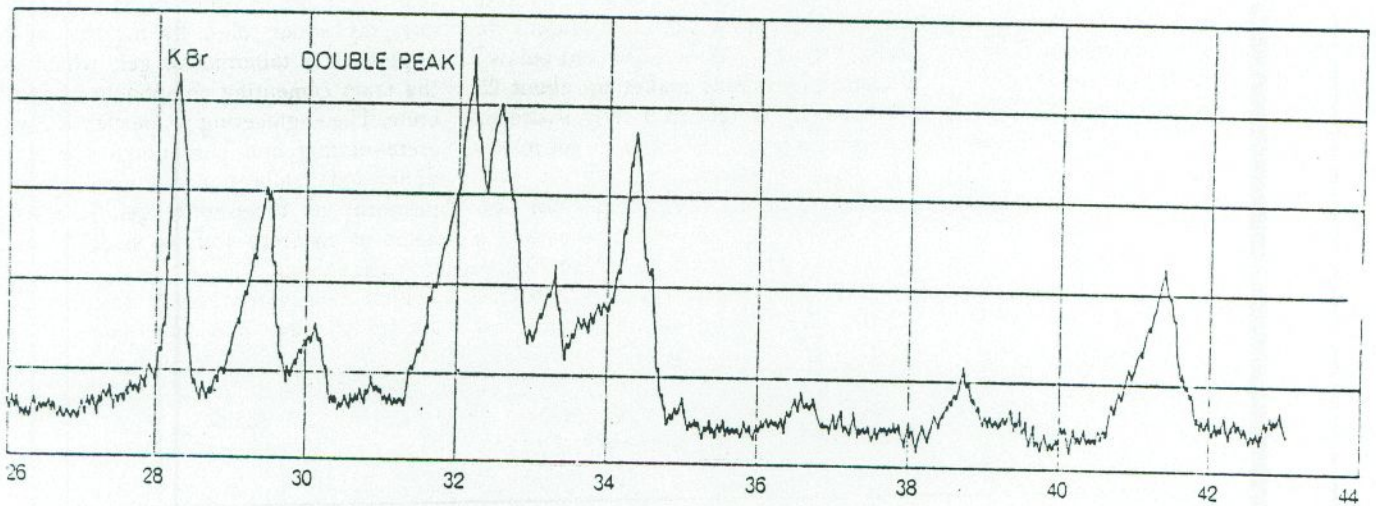
TRANSFORMATION OF COMPOUNDS occurs when water is added to portland cement. As shown in the top two lines, the two calcium silicates, which constitute about 75 per cent of a portland cement by weight, react with water to produce two new com-

pounds: calcium hydroxide and a calcium silicate hydrate called tobermorite gel. Next two lines show how the other two major compounds in portland cement react with water. The bottom line shows the reaction involving gypsum, a fifth compound in cement.



X-RAY DIFFRACTION PATTERN of tricalcium silicate, one of the major compounds in portland cement, is reproduced. The use of a particular X-ray wavelength, in this case the K-alpha radiation

of copper, causes the layers of atoms in the tricalcium silicate to diffract the rays and produce these characteristic peaks. Horizontal scale gives angles of diffraction; height of peaks indicates intensity.



EFFECTS OF HYDRATION are indicated by portions of two diffraction patterns: at top for a Type I portland cement and at bottom for the same cement after partial hydration. Each of the patterns shows at left a peak contributed by potassium bromide, which was added to the samples in known amounts for purposes of comparison. The characteristic peaks of tricalcium silicate appear at the

same angles as in the illustration at the top of the page. The double peak is contributed by the two calcium silicates; it is considerably lower in the diffraction pattern of the partially hydrated cement than in that of the cement before hydration because some of the calcium silicates have disappeared in hydration, giving way to new compounds, which appear in diffraction pattern on opposite page.

portland cement is hydrated and then we shall discuss reaction rates. In a chemical reaction heat is liberated if the sum of the energies possessed by the reactants is greater than the sum of the energies possessed by the reaction products. The reaction is said to be exothermic. If the reverse is true and energy is absorbed, the reaction is endothermic. We have already indicated that the hydration of portland cement is exothermic.

Several groups of workers have measured the individual heats of hydration of the four major compounds in portland cement and also the heat released by each compound when it is present in synthetic and in industrial cements. When the compounds are together, it is possible to isolate the contribution of each by mathematical analysis. The results of these studies are in close agreement for three of the four compounds and indicate a heat release of approximately 60 to 120 calories per gram of material. The fourth compound, tricalcium aluminate, releases about 200 calories per gram when it is hydrated by itself and about 325 calories per gram when it is part of a portland cement mixture. In the latter case the aluminate reacts not only with water but also with gypsum, a reaction that releases more energy than simple hydration does.

Portland cements have been classified into basic types by the American Society for Testing and Materials. Within each type there is considerable variation

in composition, but the different types identify cements with distinctly different properties. This difference shows up clearly when one compares their average heats of hydration. The top illustration on the next page shows the heat evolved when four types of cement were hydrated for periods ranging from three days to 13 years. The measurements were obtained by George J. Verbeck of the Portland Cement Association.

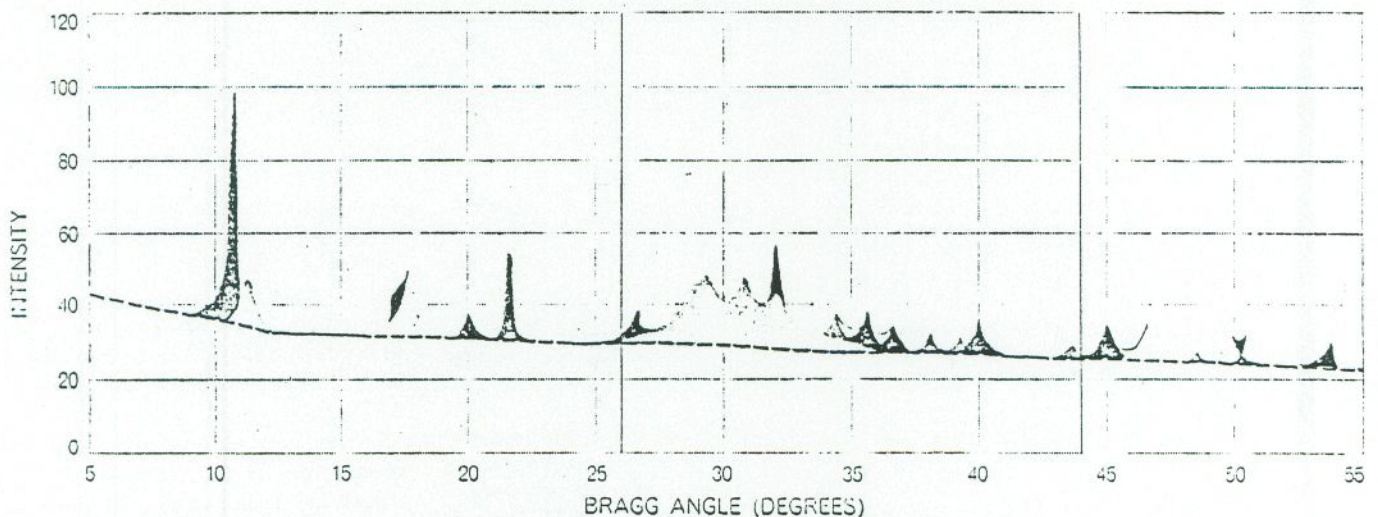
Type I, the commonest type of portland cement, releases a little more than half of its total heat of hydration in three days. Type III, the high-early-strength cement, releases 50 per cent of its heat in much less than three days. Type II, a moderate-heat cement, releases less heat over-all than do Types I and III, and more than three days are required for half of its heat to be released. Type IV, the lowest-heat cement, gives off only about half as much heat in the first three days as the high-early-strength Type III does, and over the full 13-year period it releases only about 75 per cent as much heat as Types I and III do.







The large variations in total heat release and in rate of release are achieved by altering the proportions of the four major compounds that make up portland cement. The bottom illustration on the next page shows the amount of heat released in a few hours to 100 days by these compounds. Type I cements usually contain about 50 per cent tricalcium silicate, which releases about 120 calories per gram, and about 25 per cent

dicalcium silicate, which releases only about 60 calories per gram and releases it much more slowly. It is apparent that by reversing these proportions one should obtain a cement that releases less total heat and releases it more slowly than Type I does. Indeed, the proportions are reversed in low-heat Type IV cement, which was developed specially for the Hoover Dam by the Riverside Cement Company in California.

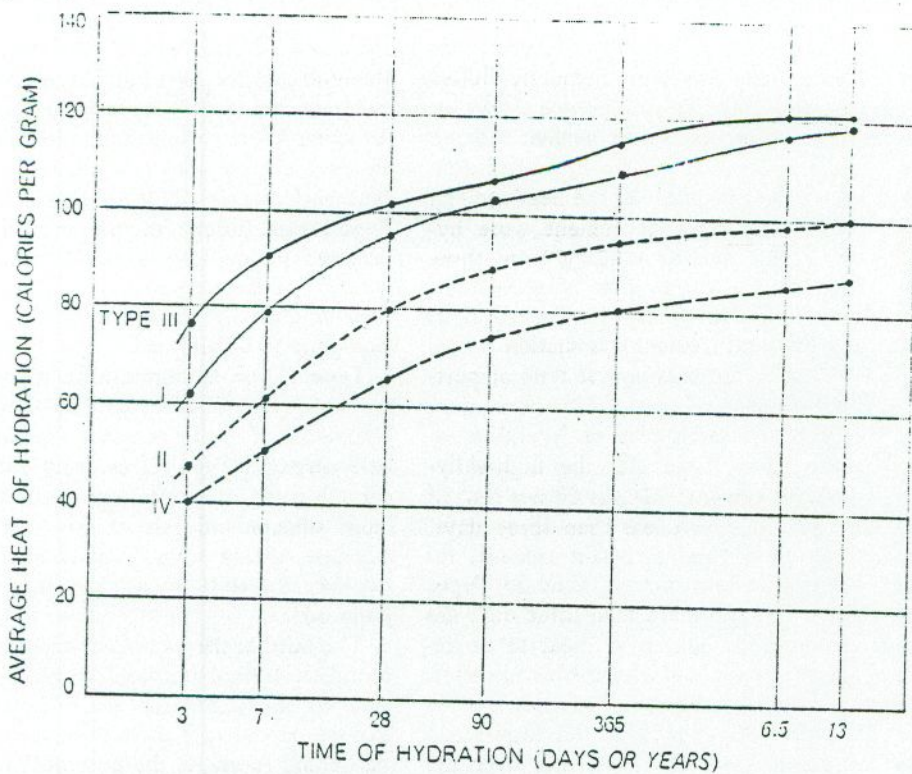
Type II, or moderate-heat, cements are intermediate in composition between Type I and Type IV cements. And high-early-strength Type III cements usually contain even more of high-heat tricalcium silicate and less of low-heat dicalcium silicate than Type I cements do [see illustration at top right on page 83].

The third of the four major ingredients found in normal portland cements—tricalcium aluminate—also has a large influence on the rate of heat release and hardening rates. As the bottom illustration on the next page shows, it has the fastest rate of reaction with water. As a result as much as 15 per cent of it can be used in Type III cements to speed the setting rate. In Types II and IV, in which low-heat release is desired, tricalcium aluminate may be almost absent. The tricalcium aluminate content of portland cement cannot be increased indiscriminately, otherwise a "quick set," or "flash set," will occur when the cement powder is mixed with water. Gypsum is added to the clinker as a "retarder" to slow down the hydration of

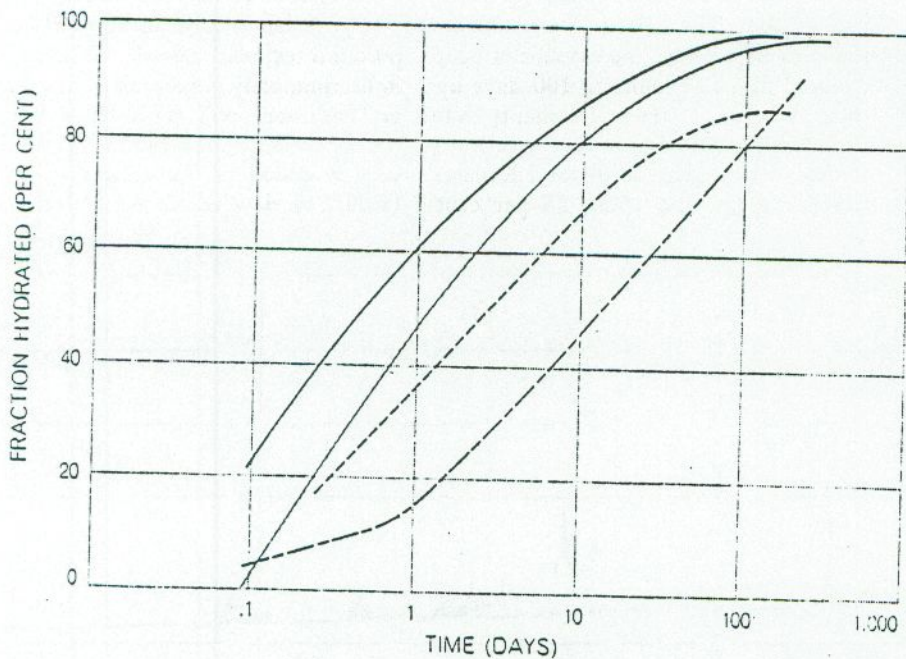


-  CALCIUM MONOSULFOALUMINATE
-  TOBERMORITE
-  CALCIUM HYDROXIDE
-  CALCIUM ALUMINOFERRITE HYDRATE
-  TETRACALCIUM ALUMINATE HYDRATE
-  MIXTURE OF COMPOUNDS

FULLY HYDRATED CEMENT shows this diffraction pattern. The peaks that appear in the diffraction patterns on the opposite page (peaks representing the major compounds in the cement before complete hydration) have disappeared because new compounds have been produced during hydration. In place of those peaks are the peaks of the new compounds constituting a completely hydrated cement (in this case Type I). Solid lines bracket area covered by patterns on opposite page. Vertical scale for intensity is arbitrary.



HEAT OF HYDRATION of the basic types of portland cement is charted for hydration periods ranging from three days to 13 years. Variations reflect the different properties of cements. Type III, for example, releasing heat rapidly, gives high early strength; Type IV, which releases heat slowly, is valuable in big structures that cannot dissipate heat easily.



- TRICALCIUM ALUMINATE —————
- TRICALCIUM SILICATE —————
- TETRACALCIUM ALUMINOFERRITE - - - - -
- DICALCIUM SILICATE - - - - -

SPEED OF HYDRATION of the four major compounds in portland cement during approximately 14 weeks is charted. If a fast reaction is desired, as in Type III portland cement, the cement should be high in the fast-reacting compounds, tricalcium silicate and tricalcium aluminate. If a slow reaction is desired, as in Type IV portland cement, the cement should be high in the slow-reacting compounds, dicalcium silicate and tetracalcium aluminoferrite.

tricalcium aluminate in portland cement. Composition, however, is not all that influences the speed of hydration. Fineness of grinding, the amount of water added and the temperature at the time of mixing all have important effects on reaction speed. To achieve a faster hydration Type III cements are ground finer than Type I cements. In fact, two cements of the same composition can be classified as Type I and Type III simply because of differences in fineness.

Let us return to tobermorite gel and observe the critical role it plays in establishing the physical and engineering properties of hardened portland cement paste. T. C. Powers and his co-workers at the Portland Cement Association were the first to show that two physical properties of cement paste—surface and porosity—are decisive in determining the two most important engineering properties: strength and dimensional stability. Powers applied the term "cement gel" to the part of hardened paste that is responsible for surface and porosity. The word "gel" signifies an extremely finely divided substance that has a coherent structure.

Later work has shown that the most important constituent of cement gel is the calcium silicate hydrate called tobermorite gel. The word "tobermorite" indicates that this substance has a composition and crystal structure resembling that of the natural mineral called tobermorite [see illustration on the cover of this issue]. The natural mineral takes its name from Tobermory in Scotland, where it was discovered.

A little simple geometry will indicate what happens to the surface area when a substance is finely divided. When a cube of a given size is divided into eight smaller cubes of equal size, the surface area is doubled. As the original cube is divided into smaller and smaller cubes, the surface area grows progressively.

Let us now suppose that out of a clinker of cement we cut a cube weighing one gram. Its surface area will be about three square centimeters. If we grind this cube to the average fineness of portland cement, the surface area will be some 3,000 square centimeters. The average diameter of a typical cement grain is 10 microns, or a hundredth of a millimeter; in a pound of portland cement there are about 150 billion such grains. The powder is so fine it passes through a metal screen that can hold water.

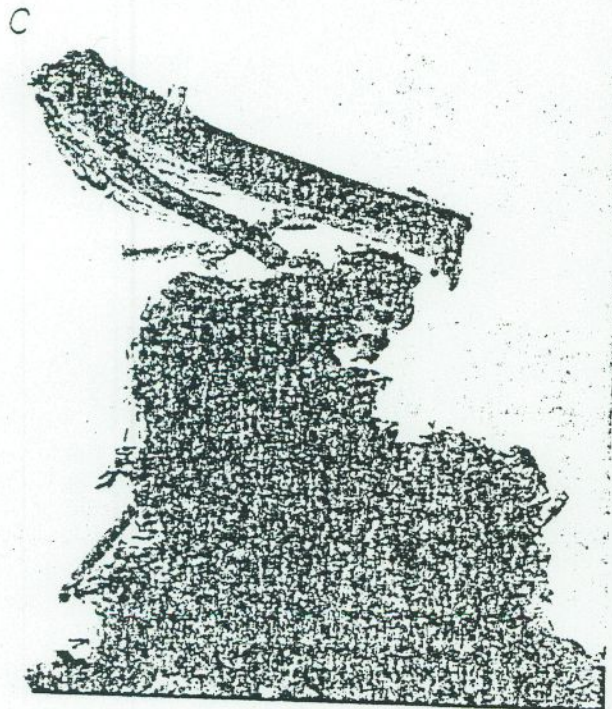
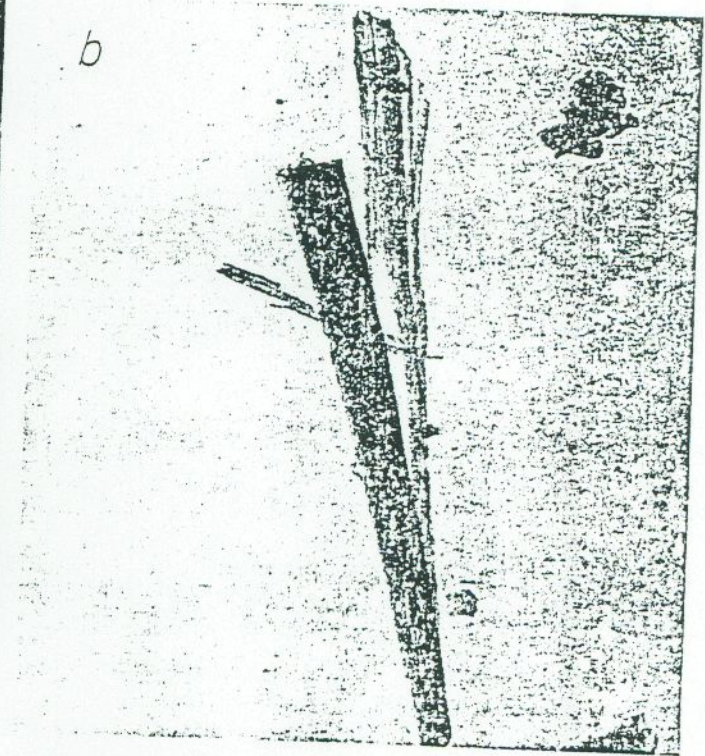
Small though the cement grains are, they are gigantic compared with particles of tobermorite gel. The surface

area of one gram of tobermorite gel is some three million square centimeters, which implies that the average diameter of a tobermorite gel particle is only a thousandth of that of a typical cement grain. Particles of such small size can be seen only in an electron microscope

[see illustration below]. Evidently in undergoing hydration the tiny grains of portland cement are replaced by still smaller particles.

One may ask: What does the small particle size of tobermorite gel have to do with the engineering properties of

hardened cement paste? The answer is that the enormous surface area of the gel gives rise to the forces responsible for the paste's cementing action. The surface forces can be visualized by imagining a cube representing a crystal of sodium chloride. A chlorine atom in



STRUCTURE OF TOBERMORITE GEL is apparent in these electron micrographs, which enlarge the gel particles some 65,000 diameters. Micrograph *a* shows an aggregation of tobermorite gel fibers obtained from a hardened paste of tricalcium silicate; in *b*, which is from a hard paste of dicalcium silicate, the

particles appear as thin, rolled sheets. Pastes of portland cement rarely show such sheets, but a few appear in micrograph *c*, which is from a Type IV cement. Usually the gel appears in the form of unrolled, crumpled sheets, as in *d*, obtained from a Type I cement. Structures give clues to moisture problem illustrated on page 90.

the body of the crystal is surrounded by six sodium atoms, four on the sides, one above and one below. Similarly, each sodium atom is surrounded by six chlorine atoms. A sodium atom located at the surface of the crystal, however, is surrounded by only five chlorine atoms: four on the sides and one below. To compensate for the missing chlorine atom the sodium atom tends to seize

some other atom or molecule from its surroundings; for example, it may attract a water molecule in the atmosphere. A chlorine atom at the surface of the crystal also exhibits a tendency to attract external substances.

This propensity of atoms or molecules on the surface of a crystal to attract substances outside the crystal is called adsorption. When two surfaces are

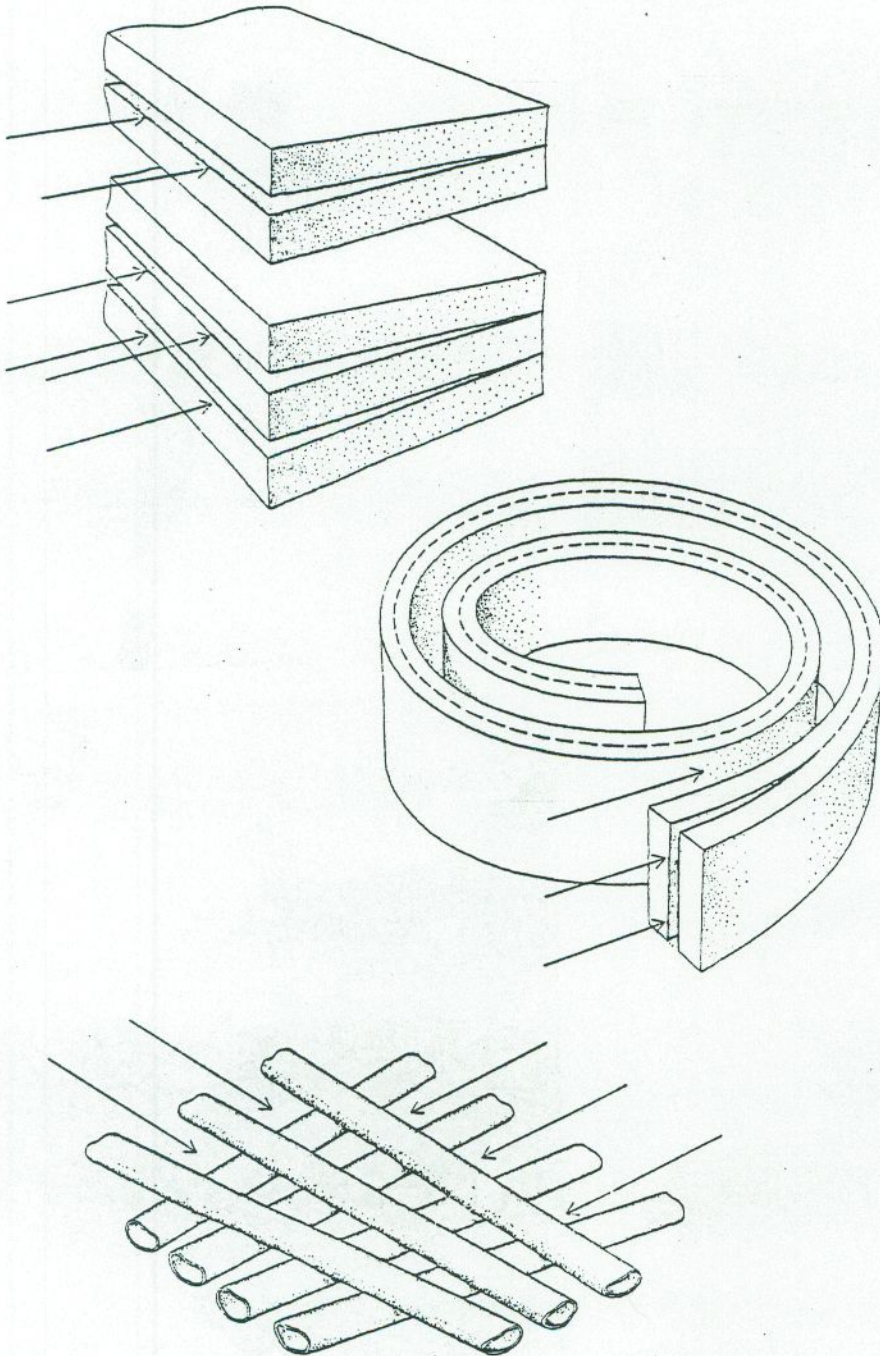
brought close together, they also attract each other and for similar reasons. This is called adhesion. The particles of tobermorite gel adhere to each other; they also adhere to small crystals in hardened cement paste, to grains of sand and to pieces of coarse aggregate, cementing everything together.

The cementing action depends on the extent and nature of the surface. There are substances such as silica gel (a form of silicon dioxide) that have more surface area, gram for gram, than tobermorite gel does, but the latter is a better cementing material because it possesses much greater force per unit of surface. On the other hand, calcium hydroxide, also found in cement paste, exerts a stronger attractive force per unit of area than tobermorite gel, but it is a poorer cementing material because one gram of the most finely divided calcium hydroxide has only about a tenth of the surface area of one gram of tobermorite gel.

In addition to surface area and surface force the other important property in determining the strength and dimensional stability of hardened portland cement paste is porosity. Inevitably there are tiny pores of molecular dimensions between particles of tobermorite gel and there are still larger pores between aggregations of gel particles. The former are called gel pores; the latter, capillary pores or cavities. Even the capillary pores are too small to be visible in an ordinary light microscope.

The volume of the pore space in a cement paste depends on the amount of water mixed with the cement at the start. When the paste sets, it acquires a stable volume that is approximately equal to the volume of the cement plus the volume of the water. Let us suppose we prepare two pastes from the same cement, using the same amount of cement but different amounts of water. After setting, the paste with the greater amount of water will have the greater volume. After hydration the two pastes will contain the same amounts of solid material, because the same amounts of cement will produce the same amounts of hydration products. The volume of one paste, however, is greater; consequently that paste will have a larger pore space.

This effect has an important influence on the strength of the hardened paste which is the dominant factor in the strength of concrete. Pores are filled with water and air and they have no strength. The strength resides in the solid part of the paste—primarily in the tobermorite



SWELLING AND SHRINKING of concrete occur with changes in moisture and present a problem of cracking. Tobermorite gel particles have the major role in the water movement, which occurs by means of the mechanisms illustrated here. At top, water penetrates between molecular layers of a tobermorite gel sheet, causing the sheet to expand. In a similar action (middle) water enters between the layers of a rolled sheet of tobermorite gel; moreover, it can enter (upper arrow) into the convolutions of the fiber, where expansion will occur by adsorption. At bottom water enters the pores between fibers of tobermorite gel.

gel. The less porous paste will produce the stronger concrete. In the mixing of concrete, therefore, no more water should be used than is absolutely necessary.

The porosity is also a vital factor in the dimensional changes of hardened paste. Two types of volume change are of practical significance. One of these is caused by the freezing of water in the capillary pores of the paste. Ice has a volume 9 per cent greater than that of water; hence when water freezes in the pores, the expansion develops internal pressures that may lead to cracking of the concrete.

The second type of volume change results from movement of water into and out of the pore system because of changes in atmospheric humidity. When the humidity increases, water enters the paste and the paste swells; when the humidity drops, water leaves the pore system and the paste shrinks. In actual practice the volume changes are quite small. A drop in the humidity of the environment from 100 per cent to 10 per cent, which almost never happens, causes a change of no more than 2 per cent in the volume of cement paste. Because the aggregates in concrete restrain the shrinkage of the paste, concrete shrinks only a tenth as much as hardened paste. Nevertheless, even this tiny volume change may produce cracking.

Of the possible improvements in concrete, the one most needed is a substantial reduction in dimensional change. One aspect of this problem, the freezing of water in the pores, has already been solved by a product called air-entraining portland cement. Small amounts of soaplike materials are ground together with the cement clinker. When the cement is mixed with water, billions of microscopic air bubbles are produced by the soaplike material and become entrained in the cement paste. The bubbles relieve the internal pressure created when water freezes in the pores. The porosity introduced by the air bubbles themselves causes only a small reduction in strength, which, if necessary, can be easily compensated by a slight reduction in the ratio of water to cement.

The problem of volume changes caused by the movement of water has not yet been solved. Before it can be solved much more must be learned about the mechanism of swelling and shrinkage, in which tobermorite gel plays a dominant role.

Some clues to the way in which tobermorite gel takes up water can be in-

ferred from close inspection of the four electron micrographs labeled *a*, *b*, *c* and *d* on page 88. Illustration *a* shows an aggregation of tobermorite gel particles obtained from a hardened paste of tricalcium silicate. The particles are straight fibers and the aggregation resembles a pile of matches in which the matches of each layer are at right angles to the matches in the layer below. Illustration *b* shows a few individual fibers obtained from a hardened paste of dicalcium silicate. The fibers are actually rolls of very thin sheets only two or three molecular layers thick. The fiber on the left is a partly unrolled sheet. Such sheets are seldom found in pastes of portland cement. Illustration *c*, obtained from a paste of a Type IV cement, shows a few rolled-up sheets. Ordinarily, however, tobermorite gel appears as unrolled crumpled sheets, as shown in illustration *d*, obtained from a paste of a Type I portland cement.

Such micrographs provide the basis for three probable mechanisms illustrated on page 90, by which water may enter tobermorite gel in hardened pastes of calcium silicates. The diagrams show (1) the swelling of stacks of essentially flat sheets, (2) the penetration of water into rolled-up sheets and (3) the penetration of water into the pores that separate crisscrossed fibers. Because tobermorite gel sheets usually do not form rolls in portland cement pastes, the second mechanism is probably not too important in the practical technology of concrete. But a fourth mechanism, which is not illustrated, may be the most important cause of dimensional changes at high humidities. We have mentioned that in addition to gel pores there are larger pores in the paste between the aggregations of gel particles. Water has ready access to these pores and swells the hardened paste.

These mechanisms do not exhaust the sources of dimensional changes in cement pastes due to moisture. The reason is that portland cement pastes contain not only tobermorite gel but also the hydration products of tricalcium aluminate, which similarly contribute to dimensional changes. The fraction of the total volume change attributable to various mechanisms has yet to be determined. When the mechanisms are quantitatively understood, one can expect to find ways to influence them. A concrete of greater dimensional stability than any now produced is a distinct possibility. Even if the new product is not "just around the corner," it will exist in the not too distant future.