

Summary

The Symposium on Blended Cements sponsored by Committee C-1 brought about an exchange of information relevant to improvement of standards for blended hydraulic cements. Awareness of the need for improved standards for blended cements has grown steadily since 1973 as a result of the national need for energy conservation and the growing recognition that blended cements can offer benefits other than reduced costs for the manufacture of cement and concrete.

The nine papers in this volume bring together much information relevant to the development of standards for blended cements and mineral admixtures. It is noteworthy that several of the papers are from European authors whose different perspectives and knowledge should prove valuable to the ASTM committees. The volume begins with papers dealing with slag-containing cements and concretes, then presents a paper concerned exclusively with fly ash-containing cements, followed by papers dealing with more than one type of blending material or mineral admixture. It ends with a paper on the current status of the development of European standards for blended cements. Taking them in order, the papers may be summarized as follows.

The paper by Daube and Bakker reviews standards and applications for portland blast-furnace slag cements from the perspective of the BENELUX countries where slag-containing cements account for about half of all the cement used. Factors such as the composition and structure of the slag and portland cement clinker, which affect the quality of slag containing cements, are discussed with reference to ASTM, BENELUX, and British standards. The terms used for cements with different slag contents in the various standards are compared, and the special performance characteristics of portland blast-furnace slag cements and slag cements are reviewed. It is pointed up that, in the BENELUX countries, there is complete interchangeability between portland and portland blast-furnace slag cements, and the contractor may use any cement which complies with cement standards when there are no special technical requirements to be met. Slag cements offer benefits in applications where resistance to sulfates or sea-water is required, or where there is a need for a cement with a low heat of hydration.

The paper on slag-containing cements by Frigione provides a good entry to the literature on these cements, as well as describing the author's research on cements in which slag is the predominant component. Frigione believes that the use of slag-containing cements will continue to grow. He presents data from a study in

which he sought correlations between slag characteristics and compressive strength of mortar, sulfate resistance, resistance to alkali-aggregate reaction, and heat of hydration. He used ASTM test methods, wherever appropriate ones were available. In the case of sulfate resistance, the test methods used were the proposed ASTM method (now ASTM Method for Length Change of Hydraulic-Cement Mortars Exposed to a Mixed Sodium and Magnesium Sulfate Solution (C 1012-84)), and the method using small cubes exposed to a low-pH sulfate solution which was proposed by Mehta. The results show that resistance to sulfates and to alkali-aggregate reaction will be high if the slag content of the cement is high, irrespective of variations in the glass content of the slag, and the gypsum content and fineness of the blended cement. In general, it appears that slags containing some small amount of crystalline material perform better than fully glassy slags, possibly because of an effect of the crystalline material on the reactivity of the glass fraction or on the nucleation of hydration products.

In a paper presenting findings from three different, but related, projects with a practical orientation, Dubovoy, Gebler, Klieger, and Whiting discuss the effects of ground, granulated blast-furnace slags on properties of cement pastes, mortars, and concretes. They note that, for both mortars and concretes, there is an optimum level of replacement of portland cement by slag for which strength is maximized; this level is usually about 50% replacement. They also found that, at normal temperatures, early age strength development is retarded when slags are used, the extent of the retardation depending on the slag. The durability of air-entrained slag-cement concretes exposed to freezing and thawing in water is essentially the same as that of portland cement concretes, though their resistance to scaling by deicing salts appears to be somewhat less. The tests of Dubovoy et al show that ground, granulated blast-furnace slags can yield satisfactory concretes, whether the slag is used as a mineral admixture or as part of a blended cement, but the differences in performance between slags are sufficiently large that each slag should be characterized individually.

The use of the chemical shrinkage of a paste of portland cement and blast-furnace slag and the difference between its uptakes of water and another liquid, such as kerosene, to provide an easy method for the evaluation of the hydraulicity of the mixture is proposed by Mills. If, as Mills believes, there is reason to expect a functional relationship between strength and chemical shrinkage, then monitoring of chemical shrinkage might provide a new approach to nondestructive evaluation of concrete quality in the field. To illustrate the concept, Mills presents results on mixtures, each made from one of two portland cements and one of four slags. The mixtures were studied either as slurries which were continuously ball-milled in pycnometer bottles for up to three years, or as pastes cast into pycnometer bottles and compacted by vibration under vacuum; companion cubes of pastes, mortars, and concretes were cast for use in measurements of compressive strength. The chemical shrinkages of both types of specimen in pycnometer bottles were determined periodically. The ball-milled specimens were

used to obtain data, such as the density of the hydration products and the mass of nonevaporable water per gram of cement at ultimate hydration, for use in interpreting the data on the cast specimens. Plots of compressive strength against the calculated volume concentration of hydration product were used to calculate the coefficients in an expression, $\sigma = AX^n$, relating strength to X , the volume concentration of hydration product. In other experiments, the volumes of kerosene taken up by water-saturated specimens which had been dried at 110°C were determined and compared with the volumes of water lost during the drying. The volume fraction, m , of evaporable water which resided in space not accessible to kerosene could be then calculated. While Mills found only a poor correlation between m and strength, he found good correlations between the 14-day values of m and drying creep and shrinkage. He concludes that m is a potentially useful parameter for estimating binder quality since, for the same porosity, a higher value of m indicates a higher volume of strongly-bound, relatively-immobile water and a lower permeance. On the other hand, drying creep and shrinkage increase with m because of the greater amount of "live" material. He further concludes that chemical shrinkage is a useful parameter for estimation of the volume concentration of hydration products. However, because the relationship between product concentration and strength is different for each cement, a separate calibration is needed for each cement.

Tenoutasse and Marion discuss the results of their research bearing on the mechanism of hydration of blended cements containing fly ash. From studies of the elements extracted from fly ashes by water, and by hydrochloric and hydrofluoric acids, they conclude that all of the sulfate and most of the potassium reside on the surfaces of ash particles, while almost all of the sodium is in the glassy phase. The effects on the particles of the treatments with water and acids were observed with the scanning electron microscope (SEM). Then, from studies of the pozzolanic reactions of the ashes with lime and with portland cement, they note that the lime etched the ash particles to give a product which, when viewed with the SEM, appears similar to that from the hydrofluoric acid treatment. With portland cement, the effects on the ash particles are also similar, but differences in the extent of attack suggest differences in reactivity between particles. At late ages, the ash particles are attacked sufficiently to leave the mullite crystals which were previously dispersed in the glassy phase. Measurements of the porosities and pore size distributions of hardened pastes of portland cement and fly ash show that replacement of cement by fly ash always increases the total porosity of the hardened paste, the effect being most obvious at early ages. By three months, however, the porosities and pore size distributions of pastes containing at least up to 25% of ash approach those of a cement paste without ash.

The problem of how to evaluate the performance of blast-furnace slags and fly ashes when blended or mixed with portland cement is addressed by Mills. He points up that, whereas reduced cost of the concrete is often the greatest incentive for using blending materials, the practitioner may have other good reasons for

their use. These include improved resistance to sulfate attack and to alkali-aggregate reactions, and reduction of the seasonal variability of the cement. Mills outlines a procedure for designing concrete mixtures containing blending ingredients which will produce concrete of the same strength as the parent portland cement. The starting point is the establishment of appropriate boundary conditions, which may include the necessary target strength taking into account the variability of strength, the maturity to be achieved, the standard deviation of the strengths of concretes made with alternative cements, and the extra moist curing required for slow-hardening cements. In examples in the introduction to his paper, Mills uses 28-day strength as one boundary condition. If, as is usually the case, workability is also to be taken into account, the mixture must meet two interdependent criteria. An example is used to show that the cost of the binder required increases with both workability and strength. Similarly, increases in standard deviation of strength and workability must lead to increased cost as the cement content is increased to reduce the risk of failure. Mills recommends the use of efficiency factors for comparing the cementing qualities of materials used as partial substitutes for portland cement. He defines a "mass-strength efficiency factor" which takes account of strength, workability and characteristic variability, and a "maturity efficiency factor" which characterizes blended cements in terms of their responses to different curing regimes; the latter is defined in terms of the number of degree-hours needed for a concrete to attain the specified strength. Experimental data used to calculate efficiency factors for blast-furnace slags and fly ashes in different concrete mixtures are presented. The efficiency factor varies with the mixture design and is not a single-valued characteristic of a given mineral admixture. The implication is that concrete mixtures should be designed to optimize the appropriate efficiency factors for each application.

The effects attainable by intentional control of the particle size distributions of the ingredients in blended cements is discussed by Helmuth, Whiting, Dubovoy, Tang, and Love. In an earlier study, they had shown that controlled particle size distribution (CPSD) portland cements have energy-saving potential because, by suitable choice of the size distribution, a given level of performance can be obtained at a lower specific surface area and with the expenditure of less energy in grinding. In the case of blended cements, they also show that there are significant benefits to be gained by control of particle size distribution, particularly in increasing early age strength development. Their initial studies were of pastes of 45 blended cements. These cements were made with one cement selected from two CPSD portland cements and a normally ground portland cement, and selections from six different powdered mineral admixtures (two fly ashes, one Class F and one Class C; one ground, granulated slag; one coarser slag; one silica fume; and a ground limestone), two water-reducing admixtures, and one accelerating admixture. Subsequently, based on the large amount of data for the pastes, they selected five of the blended cements for further testing as mortars and concretes. The concrete tests were of mechanical properties (com-

pressive and flexural strength and elastic modulus), drying shrinkage, and sulfate resistance. The final conclusions are that cement pastes, mortars, and concretes made with CPSD blended cements have properties which are approximately equal or superior to those made with normally ground blended cements of the same compositions. The major benefit in the use of CPSD blended cements may be to produce concretes with early age properties comparable to those obtained with portland cements, thereby making them more readily acceptable to users.

Many aspects of the performance of a concrete are intimately linked to the pore structure and permeability of the cement paste matrix. Because the permeability is particularly important in concretes for use in containment of radioactive wastes, Hooton has sought relationships between pore structure and permeability of portland cement pastes containing fly ash, slag, and silica fume as a step towards reducing the need for permeability measurements. His results show that replacement of a sulfate-resistant portland cement with any of fly ash, slag, and silica fume reduces the ultimate permeability to water of a portland cement paste. Silica fume is particularly effective in reducing permeability at early ages. Because the resistance of the blended cement pastes to aggressive environments cannot be explained solely in terms of differences in permeability, it appears that reduction of the calcium hydroxide content of the hardened paste by pozzolanic action is also important. Silica fume is most effective in reducing the calcium hydroxide levels, and slag the least effective. For the cement used, 20% of silica fume is sufficient to eliminate calcium hydroxide completely in 91 days of moist curing. Hooton's preliminary analyses suggest that there is no accurate way of predicting permeability from porosity or pore size parameters determined by mercury intrusion.

The last paper is of special interest from the standards viewpoint. It is a review of the present situation regarding cement standardization in Europe. The author, P. Dutron, is chairman of the European Committee for Standardization of Cements, CEN TC 51. He analyses the contents of cement standards in several European countries and describes the six categories of cements—portland cement and five categories of blended cements (composite cements)—defined in the draft CEN Standard 197-1. Each category of blended cement may contain at least 5% of other blending materials than those indicated in its name. For example, portland pozzolana cement, Category II-Z, must contain 65 to 90% of clinker and 10 to 35% of fly ash or pozzolana; it may also contain up to a combined total of 5% of blast-furnace slag and filler. In general, the principal of specifying 28-day strengths with both upper and lower limits "is taken for granted." Now that the CEN standard has gone beyond the preliminary voting stage, it is to be submitted to ISO Committee TC 74. The paper gives figures showing the large differences in some national productions of cements in the categories proposed in the draft CEN cement standard. The author predicts that, between now and the year 2000, the use of blending ingredients will increase substantially in many regions of the world, including North America. Eventually,

“pure portland cements will come to be regarded as special cements reserved for applications where exceptional performance is required, particularly as far as mechanical strength is concerned.”

Overall, the Symposium gives an interesting and thought-provoking exposure to opinions and research results which should help improve ASTM standards for cements and mineral admixtures.

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