

THE FUNCTION OF WATER IN HARDENING CONCRETE

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SYNOPSIS

A mental picture of the function of water in concrete is obtained by assuming that, in an ideal cement composed only of the calcium silicates, the cement hydrates as circumstantial evidence indicates it might. In this way structures and actions too fine and intricate to be seen even with the best microscope are examined.

After the cement has hydrated for a week or more the temporary water voids have been filled with hydration products which apparently have come from the outer surfaces of the cement grains. The water has transformed the calcium silicates into crystalline hydrated lime and a non crystalline substance called gel which occupies about 12 per cent of the volume of the concrete. The gel can occupy such a large volume because of its minutely porous, frame-like structure. The gel is the cementing agent, apparently solidifying the mass by growing into the void spaces with the advent of water.

The water in concrete fills voids with gel incidentally to its principal concern of arranging the calcium silicate in gel form so that it can cling to all sides of each molecule. When voids of limited size are provided the water finds it necessary to fill them with a dense strong gel. After the water has hardened the concrete by filling the pores with gel it has served its purpose. It is not necessary for the continued existence of the gel. Ultimate strength is reduced by drying because of the destructive internal stresses caused by gel tending to shrink when other constituents do not. The water needed for chemical combinations is about 10 per cent of the weight of the cement but for the production of gel at least three times as much is needed.

Progress has been made in scientific research by applying assumed knowledge of infinitesimal and unknown things to untried cases. Likewise in cement and concrete research it is believed that progress can be made by assuming cement to hydrate as circumstantial evidence indicates that it might hydrate. In this way a reasonable mental picture is obtained of structures and actions too fine and intricate to be seen with the best microscope, but a picture that permits one to predict what may happen when the cement hydrates in untried circumstances. If the predictions prove out, the picture becomes a little clearer, if not, it must be modified. As a justification of this procedure, it can be stated that the variables in cement and concrete research are so many that if all combinations and permutations were to be tried, all of the laboratories in the country could not accommodate the trials in a lifetime. Furthermore, without a reason-

able picture of cement hydration, the most important factors are likely to be overlooked.

The present discussion deals with an assumed picture of cement hydration to show the function of water in hardening concrete. The picture is simplified for the present purpose by further assuming the cement to be an ideal one composed only of the calcium silicates, which constitute about 75 per cent of an average cement.

Water makes up about 20 per cent of the volume of a fresh concrete of good quality. This is near the minimum that can be used under ordinary conditions. Air bubbles make up about one per cent. The spaces occupied by water may be termed "temporary water voids" and the air bubbles may be termed "air voids". The temporary water voids are made up of countless, connected spaces between particles. If the proportioning of the concrete is good, the water-filled spaces

are narrow and tortuous as compared with the much larger but isolated air bubbles. Because the temporary water voids have many times the volume of the air voids and because they are continuous throughout the concrete, they are of greater importance. Their average width is probably about 5 to 10 microns, or considerably less than one thousandth of an inch. They are large enough to permit easy percolation of water under slight pressure, but yet they are barely large enough to be seen nicely in a good microscope.

After the cement has hydrated for a week or more, the concrete structure appears different. No pore spaces except the air voids are visible even with the best microscope. The temporary water voids have been filled with hydration products, which apparently have come from the outer surfaces of the cement grains. The smallest grains have been transformed entirely into hydration products, but only the surface of each of the larger grains has been altered. The calcium silicates upon hydration have yielded two substances, one of which is white, crystalline hydrate of lime, and the other is a non-crystalline material called gel. With an average cement and after a month of moist curing, the hydrated lime is likely to make up about 2 or 3 per cent of the concrete volume. But the temporary water voids originally comprising 20 per cent of the concrete volume have been practically filled and cement particles have been consumed to an extent of about 5 per cent of the concrete volume, from which it follows that hydration products now fill about 25 per cent of the volume. The 2 or 3 per cent of the volume occupied by the hydrated lime and about 6 per cent occupied by miscellaneous hydration products are overshadowed by the 16 or 17 per cent remaining to be occupied by the gel. For this reason, and for others not yet discussed, the most impor-

tant hydration product is therefore the gel.

The principal gel of portland cement may be pictured as an intricate, brush-like frame, built or grown from compact grains of cement. The building does not represent any great increase in solid volume but rather a rearrangement of the invisible building stones of the cement to make the porous frame that is the gel. Although no pores can be seen with the best microscope, the gel is nevertheless porous and absorption tests show that the total volume of pores in hardened concrete is not vastly less than in fresh concrete. Through the process of hydration, the cement grain has been used to build into all the temporary water voids the gel network that knits all particles together as though a solid. It is now very difficult to pass water through the concrete. The extremely fine structure of the gel is evidenced by the fact that the rate of water percolation through the concrete before hydration is about 10,000 times as great as the rate under identical pressure after hydration. The hydration has subdivided all except the largest of the seemingly small water voids into much smaller compartments by filling them with a rigid gel framework. The maximum size of void that has been filled is perhaps 50 microns in width, but this varies with such conditions as time and temperature.

The development of cement gel has such possibilities that if an observer could be gifted with an eye to see invisible detail in a concrete mixture, he could probably manipulate the ingredients to give almost any desired properties. It is therefore instructive to guess what he might see.

With his gifted eye, the observer sees the cement grain as a compact bundle of building blocks, molecules of tricalcium and dicalcium silicate, seemingly adapted to be fitted together in chains or columns. The tricalcium silicate blocks are por-

vided with an abundance of keystones in the form of lime molecules, which when removed permit the blocks to be taken easily from the bundle. The dicalcium silicate blocks are similar except that they are packed more tightly and with fewer keystones, so they are very difficult to remove from the bundle.

Looking into the concrete mixture, the observer sees cement grains distributed through the water-filled pores like bundles of shingles on a roof to be covered. The water molecules rush about, bombarding the surfaces of the cement grains and pulling out first keystones and then building blocks. The blocks are erected on the surface of the grain in the form of small, braced columns. The blocks are linked together with water molecules, which attach themselves on all sides of each block. It is the later desertion of these water molecules when the concrete dries out that permits the blocks to settle together and causes the concrete to shrink. Due to the fact that the water molecules cluster around each building block, passageways are provided on all sides of the columns and thus access of a rather poor sort is maintained to the unused blocks below. The unused blocks are always obtained by first pulling out keystones, which are not used in the building. They are carried off by some of the water molecules to the nearest open pore and placed there in rows and tiers, one water molecule remaining with each keystone and thus growing a crystal of calcium hydroxide. The keystones facilitate the work to such an extent that where they are plentiful in the bundle of blocks, about fifty blocks are removed and erected to each one that is handled where keystones are scarce. The same sort of structure is built in either case, the differences being only in the rate of construction and in the number of keystones to be discarded.

In a few hours the smallest pores are filled with a sparse framework and the

concrete is pronounced "set." Only an insignificant number of the silicate blocks have been used but it has become increasingly difficult for the water to penetrate to the bottom of the gel and extract more of them. The work goes on at a decreasing rate of progress, and larger pores are gradually filled with the silicate framework, while that in the filled pores is made stronger and denser, as there are left fewer water molecules around each block. The supply of silicate molecules or blocks in the cement grains is so great that it does not seem possible that all of them can ever be used. If water is available, the gel should continue indefinitely to grow denser and to fill larger pores. It seems doubtful, however, that the gel in the larger pores will become as strong and dense as that in the smaller pores during the life of a structure.

The water in concrete is not primarily concerned with the filling of pores with gel. It is concerned only with arranging the calcium silicate in gel form so that it can cling to all sides of each molecule. The engineer takes advantage of the fact that when pores of limited size are provided in which to arrange the gel, the water finds it necessary to fill the pores with a dense, strong gel.

After the water has hardened concrete by filling the pores with gel, it has served its purpose. Water is necessary for the hydration of cement and it is a permanent constituent of some of the hydrated compounds, but it is not necessary for the continued existence of the gel that gives concrete its strength. The gel can be dried without destroying it. Drying is objectionable mainly because of the shrinkage and consequent stresses that result when the silicate molecules fall together. The ultimate strength is reduced because of the destructive internal stresses that result from the gel tending to shrink while other constituents do not. A gel shrinkage of at least 3 per cent by volume is estimated to occur

due to complete drying, but fortunately the gel in service concrete does not shrink this much. The reasons are that the gel has a strong enough affinity for water to retain a large amount and that the pores are so small that loss of evaporable water by diffusion to the surface is very slow and seldom if ever complete.

It is illuminating to note how hydration causes heat liberation of cement. If dicalcium silicate could be changed from its crystalline form to gel without water, there would be practically no heat liberation. The heat of hydration of dicalcium silicate in cement is largely due to the wetting of the gel. The amount of this heat is appreciable because of the tremendous amount of surface to be wetted in the gel. If dicalcium silicate were to be hydrated without loss of heat, its temperature would rise considerably. If the water could then be removed without removing heat in so doing, the temperature would drop again to about the initial value and the dicalcium silicate that was changed to gel would remain as gel.

In the case of tricalcium silicate, important amounts of lime, the keystones mentioned above, are cast off during gelation and the observed heat of hydration is about one-half due to the wetting of the gel and about one-half due to the hydration of the lime. There is practically no net heat liberation due to changing the tricalcium silicate into dry gel and calcium oxide, the heat liberation observed during hydration is attributed largely to the wetting of the gel and the hydration of the calcium oxide.

The amount of water necessary for the hydration of cement is not definite because the degree of hydration is automatically adjusted to suit the amount of work the cement has to do. In what is called a good concrete mixture, there is enough cement to produce gel and other

hydration products to fill much more void space than exists. The cement then does not have much work to do and hydration does not proceed far. When leaner mixes and higher water contents are used, the amount of void space to be filled by each unit of cement is greater. The cement in a sample from a concrete road three years old when examined petrographically was found to be almost completely hydrated. Analyses indicated the original mix to have been oversanded and to contain a large amount of mixing water. The cement in a corresponding sample of dense, rich concrete was found to be only partially hydrated at the same age.

In considering the limiting case of complete hydration, the water requirement for definite chemical combinations is distinguished from that necessary for gelation. The water needed for definite chemical combinations is only a little more than 10 percent by weight of the cement, while that needed for the manufacture of the gel is believed to be at least three times as great. Temperature and time, however, probably modify the water requirement. Tests are now in progress at the Massachusetts Institute of Technology to determine the relative degrees of hydration of cement and its pure compounds at various ages under different moisture and temperature conditions.

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