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Concrete Mixture Proportioning with Water-reducing Admixtures to Enhance Durability: A Quantitative Model

Kenneth C. Hover

Cornell University, 302 Hollister Hall, Ithaca, NY 14853, USA

Abstract

Durable concrete is characterized as concrete with a low porosity, in which the individual grains of cement are tightly packed before initiation of hydration. Such concrete is typically characterized by a low water/cement ratio, which is described herein on a volumetric, rather than a mass basis. Low water/cement ratio is responsible for improved mechanical properties and for enhanced durability. It is shown, however, that use of a low water/cement ratio necessitates either a sacrifice in workability, or the use of high cement content, neither a desirable consequence. The use of water-reducing admixtures is discussed as an alternative. The use of normal-, mid-, and high-range water-reducing admixtures is described in the context of a series of graphs based on the water demand relationships implicit in the ACI 211.1 procedure for proportioning mixtures. By introducing the concept of water-reducer 'effectiveness', these graphs can be used to describe the differences among normal, mid-range, and high-range water reducers, and can be used to illustrate the use of water reducers to reduce water content, reduce water/cement ratio, and to increase workability. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Keywords: water-cement ratio, durability, mixture proportioning, water-reducers, superplasticizers, microstructure, admixtures.

INTRODUCTION

This paper focuses on the use of normal-, mid-, and high-range water-reducing admixtures for the purpose of increasing the durability of concrete, primarily by means of decreasing permeability and improving mechanical properties. Such improvements not only slow the rate of ingress of water, oxygen, carbon dioxide, and dissolved solids, but also provide increased resistance to stresses generated by external or internal loads. External loads include typical service loads, impact, or abrasion, while internal loads include internal expansion of freezing water, alkali-silica gel, swelling aggregates, Ettringite crystals, or thermal stresses. At the heart of this paper is the principle that all such benefits are derived from a densified microstructure of the hardened cement paste. This densification can be theoretically achieved from judicial use of water and cement alone, but pragmatically, can only be realized in other than laboratory conditions through the use of chemical admixtures, or mineral admixtures, or both.

When concrete is exposed to freezing temperatures while in a near saturated condition, air entraining admixtures can be added to the concrete to provide necessary frost resistance, another aspect of 'durability'. Air entrained concrete is a separate topic within concrete material technology (and discussed in detail elsewhere[1–4]), and is not addressed in this paper.

BACKGROUND: PASTE MICROSTRUCTURE

The fundamental porosity of portland cement concrete influences all of its material properties. Pores exist within the coarse and fine aggregates themselves, at the paste/aggregate interface and within the paste. Voids in the paste range from capillary pores of 10 nm to 1 μm in approximate diameter[5,6] to gel pores of only 1–10 nm in equivalent diameter. Aggregate pores are minimized by appropriate aggregate selection, as little can be done to alter aggregate porosity. Cohen[7] showed how mineral admixtures can dramatically reduce paste/aggregate interface porosity. Our primary subject in this paper, however, is the paste porosity itself, as indicated in Fig. 1.[8]

The 'fuzzy' ball-shaped objects are hydrating grains of cement, with hydration products forming on the grain surfaces. Cement grains connected to their neighbors via hydration products provide the microstructural framework in the hardened paste for the transfer of loads. The large volume of interstitial void space evident in the figure is striking, however, and it is through these voids that deleterious gases, liquids, and dissolved solids move through the paste. It is also evident that an improvement in the mechanical behavior of the paste, as well as an improvement in durability could be achieved by finding ways to move the cement grains closer to one another, enhancing their mutual bond, and reducing the interstitial void space. It is also evident that it would not be necessary to eliminate the void space altogether to improve durability; it would be necessary only to block the connectivity of the pores so that gases and liquids could no longer permeate the paste.

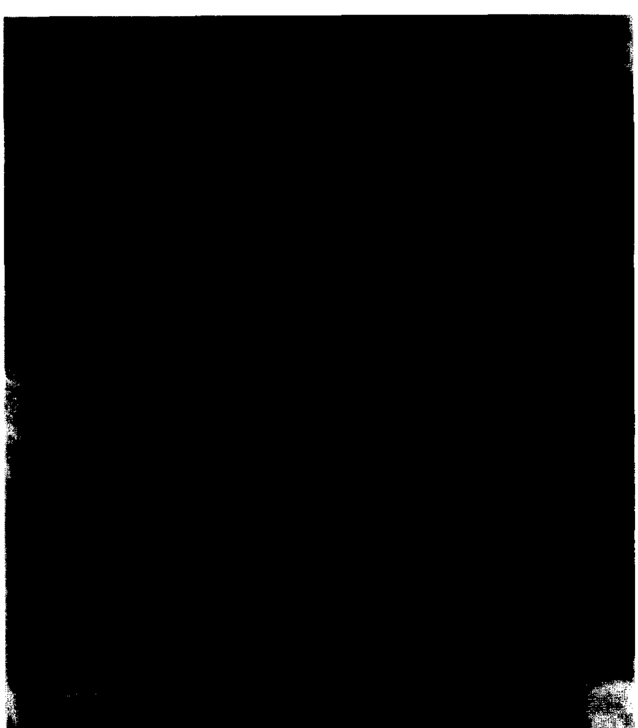

Fig. 1. Scanning electron microscope image of hardened cement paste at age 7 days.

For these reasons, most of our standard practices for concrete construction have as their objective the minimization of paste porosity, which consequently increases both strength and durability. Low water/cement ratio, control of water addition, consolidation of fresh concrete, and curing so as to maintain appropriately warm and moist conditions for development of the hydration products all reduce porosity and decrease the average proximity of cement grains. Curing is essential because grain-to-grain bonds are established as hydration products extend from grain surfaces, and such development is temperature- and moisture-dependent. Consolidation attempts to remove additional void space contributed by air trapped in the concrete as a result of placing. Control of water addition seeks to minimize the void space occupied by mix water, as does control of water/cement ratio as discussed in the next section.

CONTROL OF WATER/CEMENT RATIO: ESSENTIAL WITH OR WITHOUT ADMIXTURES

When the relationship between the total mix water and the total amount of cement is expressed as a volume ratio rather than the more common weight or mass basis for water/cement ratio, the importance of the relationship becomes clear, as shown in Fig. 2.

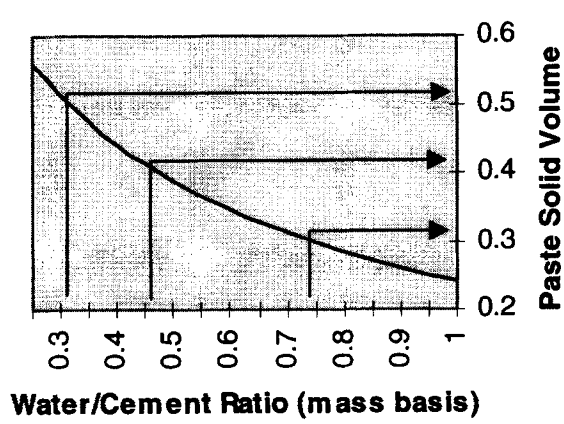

Fig. 2. Solid volume fraction of cement paste as a function of water/cement ratio. Water/cement ratios of about 0·33, 0·48 and 0·75 correspond to paste solid volumes of 50%, 40% and 30%, respectively.

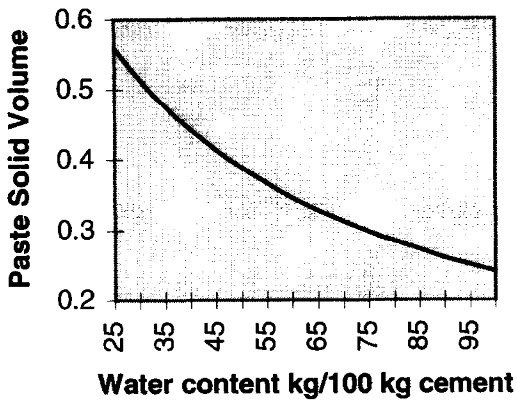

Fig. 3. Solid volume fraction of cement paste as a function of water content per 100 kg of cement.

As seen in Fig. 2, lowering the water/cement ratio increases the solid volume of the paste, reducing pore space and decreasing the proximity of cement grains. This has been examined graphically elsewhere.[9] These same data can be plotted as a function of water content as in Fig. 3.

Using a cubic lattice arrangement of cement grains in paste (as developed by Powers for the spatial distribution of air voids in paste),[10] the average space between adjacent cement grains can be estimated as a function of the water/cement ratio, as shown in Fig. 4.

Figure 5 shows the impact of water/cement ratio on both compressive strength and permeability, based on data from ACI 211.1[11] and Powers *et al.*[12]

On the basis of any of these arguments, one can justify the quality-control emphasis (if not preoccupation) on control of water content, and

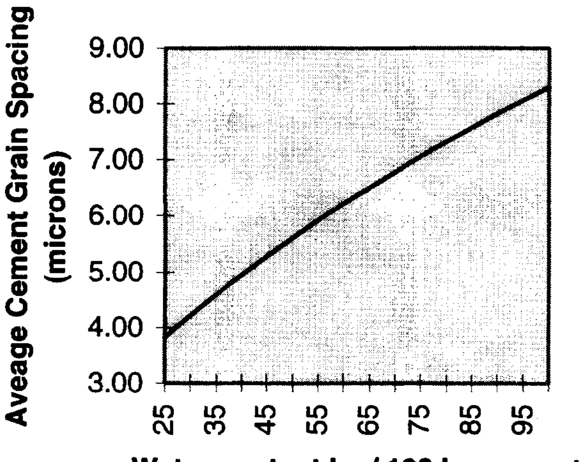

Fig. 4. Average clear spacing between cement grains as a function of water content per 100 kg cement, assuming a cubic lattice arrangement of cement grains in the paste.

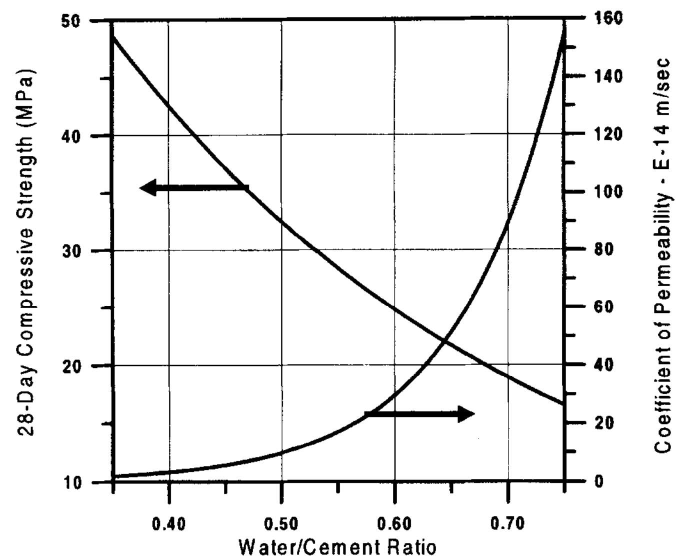

Fig. 5. Impact of water/cement ratio on compressive strength and permeability.

the use of mixtures with low water/cement ratios for the development of both strength and durability. Were this practically and economically achievable in the field, admixtures would not be the virtual necessity they have become for high strength or high durability concrete.

COMPLICATIONS IN ACHIEVING LOW WATER/CEMENT RATIO MIXTURES

A low water/cement ratio can be achieved in two obvious ways: establish the desirable water content commensurate with required workability and then increase cement content accordingly; or, select a desirable cement content and decrease the water content accordingly. Both are problematic, and both are related to the fundamental issue of workability.

First of all, it is essential that the fresh concrete has sufficient workability to enable mixing, transport, placing, consolidation, and finishing. To ignore workability as only a construction problem is to ignore one of the strongest driving forces in the concrete industry. Concrete with inadequate workability will either suffer due to lack of consolidation or poor finish, or its workability will be modified by the addition of water in the field. The gentlemen shown in Fig. 6 are not indifferent to the workability of the concrete—indeed the outcome of their day's work, and how they feel at the end, are dependent on it!

Secondly, water/cement ratio and slump are independent characteristics of a concrete mixture. It is possible to create a mixture with a w/c of 0·40 and a slump of 150 mm, or a mixture with a w/c of 0·60 and a slump of 25 mm. The reality is that workability (slump) is influenced by a host of factors, but is influenced predominantly by water content, whereas w/c is a function of both the water and cement contents.

An estimate of the water content required for a given slump (known as 'water demand') is shown in Fig. 7, based on data presented by ACI committee 211 on mixture proportioning.[11,13,14] As the nominal size of the coarse aggregate decreases, the water demand for any given slump increases (due to increasing cumulative aggregate surface area). In preparing a non-air-entrained mixture design that will achieve a 100 mm slump, for example, the water demand increases from about 180 to about 232 kg/m^3 as aggregate size drops from about 40 to about 10 mm, independent of water/cement ratio (according to ACI 211.1)[11]. For any given aggregate size, choice of design slump fixes the required water content, which in turn fixes the cement content for any given water/cement ratio. An example of these interrelations is shown in Table 1 for the particular case of a mixture incorporating 20 mm coarse aggregate.

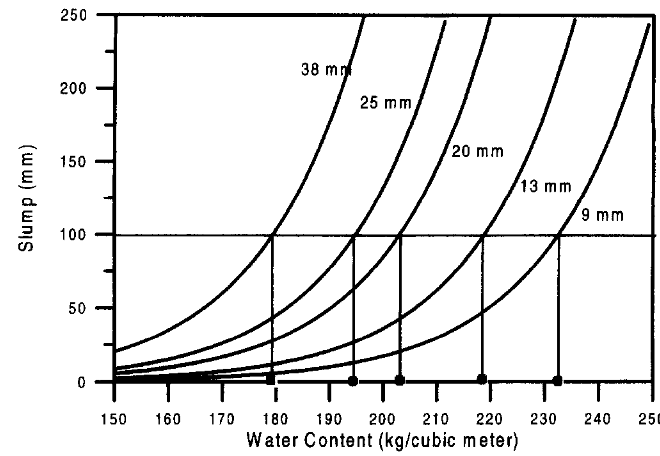

Fig. 7. Estimated slump as a function of water content for various sizes of coarse aggregate.[11,13,14]

Fig. 6. Typical concrete placing operation.

As a consequence, the independent selection of a 100 mm slump and a w/c of 0·40 forces a cement content of 508 kg/m^3 (855 lb./CY or a '9 sack' mix in North American terms). Theoretically, then, high slump and low water/cement ratio are not mutually exclusive. They are mutually achievable through an extraordinarily high cement content, which is not only expensive, but will produce high heat of hydration, and may contribute to increased creep and shrinkage by virtue of a high paste volume and a low aggregate volume.[15]

An alternative is to pre-select a more reasonable cement content, say 400 kg/m^3, and use a

Table 1. Cement content (kg/m^3) for various water/cement ratios for mixtures incorporating 20 mm coarse aggregate

Slump (mm)	*Water demand (kg/m^3)*	*w/c = 0·35*	*w/c = 0·40*	*w/c = 0·45*	*w/c = 0·50*	*w/c = 0·55*
25	177	506	443	393	354	322
50	190	543	475	422	380	345
75	198	566	495	440	396	360
100	203	580	508	451	406	369
150	211	603	528	469	422	384

water content of 160 kg/m^3 to obtain the desired w/c of 0·40. According to Fig. 7, a water content of 160 kg/m^3 will yield a slump of about 10 mm. While this is theoretically reasonable, the gentlemen in Fig. 6 are not interested in theory, and it is doubtful that the concrete would be placed at this low water content. Water-reducing admixtures can be employed to realize the concrete performance associated with the w/c of 0·40, and provide practical alternatives to the disadvantages of excessively high cement contents or excessively low water contents.

WATER REDUCING ADMIXTURES

As their generic name implies, these admixtures reduce the amount of water required to achieve a given degree of workability. A water reducer with a 10% 'effectiveness' would enable a 10% reduction in water content with no loss in slump. Thus, in the example from the previous section, the water demand of 203 kg/m^3 would become 183 kg/m^3 in the presence of a 10% water reducer. The approximate ranges of effectiveness of the water reducing admixtures currently available are shown in Table 2.

Water reducing admixtures achieve these levels of effectiveness primarily through de-flocculation of cement grains via modification of electrical charges on the cement surfaces.[5,16–18] The effectiveness will depend on the dosage used, temperature, cement chemistry, fineness, and other mixture characteristics. While water-reducer effectiveness is difficult to predict reliably, it can be determined readily from a few trial batches. Normal (or 'normal range') water reducers have been available for over 30 years, while the high range or 'superplasticizers' have been popular for about the last 20 years or so. The newest product is the mid-range water-reducer, occupying a vital position in the spectrum of water-reduction capability.

Figure 8 is a modified version of Fig. 7, in which the water demand for 20 mm coarse aggregate is shown as a function of water-reducing admixture effectiveness.

Continuing from the previous example of a mixture with a 20 mm nominal coarse aggregate size, Table 3 shows revised water demand and cement content for various levels of water-reducer effectiveness.

From the table values it is seen that the cement content for w/c = 0·40 approaches 405 kg/m^3 as the admixture effectiveness

Table 2. Water reducing admixtures

Approximate ranges of water reduction effectiveness	*Nomenclature*
5–7%	Normal water reducer
7–15%	Mid-range water reducer
15–30%	High-range water reducer or superplasticizer

Note: effectiveness varies with a large number of factors, especially admixture dosage.

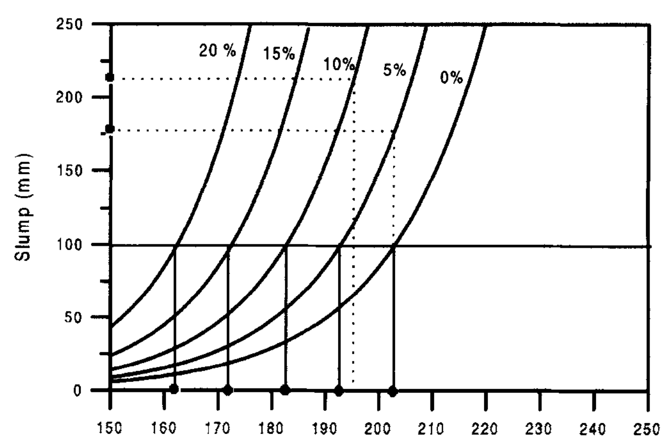

Fig. 8. Relationship between water content and slump for a mixture incorporating 20 mm coarse aggregate with various levels of water-reducing admixture effectiveness.

Table 3. Cement content (kg/m^3) as a function of WRA effectiveness for a mixture incorporating 20 mm coarse aggregate, and a slump of 100 mm

WRA effectiveness	*Water demand (kg/m^3)*	*Water/cement ratio*				
		0·35	*0·40*	*0·45*	*0·50*	*0·55*
0%	203	580	508	451	406	369
5%	193	551	483	429	386	351
10%	183	523	458	407	366	333
15%	172	491	430	382	344	313
20%	97	463	405	360	324	295

approaches 20%. Achieving such effectiveness would require a superplasticizer. Using a mid-range water reducer (15% effectiveness) the cement content can get down to 430 kg/m^3 or thereabouts, for a water content of about 172 kg/m^3.

Returning to Fig. 8, the dashed lines show another way to take advantage of water-reduction technology. Using a combination of the original 203 kg/m^3 water with a normal-range water reducer (5% effectiveness) produces a mixture with a slump of about 175 mm. For an even more workable concrete, sometimes called 'flowing concrete', a combination of about 195 kg/m^3 and a 10% water reducer can be used. Achieving a 10% water reduction can be accomplished with high doses of a normal range water reducer, or with more moderate doses of a mid-range product.

This latter example demonstrated that workability (slump) can be increased through use of water reducers, while holding water and cement content constant (and thus maintaining water cement ratio constant). The first example showed that slump can be maintained while reducing both water and cement contents (at constant w/c). Still another variation on this theme is to reduce water by means of a WRA, but to keep the cement content constant. Returning to the first example, a mixture is contemplated with 203 kg of water and 508 kg of cement per cubic meter (w/c = 0·40). Assume that a lower w/c of 0·35 were required to increase both strength and durability. A reduction in water (to $0{\cdot}35 \times 508 = 178$ kg/m^3) would reduce the slump to about 25 mm. An increase in cement content (to $203/0{\cdot}35 = 580$ kg/m^3) would make an already 'rich' mix even richer and more objectionable on the basis of cost, shrinkage, creep, and heat generation. However, a combination of 178 kg/m^3 water and about a 12% effective water-reducer would maintain the 100 mm slump at a cement content of 508 kg/m^3, for a w/c of 0·35.

DISCUSSION

Application of the principles discussed requires knowledge of the effectiveness of the admixtures. As pointed out, this depends on a large number of factors such as the chemical composition of the admixture itself, dosage, mixture ingredients and proportions, time, and concrete temperature. The effectiveness must be determined, therefore, from trial batches combined with field experience. This can be done practically and effectively, however, as has been done by the author on several major concrete projects including the Interstate-90 Floating Bridge project in Seattle, Washington in 1992. Careful mixture proportioning had been done in advance by LaFraugh,[19] and then modified on the basis of slump measurements on-site after the controlled addition of various dosages of water reducer. After several such measurements it became possible to predict the dosage required to achieve the desired workability and mixture proportions. Similarly, mix design for concrete floors at the veterinary hospital at Cornell University (Ithaca, NY) was adjusted on the basis of slump measurements after careful addition of water-reducer. From such data it was determined that a mid-range water-reducer produced the desired result of sufficient workability and a minimized cement content.

Secondly, one can theoretically extend the water-reduction philosophy to extraordinarily low total water contents combined with high doses of powerful water reducers. This is undesirable for several reasons. First, cost of the admixture increases with dosage. Second, many water-reducing admixtures have a tendency to retard set, and more so at higher doses. Third, workable mixes obtained with high doses of admixture and low water contents tend to be sticky, hard to finish, and have a 'jelly-like' consistency. It is often useful, therefore, to make sure that the water content of the mixture is at least that which would have produced a slump of 25–35 mm in the absence of the WRA. Further, there have been reports that water-reducer addition can in some cases lead to an inconsistent setting time. All of these problems are minimized by using the lowest dosage of WRA that provides the desired effectiveness. This is why a mid-range water-reducer is preferred to a high dose of a normal range WRA for the same water reduction effectiveness. Similarly, a high-range water reducer at a low dose is preferred to a mid-range at a high dose.

SUMMARY

The use of water reducing admixtures enables the benefits of low water/cement ratio to be realized under practical field conditions. Water reducing admixtures can be used to decrease water content with or without a proportional reduction in cement content, or these admixtures can be used to increase workability with no change in water or cement content. These outcomes can be visualized graphically by introducing the concept of water-reduction effectiveness, which is in turn influenced by several factors. Effectiveness can be determined in the field. When water content is reduced and water/cement ratio is held constant, the WRA might correctly be called a water reducer, a cement reducer, or a paste reducer. Reductions in paste diminish shrinkage, and reductions in cement content reduce heat and cost.

When water content is reduced with no reduction in cement content, the water/cement ratio of the paste is lowered, resulting in an increased quality concrete without additional cement, and with a net reduction in paste volume. Under this circumstance a WRA may be called a 'water/cement ratio reducer'.

When neither water nor cement contents are altered in the presence of a WRA, the workability is increased. Although high slump or 'flowing' concrete can be produced, it is always necessary to make sure that the mix does not segregate in placement.

REFERENCES

1. Roberts, L., Air content, temperature, unit weight, and yield. In *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, Ch. 8, eds. Kleiger & Lamond, ASTM STP 169C, Philadelphia, 1994, pp. 65–71.
2. Newlon, H. & Mitchell, T., Freezing and thawing. In *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, Ch. 16, eds. Kleiger & Lamond, ASTM STP 169C, Philadelphia, 1994, pp. 153–163.
3. Kleiger, P., Air entraining admixtures. In *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, Ch. 44, eds. Kleiger & Lamond, ASTM STP 169C, Philadelphia, 1994, pp. 484–490.
4. Hover, K. C., Air content and unit weight of hardened concrete. In *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, Ch. 28, eds. Kleiger & Lamond, ASTM STP 169C, Philadelphia, 1994, pp. 296–314.
5. Mehta, P. K. & Monteiro, P. J. M., *Concrete: Structure, Properties, and Materials*, 2nd ed. Prentice Hall, Englewood Cliffs, NJ, 1993, p. 27.
6. Cook, R. A., A generalized form of the Powers model of cement hydration, Ph.D. Dissertation, Cornell University, Ithaca, 1992, pp. 7–10.
7. Cohen, M. D., Goldman, A. & Chen, W. F., The role of silica fume in mortar, transition zone vs. bulk-paste modification. *Cement and Concrete Research*, **24**(1) (1994) 95–98.
8. Soroos, E., Hover, K. C., Report of Scanning Electron Microscopy, Cornell University, Ithaca, May, 1994.
9. Hover, K. C., A graphic approach to concrete mix design per ACI 211.1. *Concrete International*, September (1995) 49–54.
10. Powers, T. C., Void spacing as a basis for producing air entrained concrete. *Journal of the American Concrete Institute*, **50** (1954) 741–759.
11. American Concrete Institute Committee 211, *Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete (ACI 211.1-9 1)*, American Concrete Institute, Detroit, 1991, 38 pp.
12. Powers, T. C., Copeland, L. E., Hayes, J. C. & Mann, H. M., Permeability of Portland cement paste. *Journal of the American Concrete Institute*, **51** (1954) 285–298.
13. Hover, K. C., Computer-aided concrete mix design. In *Proceedings of the Second International Conference on Civil and Structural Engineering and Computing*, Vol. 1, ed. B. V. H. Topping, Institution of Civil Engineers, London, December 1985, Civil-Comp Press, Edinburgh, pp. 386–391.
14. Hover, K. C. & Stokes, T., Making cents out of water/cement ratio. *Concrete International*, May (1995) 52–54.
15. Hansen, W., Constitutive model for predicting ultimate drying shrinkage of concrete. *Journal of the American Ceramic Society*, **70**(5) (1987) 34–39.
16. Mindess, S. & Young, J. F., *Concrete*. Prentice Hall, Englewood Cliffs, NJ, 1981, 671 pp.
17. Rixom, M. R. & Mailvaganam, N. P., *Chemical Admixtures for Concrete*, 2nd ed., E. & F.N. Spon, London, 1986, 306 pp.
18. Dodson, V. H, *Concrete Admixtures*, Van Nostrand Reinhold, New York, 1990, 211 pp.
19. LaFraugh, R. W., Concrete Mix Design Development, 1-90 Pontoon Replacement, Wiss, Janney, Elstner Associates, Seattle, December, 1991, 69 pp.