Calculation of Compounds in Portland Cements

The National Bureau of Standards–National Institutes of Standards and Technology has had an illustrious history of research on the most widely-used, man-made materials of construction, cement and concrete—materials which are often taken for granted, because of their commodity nature and generally successful use in the structures that comprise about 80 % of the Nation's fixed wealth. The level of NBS-NIST's cement and concrete materials research effort, in contrast to its structural research effort, has varied substantially over the century, with two highly productive periods separated by an almost dormant period from about 1960 to 1980. While some important contributions were certainly made prior to 1924, an outstanding period stretched from 1924 to 1954 when a strong NIST cement research program was complemented by an equally strong and synergistic industry-supported program, the Portland Cement Association Fellowship at the National Bureau of Standards. The Director of the PCA Fellowship for the whole of its 30-year life was Dr. Robert Bogue, a major figure in the history of cement research.

Robert Herman Bogue, a physical chemist, was born in Southborough, Massachusetts, on September 27, 1889. Before taking the position as Director of the PCA Fellowship in 1924, he had obtained degrees from Tufts University (B.S., 1912), Massachusetts College (M.S., 1915), and the University of Pittsburgh (Ph.D., 1920), and had gained professional experience as an Assistant Professor at Montana State College, 1915-17, a Fellow of the Mellon Institute, 1917-22, and an Associate Professor at Lafayette College, 1922-24. His research interests at that time appear to have been the chemistry of gelatine and the colloidal behavior of proteins—subjects remote from the inorganic materials that would be central to the rest of his professional career.

As Director of the PCA Fellowship, Bogue exercised a remarkably far-sighted leadership that made the Fellowship a major contributor to what would now be described as the materials science of concrete. Among Bogue's personal contributions was a landmark paper, *Calculation of Compounds in Portland Cement* [1], published in 1929. To understand the significance of the paper, it is necessary to know a little about portland cement and its manufacture.

Portland cement was invented in 1824. Its essential ingredient is cement clinker, a granular product from the high temperature (~1500 °C) processing of an appropriately proportioned, finely-ground mixture of minerals that are sources of the common oxides CaO, SiO_2, Al_2O_3, and Fe_2O_3; (for convenience in this paper, and in accord with cement industry usage, these oxides will frequently be referred to by the single letters C, S, A and F, respectively). Typical raw materials that are sources of these oxides in clinker production are, in the same order, limestone, quartz sand, clay, and iron ore. The cement manufacture ends with the intergrinding of clinker with a mass fraction of about 5 % gypsum ($CaSO_4 \cdot 2H_2O$) to produce the fine cement powder, usually gray in color, of which almost 100 million tonnes (1 tonne = 1000 kg) are produced in the U.S. each year. (The gypsum is added to control the rate of setting of the cement.)

Until the publication of Bogue's paper, there was much controversy about the compositions of the compounds present in the clinker, even though the elemental compositions of clinker and cement (always expressed in terms of simple oxides) were determined routinely in cement plants and other laboratories. Publication of the paper obviously met an objective Bogue had set for the Fellowship since, in the text of an address given to the American Concrete Institute [2] two years earlier in 1927, he wrote: " . . . this is an age of advancement. The cry for new knowledge is in the air. . . . . Questions are being asked now in all seriousness which a few years ago would have been regarded as absurd because unanswerable. . . . . All of this brings us to the belief that an unraveling of the laws governing the constitution of cement clinker and the behavior of the constituents of cement when made into concrete may hold developments which today can only be sensed but not definitely apprehended." In the same address, he made the nature of the problem to be solved clear by saying, "Of fundamental importance, above all others, and for the reasons given above, are the studies which will give us information of the nature of the constituents in clinker. Some of these have been known for some time. Others have been guessed at, but the guesses of the various authorities do not always agree. One group believes that a complex compound containing lime, alumina, and silica is present in clinker; another group, that lime and one of the silicates form a loosely bound compound known as a solid solution; and still another group, that the lime and silica form two separate silicates. . . . . But other components than lime and silica are present, and we must learn the manner of their combination. Into what compounds do the alumina, iron oxide, and magnesia go? What change is observed in the composition of the product resulting from the use of different percentages of these and still other constituents of the raw material?"

From petrographic studies, Bogue knew that portland cement clinker usually contained four main compounds (referred to as alite, belite, celite and felite) of unknown composition (Fig. 1), but there was, as yet, no practical way of determining their quantities. From the growing, but still incomplete, knowledge of the phase relationships in the CaO-SiO_2-Al_2O_3-Fe_2O_3 (or C-S-A-F) system, Bogue concluded that the main compounds in clinker were tricalcium silicate (Ca_3SiO_5 or C_3S), dicalcium silicate (Ca_2SiO_4 or C_2S), tricalcium aluminate ($Ca_6Al_2O_6$ or C_3A), and tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$ or C_4AF), and that the quantities of each could be calculated from the oxide composition of the clinker, provided the high temperature reactions had gone to completion in producing the equilibrium products and no significant amount of unreacted material remained. On this basis, at least to a useful approximation, Bogue was successful in unraveling "the laws governing the constitution of cement clinker" and he presented a set of simultaneous equations, together with nomographs, for calculating the amounts of the major compounds—the "potential compound composition"—of a clinker or a portland cement from the results of analyses for the major oxides (CaO, SiO_2, Al_2O_3, and Fe_2O_3) together with determinations of MgO, loss on ignition, and acid-insoluble residue. He realized that the compounds were unlikely to be pure because of the presence of unwanted minor oxides in the raw materials, but he did not have data that would enable him to take the minor oxides into account in his calculations. In spite of this limitation, Bogue believed that the calculated amounts of the compounds were close enough to reality to be useful. That this is true is amply demonstrated by the fact that Bogue's equations became, and 70 years later still remain, the basis for the classification scheme used in the ASTM C-150 specification for portland cement.

Ability to calculate compositions of cements in terms of the amounts of the main compounds present provided a valuable new tool for explaining, or predicting, differences in engineering performance among portland cements. This was true even though, when he wrote his paper, Bogue did not know that the composition of the

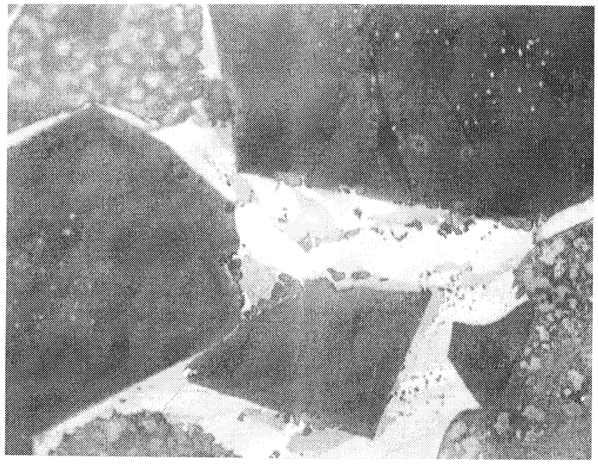

Fig. 1. Polished and etched section of portland cement clinker showing evidence of four major compounds (phases) such as would have been seen by Bogue (courtesy of Paul Stutzman).

aluminoferrite phase could vary much more than the compositions of the other major compounds; the "C_4AF" phase is, in fact, a member of a solid solution series of which the end members are $Ca_6Al_4Fe_2O_{15}$ and $Ca_2Fe_2O_5$ (or C_6A_2F and C_2F); however, for most portland cements, the composition of the aluminoferrite phase is reasonably close to the composition assumed by Bogue.

The ability to calculate the amounts of the major compounds in a clinker or cement had important implications. There was now the possibility of studying relationships between the amounts of the compounds in a cement and the cement's engineering performance in concrete, especially in relation to "durability." Beginning in 1940, this led to the inclusion of the Bogue equations in the ASTM specification for portland cements, because it was then certain that the amounts of the major compounds was one of the factors that determined engineering performance. The ASTM Type of a portland cement (I, II, III, IV or V) [3] is still determined, at least in part, by its "potential compound composition," colloquially referred to as its "Bogue composition." Thus, an ASTM Type IV Portland Cement is a "low heat cement," required to be low in C_3S and low in C_3A; it was developed for use in massive concrete structures, specifically for construction of the Hoover Dam. An ASTM Type V Portland Cement is a "sulfate-resistant cement," which is required to contain a maximum of 5 % by mass of C_3A; it was developed for use in concrete that will be in contact with sulfate-rich soils or waters; and an ASTM Type II Portland Cement (containing a maximum of 8 % by mass of C_3A) is both a "moderate heat" and a "moderately sulfate resistant" cement. There is no need to explain to a cement chemist, whether in the

United States or in many other countries, what is meant when the "Bogue composition" is referred to.

Bogue's legacy from his years as Director of the PCA Fellowship is reflected not only in his technique for calculating phase compositions of cements but also in many experimental studies, often carried out with his participation, of phase relationships in systems relevant to cement and concrete. Representing H_2O, K_2O, and Na_2O by H, K and N, respectively, some of the systems studied were of the anhydrous systems: C-A-S, C-N-A, C-M-C_2S-C_5A_3, C_2S-KCS, N-C-A-S, and C-CA-C_2F; and the hydrous systems studied included: C-S-H, the garnet-hydrogarnet system, C-A-H, C-N-S-H, and hydrogarnet in C-A-S-H. Bogue was clearly one of the more eminent cement chemists of his day, and his scholarly text, *The Chemistry of Portland Cements* [4], remained the single most comprehensive and authoritative source of knowledge of cement chemistry from the time of its first publication at least until the mid-70s.

It was probably a coincidence that, in 1929, the year Bogue's paper was published, the NBS Director responded to a Congressional request to set up a program to ensure that cements used in federal construction projects be of the required quality. This began as an NBS-managed and operated program which, over several years, evolved into a partnership with ASTM as the Cement Reference Laboratory (CRL). The CRL evolved further and enlarged its scope to include concrete, becoming what is now the ASTM-sponsored Cement and Concrete Reference Laboratory (CCRL). In its present form, the CCRL is a research associateship which, through laboratory inspection and proficiency sample programs, provides quality assurance to testing laboratories that use ASTM standards, including ASTM C-150 with its Bogue calculations, in the testing of cement and concrete. An important development made to improve the efficiency of the CCRL proficiency sample program was described in the 1959 paper, "Statistical Aspects of the Cement Testing Program" [5] by the renowned NBS statistician, W. J. Youden. Youden showed how the amount of information obtainable from an interlaboratory test program could be increased substantially by issuing proficiency samples in pairs—a procedure which is widely used both nationally and internationally.

While Bogue's paper gave new insight into the amounts of the major compounds in portland cements, it did not provide any clue as to how the compounds might be distributed within and among individual cement particles. Indeed, in spite of the fact that particle size distribution and fineness are important characteristics which affect the performance of cements, there were no useful ASTM standard methods for their determination until the sedimentation method for determination of particle size distribution was adopted in 1933 and the air permeability method for determination of fineness was adopted in 1943. Both methods are still commonly known by the names of the NBS researchers who developed them, Wagner and Blaine, respectively. Attainment of the capability to determine the distribution of the cement compounds within cement particles was long delayed. It was not until 1997 that another researcher at NIST, Dale Bentz, showed its importance (Fig. 2) in accounting for differences among cements [6]. In Bogue's day, this might have been viewed as an attempt to answer one of those questions that "would have been considered absurd because unanswerable."

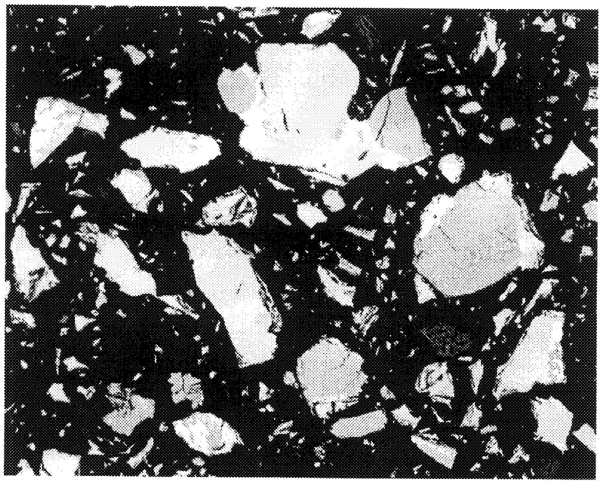

Fig. 2. Modern technology: Backscattered electron image of a polished section of portland cement particles from CCRL Proficiency Sample No.115 embedded in an epoxy resin. The major portland cement clinker phases in the cement particles can be identified, with reasonable confidence, by their grey levels in the image and the habits of the crystals. More definitive information about the distribution of the cement phases within and among the particles can be obtained using x-ray imaging to apply false color based on the elemental compositions of the individual crystals. (Micrograph courtesy of Paul Stutzman).

As mentioned earlier, NBS research into the materials science of cement and concrete fell to a low level between 1960 and 1980. Then in 1981, in response to the national need for research on cement and concrete made apparent by the Nation's failing civil engineering infrastructure, NBS established a cement hydration competence project. The complexity of cement chemistry and of the physical and mechanical changes accompanying the cement hydration reactions suggested that computer simulation should be an important part of the program. In 1986, a paper by Hamlin Jennings and Steven Johnson of NBS, *Simulation of Microstructure*

Development During the Hydration of a Cement Compound [7], received the Best Paper Award from the Cements Division of the American Ceramic Society and was featured on the cover of the magazine Science News. This was the beginning of a program which has made NIST the world leader in the computational materials science of concrete and other cement-based materials. The series of publications has progressed from simulations of the 3-dimensional random porous structures formed in hardening cement pastes to calculations of the diffusivities and elastic moduli of the structures; to the rates of reaction and heat evolution during the hardening of cement pastes taking into account the experimentally-determined phase composition (which is not dependent on Bogue's calculation method) and phase distribution; to the effects on diffusivity of concrete attributable to the aggregates imbedded in the hardened cement paste and the interfacial zones around them; to calculations of the service life of chloride-exposed, steel-reinforced concrete, to the rheological properties of concentrated dispersions of irregularly-shaped particles with predictions of the effects of interparticle forces; to the effects of embedded electrically-conducting fibers on the electrical properties of mortars; to the effect of randomly-distributed thermoplastic fibers on the fire resistance of high-strength concrete; and to the moisture distribution in concrete under a variety of curing conditions and its effect on shrinkage. Together, these developments illustrate the concept of virtual cement and concrete in which the properties of concrete mixtures made from as-yet-unavailable hypothetical materials might be predicted, thereby providing a powerful new tool for product development. As papers on the simulation models are approved for publication, they are added to the web-based *Electronic monograph on the computational materials science of concrete* [8] initiated by Edward Garboczi and Dale Bentz in 1996, more recently joined in the venture by Kenneth Snyder, Nicos Martys, and Chiara Ferraris. The continually-evolving monograph (Fig. 3) is a repository for NIST's contributions to the computational materials science of concrete

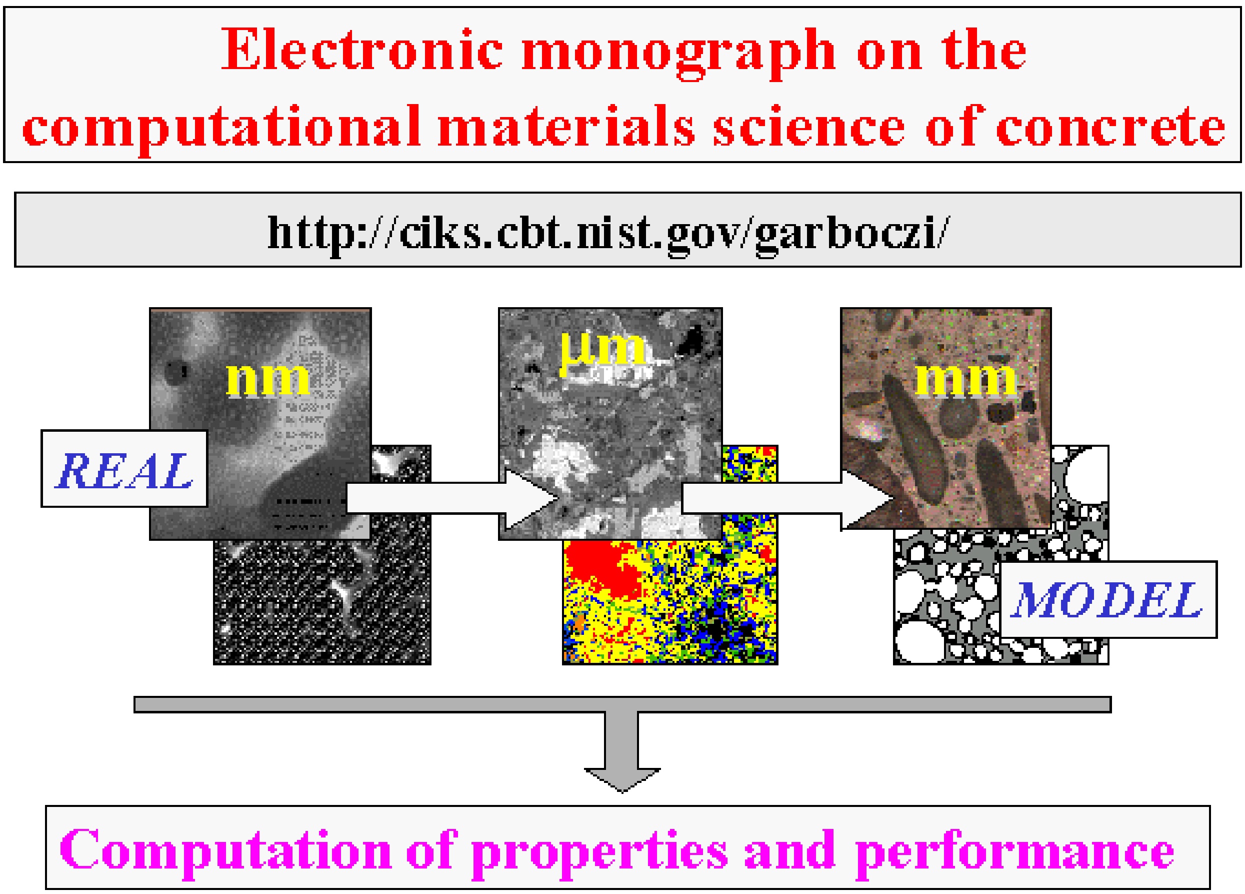

Fig. 3. Announcing the web-based *"Electronic monograph on the computational materials science of concrete"*—equivalent to about 1500 printed pages of NIST models for predicting the structure and properties of cement and concrete, and growing by several hundred pages each year.

through which they are made available to the world. The monograph has now reached the equivalent of 1500 printed pages in length and continues to grow. In a typical month, the monograph's web-site is accessed by more than 1000 persons from about 40 countries.

The advances in computational materials science of concrete have been complemented by advances in techniques for cement characterization, particularly in electron micrographic petrography, and application of quantitative x-ray diffraction analysis. NIST research in both areas has led to new ASTM standards, and both techniques have been applied to characterization of a suite of three portland cement clinkers which have been designated NIST Reference Materials.

From his writings, one feels that Bogue would have appreciated the recent work at NIST because it seems to be in complete philosophical accord with his views and because it has benefitted so much from the program he led from 1924 to 1954. For example, early in the life of the PCA Fellowship, Bogue commented, "Just in what department our investigations will prove to be of greatest value, we do not know, but we are convinced that scientific information on the nature of the compounds of clinker and of the reactions of these compounds, holds promise of application in many directions. Perhaps the eventual direct application may be in manufacture, in raw material, in control, or it may be in the utilization of cement in concrete. . . . This is one of our ambitions; one of the reasons for our existence. The other is to extend the field of usefulness of concrete by the development of a material which will possess to a higher degree the virtuous qualities for which concrete is now well known. Or, perhaps, even go beyond these to the opening up of new possibilities in construction, or art, or industry which are not yet conceived. In the case of many commodities, supply follows the demand, but in the case of the new discoveries of science, a market is born where none existed and the creation of the product opens to reality trails of progress, of achievement, which formerly were lighted only by the Aladdin's Lamp of Imagination." The range of impacts of Bogue's work illustrates the correctness of his vision.

Prepared by Geoffrey Frohnsdorff.

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