

The Growth of Basic Research on the Properties Of Concrete in the PCA Laboratories

T. C. POWERS

•OF the multitudes of different conditions, situations and fortunes that make up our individual lives, there is one sector in which we meeting here have an involvement in common: to one degree or another we are faced with the necessity of trying to understand concrete. To some of us, the study of concrete is our bread and butter; to others concrete is a challenge that has stimulated our curiosities, and to a degree made us its captives; and to some it has been both bread and butter and the object of compelling curiosity. On this occasion we are celebrating a certain growth of scientific knowledge about concrete, and we shall soon begin hearing reports on the fruits of some of our current labors.

However, Dr. Brunauer started this meeting by making some remarks about me, and I should like to say something about that. First of all, I thank Committee MC B-6 for sponsoring this meeting. And I thank Dr. Brunauer for his more than generous remarks; although my vanity feeds on them as you might expect, I am at the same time sure that no one intended to imply that our gain of knowledge about concrete during recent years was due to any one man, any one group, or any one nation. I shall use this occasion to tell something of the degree to which I have become indebted to others, and to emphasize the interdependence which characterizes our efforts, and I think all human endeavor.

I should like to insert now some autobiographical remarks which will call to mind something of the nature of concrete research as it was done in the early part of this century.

After gaining my first field experience with concrete during construction of a dam in Oregon, I nursed a ready-mix concrete business through its first year, only to be overwhelmed by the consequences of the fateful October of 1929. In the spring of 1930, I received a letter from F. R. McMillan, then Director of Research of the Portland Cement Association, tentatively offering a position in Chicago. Mr. McMillan said in his letter, "Our work is tending more and more toward the fundamental approach and away somewhat from the customary method of making and breaking specimens. I will therefore be particularly interested in the training you have had in chemistry and the fundamental sciences, as well as the work you have done more recently in concrete."

In reply, I said something about liking the fundamental approach and gave him the requested information. I was hired, and began work in Chicago in June 1930.

Aspiration toward fundamental research was quite out of line with the education in science I was able to offer, and thus it was somewhat surprising that I was hired. However, I can guess what Mr. McMillan had in mind: six years earlier the Portland Cement Association had established a research group here in Washington, D. C., for basic research on the chemistry of cement. This organization came to be called the Portland Cement Association Fellowship at the National Bureau of Standards. The early work of the Fellowship was done by Ashton, Brownmiller, Hansen, Lerch, and Taylor, under the direction of Dr. Bogue, and it had been fruitful. Thus it seemed that scientific research directly on concrete might bring comparable rewards. But somehow it was thought that the same high level of scientific training needed for research in cement chemistry was not needed for dealing with concrete.

I don't know which of us discovered the mistake first, Mr. McMillan or I, but after two or three years in Chicago, I realized that I was not able to do much more than employ conventional methods of a testing laboratory. I began to look for ways to live up to my end of the bargain.

One of my assignments on arrival in Chicago was to assist with freezing and thawing tests. Cubes of mortar made with New York sands were being repeatedly frozen and thawed. Periodically the cubes were examined and a description of the condition of each cube was written in a notebook; no quantitative measurements were made. Then I ran across this oft quoted paragraph attributed to Lord Kelvin:

"When you can measure what you are talking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely in your thought advanced to the stage of a science."

That observation struck home, and became my credo. Research gradually became a quest for numbers having meaning with respect to structure. But before describing that quest, let me call to mind a few aspects of early concrete research.

During the early 1930's, concrete research in our laboratories was mostly an elaboration of the techniques of routine concrete testing, as I have already indicated. When we discussed concrete, we naturally did so in such terms as consistency, workability, durability, unsoundness, shrinkage, abrasion resistance, sulfate resistance, frost resistance—all these words being attempts to designate properties of concrete in terms suggested by direct observation. It was already apparent to some, Mr. McMillan for example, and it gradually became apparent to me, that studies made exclusively from this point of view were likely to fall short of expectations.

Nevertheless, it must be said that this kind of work had great value; it had already produced the practical basis for much of present-day concrete technology. But the period of diminishing returns from empirical research on concrete had already begun, certainly no later than 1930. The problems and perplexities that remained to be dealt with by research had become mostly those that would not yield to the then prevailing methods, and thus the time had come to increase the application of scientific methods to concrete research.

The time was ripe for a change, not only because of the need of new information, and especially the need of better understanding, but also because the climate of knowledge and needs had become right for it.

How ripe the time had become may be indicated by several observations. In the first place, scientific research on cement chemistry had been under way for many years in many places; the PCA effort in this direction under Dr. Bogue has already been mentioned. By 1934, we had on the one hand a considerable fund of scientific knowledge of cement chemistry, and on the other hand a fund of engineering data and experience on the properties and behavior of concrete.

A gulf had developed between the two areas of knowledge. Attempts to bridge it usually took the form of using different cements in mortars or concretes, and attempting to correlate cement characteristics expressed in the language of the chemist, with concrete characteristics expressed in terms of the concrete engineer. There was a good deal of success, but also some dubious results. For example, some tests proved that it was necessary to exclude certain types of portland cement in order to obtain what was called frost resistant concrete; but, sad to say, different tests could not agree on which type was to be excluded. (Now we know that so far as frost action is concerned, all types are equally usable, and that no type will make concrete that can safely be frozen in the water-soaked condition, unless entrained air is used. What is more, we know why that is so.)

As I was saying, cement chemistry seemed too far removed from concrete technology to permit reliable interpretation of various correlations pointed out in current research papers. The idea began to grow that it should be possible to find within the concrete specimen itself, particularly within the paste component, specific structural features that would account for observed properties of concrete. Since hardened cement paste is a component of mature concrete, whereas anhydrous cement is not, we would no longer be limited to methods of statistical correlation.

Others, especially some workers in Europe, were apparently already thinking along these lines, and they began examining pastes by strange methods. There was Leopold Jesser who produced water vapor sorption isotherms before 1927; Werner and Giertz-Hedstrom produced isotherms in 1931; Berchem did so in 1936. Von Grönow had

studied the freezing of water in cement paste in 1936. In France, Freyssinet was thinking in terms of colloid and capillary structure, and offering hypotheses concerning strength, volume changes, and creep, before 1933. And of course Michaelis and Le-Chatelier had thought about structure long before these dates.

In the PCA concrete laboratory, we began our work in the, for us, new direction about 1934 by studying the structure of paste, both in the freshly mixed and hardened state. We measured bleeding characteristics and rheological properties of fresh pastes and concretes. From such data we learned that fresh paste has structure. By 1940, Dr. Steinour had firmly established the nature of that structure and by so doing he had given us the nature of the framework from which the final structure called hardened paste is developed. (In Germany, it is called cement stone.) In freshly mixed paste the particles hang together, yet they are separated from each other by small water-filled spaces. We have come to recognize this structure as the resultant of forces of attraction and repulsion between cement particles. Particles are held in a complex field of push and pull forces and because of this, fresh paste is a soft-solid, able to support finite shear stress.

Our work on the structure of fresh paste lasted more than five years. During the same period we began to study the freezing of water in hardened cement paste. Some of this work was done at MIT in Cambridge, Mass., where, in 1936, PCA sent me to take a course of study in colloid chemistry. The experimental work done there was not very successful, but it was a stepping stone to later work that met with considerable success. Also, as early as 1934 I had begun some studies of the submicroscopic structure of hardened paste, which began to produce usable data in 1937.

Even in 1936 it was possible to develop tentative concepts about the structure and properties of hardened cement paste that were in many important respects not substantially different from the concepts we have today. This was possible on the basis of data we had obtained, and data already published, mostly in Europe. We had to guess about many things that have since become more or less common knowledge, but generally they were well founded guesses. For example, we knew from the nature of the adsorption isotherm that not all the water in cement paste could freeze at one temperature; moreover we could guess how it would freeze.

The principal mechanism of shrinking and swelling was identified, and fairly well understood. The role of capillary forces, and of viscous friction in bleeding was predicted with fair accuracy.

In short, even imperfect knowledge of physical and colloid chemistry, together with data then available, made it possible to begin basic research with a good working hypothesis; a good foundation had been laid before we began. Our job was to convince ourselves that the early indications were in fact what they seemed to be, and then to build on that foundation.

After returning from Cambridge, I prepared a document entitled "The Application of Colloid and Capillary Theories to Concrete Research." It was a 60-page working hypothesis, and a proposal for future basic research on concrete; it ended with the following remarks:

"The foregoing discourse shows how the behavior of concrete from the time of mixing to the end of its useful life is conditioned by the chemical and physical relationships peculiar to the colloidal state and to the capillary dimensions of the interparticle spaces, both before and after hydration. In general, . . . the statements are inadequately supported by data, and without some perhaps unwarranted assumptions, and out-and-out conjectures, much of the discussion could not have been offered at all. Yet it is clear that some such picture . . . is essential not only to a full understanding of portland cement as it is now, but also . . . to accomplishing needed improvements. . . ."

After this proposal was made, the staff for this program was enlarged from two to six, Dr. Brownyard joining up in 1937. Then, in 1940, through the support of Mr. Mc-Millan and Mr. Frank T. Sheets, then president of the Association, additional funds were made available and the professional staff was enlarged to eleven. Dr. Steinour came from California, Prof. Pickett from Kansas, and William Lerch was transferred to Chicago from the Fellowship laboratory in Washington.

Mr. Lerch brought with him from Washington ideas about the early reactions between cement and water, and he launched into studies resulting in his well-known papers on the optimum gypsum content of cement.

At the same time a project had been started under the title "Studies of the Cracking Tendency of Concrete." This title is significant; it is an indication of how difficult it was for me, and for some of my associates, to cast off the traditional approach to research on concrete. We had two kinds of tests for so-called cracking tendency, by means of which we could line up materials in order of relative merit. But the difficulty was that the two kinds of tests did not agree as to what the order should be. I began to see the light in this area of research after Prof. Pickett came. He pointed out that since there is no such property as cracking tendency, we could hardly hope to measure it. What we could measure were stresses and strains and time; and that is what Pickett and his associates did, learning a good deal about shrinkage stresses and creep. This work was coordinated with concurrent studies on the properties of paste. That is to say, while we gradually built up a many-faceted program of studies of cement paste and concrete, the backbone of the program was the work on the physical structure of hardened paste. As I said before, it was possible as early as 1936, which was before we had very much new data, to imagine the kind of structure it must be, but we had no way to test adequately the correctness of our ideas. We needed more quantitative data, and as long as we had to rely on indirect methods of observation, we needed more than one line of evidence that would, it was hoped, converge to the same conclusions.

In hopes of finding structural features that could be expressed in numbers, we had already taken hold of a method that had been used in Europe. The method was based on the theory of capillary condensation, and it employed the Kelvin equation for the relationship between the surface curvature of water droplets and the escaping tendency of water molecules, expressed as relative vapor pressure. By assuming the pores in a sample to be cylindrical, and by making another assumption or two, we were able to calculate the size of a pore from the relative vapor pressure and the temperature of the water contained in the pore.

Working with this kind of information, we tended to think in terms of pore-size, and pore-size-distribution, and we continued to do so until 1938. But satisfactory interpretation eluded us; we could not conceive of a model resting on such ideas that would stand critical examination.

I mentioned a terminal date—1938. That was the year that Brunauer, Emmett, and Teller published their first paper on multimolecular adsorption, and showed how their experimental method could be applied to the measurement of internal surface area in porous bodies—the BET method. That paper started our imaginations working along different lines. Whereas we had been more or less forced to think of submicroscopic holes in a mass of amorphous solid material, we could now think of the solid material as being composed of semi-discrete particles, and the pores as interstitial spaces in aggregations of such particles, mostly submicroscopic.

Actually we had returned to a concept published by Freyssinet in 1933; he proposed that the properties of cement paste depended on what he called corpuscles, their concentration and their surface area. Indeed, we had returned to the general concept that all material is essentially particulate.

Again you see, the foundation had already been laid; the time was ripe for us to take advantage of Brunauer's contribution just as soon as his paper appeared.

Having learned how to measure internal surface area, and knowing also the volume of interstitial space with fair accuracy, we could at once arrive at the order of size of Freyssinet's corpuscles—we called them gel particles. Also, we learned the order of size of the pores. We had finally obtained numbers that could put some dimensions in our picture of structure; we could build our imaginary model more or less to scale; we could do a little more than just confirm the belief of many before us that hydrated cement is mostly colloidal material.

I must pause here to say that in 1938 Brunauer was to me only a name in a by-line. I had not met Dr. Brunauer and was not to meet him until after 13 years had passed. I could not then have imagined the circumstances that finally made him my friend and

colleague; still less could I have dreamed of the day he would propose a meeting such as this. As you can see, it was his early work that pulled us out of the doldrums of stagnant ideas. In recent years he has furnished sustenance and inspiration for progress at new levels.

Returning now to the era following 1938, I must point out that although the appearance of the BET theory gave us a definite breakthrough, we were not sure at that time that a breakthrough had actually occurred. The theory was new, and relatively untried; there were reasons to doubt its applicability to our particular data.

Nevertheless, it became the basis of our new working hypothesis, and it served us well. It led us into a study of the energetics of adsorption, and soon we had a much improved basis for understanding volume changes, the freezing of water in small places, and other properties related to interfacial energy. We could at last begin to interpret properties of concrete in terms of numbers found, so to speak, inside cement paste.

This era was ended by our involvement in World War II. I mentioned before that in 1940 our staff totaled 11. That strength was maintained only two years, for in 1943 the staff began to disintegrate, and by 1945 only Steinour and I remained. Virtually all experimental work stopped. All we could do was to write papers based on work already done, and to lay plans for the future.

The program remained completely dormant until June 1947. Then we found Dr. Copeland and began rebuilding a staff, but hardly a new experiment was made until 1948. (At that time, Dr. Steinour, assisted by Dr. Seligmann, organized a literature research group which later became an independent section.)

Having lost its momentum, post-war basic research gained headway slowly, but finally it almost regained pre-war strength; indeed, in some respects pre-war levels were exceeded. Some techniques were improved, some discarded, and new techniques were introduced.

Post-war studies gave us more numbers related to structure. By studying the flow of water in cement paste we found a measure of surface area which was in harmony with values obtained by water vapor adsorption. The same studies enabled us to distinguish between systems containing continuous capillaries and those containing only discontinuous capillaries. Copeland and Bragg measured the small-angle scattering of X-rays by cement paste and found support for previous conclusions as to particle size. Helmuth carried out definitive work on the mechanics of frost action.

In the meantime similar work was under way in other laboratories, and some important contributions were coming in. Without attempting to mention all who have contributed, I shall mention a few. There was work with the electron microscope in Europe and Japan; especially important was that by Grudemo in Sweden, and that by Czernin in Austria. Beginning in 1957 Grudemo spent a year in our laboratories making use of our newly acquired electron microscope. He left us a legacy of important pictures and diffraction data.

Dr. Mielenz and his co-workers, then at the Bureau of Reclamation, contributed much to our knowledge of bubble systems in cement paste, as did also workers in Australia.

In Denmark, Plum and his associates studied the physico-chemical mechanics of alkali-silica expansion.

At the National Bureau of Standards, Blaine, Hunt, and Tommes produced significant data, particularly that pertaining to the instability of virgin paste structure.

At the National Research Council of Canada, Sereda and his associates entered the field, contributing some elegant techniques and new ideas.

A glance at today's program is suggestive of other fields of work. Also it reflects the tendency in recent years for the results of basic studies to find application in experimental work dealing more directly with concrete.

At the start of our post-war era, we were very much aware of the incompleteness and faultiness of work already completed. Especially, we felt the lack of knowledge about the chemical structure of hydrated cement paste. We often spoke of internal surfaces, but we had no clear concept of what kind of solid material the surfaces bounded. Indeed, our ideas of the nature of a solid surface as "seen" by adsorbed

molecules was not well developed, and some critics doubted that "real" surfaces are involved; some still do. Although some work on the chemistry of the hydration products had been attempted after 1947, it was not until 1952 when Dr. Brunauer joined the staff and surveyed the problem that a well-conceived investigation got under way.

The work accomplished by Brunauer, Copeland, Kantro, Helmuth, Weise and others, together with important work done in Europe, has already removed a great deal of the uncertainty of 1947. The calorimeter, the X-ray, and various special techniques have provided us with a new array of numbers that tell us about the molecular and ionic structure of the solid material in cement pastes.

I must say something more about the work done with the electron microscope. Following up earlier work by Czernin and his collaborators with the surface-replica technique, Copeland and Chang have recently produced stereomicrographs which enable us to see clearly the actual structure of hardened cement paste.

It is especially gratifying that these marvelous pictures by Copeland and Chang have not required a material change of concepts already developed from the various numbers garnered by indirect methods of exploration. At the same time, the stereomicrographs suggest some possible modifications; I am thinking particularly of the relationship between the distinct bodies of cement gel that can be seen in the stereomicrographs and the definition of cement gel earlier derived. There is a possibility that the two do not match exactly, and if they don't, it might be possible now to revise the older model.

Reaching the end of this discourse, I fear I have given too much the impression that we in Chicago began basic research on a small scale and then carried on an orderly accumulation of significant data, the process being interrupted only by an inconvenient war. If so, I have deceived you, not purposely, but because of the desire to present an orderly chronicle. A realistic story would have abounded in incomplete sentences, and the theme would frequently have been swamped by inconsistencies and illogical changes of subject. As a matter of fact, we bumbled and fumbled as we groped for data we could understand. Although we did probably more than our share of that, I do not hesitate to confess it, for it seems to me that such is the characteristic of all human endeavor that goes beyond previously trodden paths.

Personally, I am grateful for the exciting years I have been telling of, and for the company of those who shared them with me.