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Determination of Silica-Fume Content in Hardened Concrete by AC Impedance Spectroscopy

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ABSTRACT: A nondestructive method based on AC impedance spectroscopy was applied to studies of the electrical behavior of hydrated portland cement concrete containing silica fume. Silica fume content significantly influenced the impedance behavior of hydrated portland cement concrete. Correlations between the high frequency arc (HFA) diameter and the silica-fume content in concrete were obtained. Empirical relationships for concrete binders at early and more advanced hydration can be expressed as

$$D_{HFA} = K_o\beta_{sf} + C \text{ for early hydration times} \quad (1)$$

and

$$D_{HFA} = C'(Ko')\beta_{sf} \text{ for advanced hydration times} \quad (2)$$

where D_{HFA} is the high frequency arc diameter, β_{sf} is the silica-fume content, K_o, K_o', C, and C' are constants related to hydration times and *W-C* ratio, and so forth.

KEYWORDS: concrete, portland cement, silica fume, AC impedance spectroscopy

The quality of concrete materials is important as it affects the service life of concrete structures. Cement and aggregate content and *W-C* ratio of the original concrete mixture are important factors affecting quality. ASTM standards C 457, C 856, C 823, C 295, C 1078, and C 1084[3] all provide guidance for the determination of cement content and *W-C* ratio. Sampling and analytical methods to be used to determine the cement content, aggregate content, aggregate grading, *W-C* ratio, type of cement and aggregate, chloride, sulphate and alkali contents are described in a recent revision of a 1988 British Standard.[4] The determination is more difficult in concretes containing various chemical and mineral admixtures such as fly ash, silica fume, and slag.

In previous work, it was demonstrated that AC impedance spectroscopy is a useful tool for investigating changes of both microstructure and ionic concentration of pore solution in a hydrating cement paste system (Gu et al. 1992, 1993a, 1993b). The impedance behavior of hydrating cement-silica fume mixtures was significantly different from that of pure cement paste. An early appearance of a high frequency arc and rapid growth of HFA diameter with hydration time occurs in pastes containing silica fume. This behavior is due to the combined effect of accelerating hydration reactions through consumption of calcium hydroxide and microstructural changes in the matrix. In this paper, an AC impedance method to determine silica-fume content in hardened concrete is described.

Concepts and Principles of AC Impedance Spectroscopy in Cement and Concrete Systems

Impedance spectra are recorded over a wide range of frequencies (from MHz to Hz). They provide information on the evaluation of cement paste and concrete microstructure and hydration. A typical impedance spectrum for a cement system (two- or three-point measurement) is plotted in the real versus imaginary plane in Fig. 1*a*. A single arc in the high frequency range and a small part of a second arc in a relatively low frequency region is illustrated. The HFA is attributed to the bulk paste impedance behavior, and the second arc is due to the cement-electrode surface capacitance contribution. The intercepts R_1 (at the high frequency end, in the range 10 to 32 MHz) and $R_1 + R_2$ (at the minimum between the electrode arc and bulk arc, at frequency circa 100 KHz) are important parameters providing information related to the cement paste and concrete microstructure profile. The HFA diameter is determined from equivalent circuit modeling (Fig. 1*b*). Ideally, the value of R_2 should be equivalent to D_{HFA} if the HFA is a perfect semicircle. An ideal response however is rarely observed. Most materials exhibit an inclined semicircle with the center depressed below the real axis by an angle θ, (Fig. 1*c*). The value of D_{HFA} is then equal to $R_2/\cos(\theta)$.

From previous investigations (Xie et al. 1993; Gu et al. 1993c; Xu et al. 1993) it is noted that: (1) the high frequency resistance R_1 is an inverse function of both porosity and ionic concentration

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[3]C 457—Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete.
C 856—Practice for Petrographic Examination of Hardened Concrete.
C 823—Practice for Examination and Sampling of Hardened Concrete in Constructions.
C 295—Guide for Petrographic Examination of Aggregates for Concrete.
C 1078—Test Methods for Determining Cement Content of Freshly Mixed Concrete.
C 1084—Test Method for Portland-Cement Content of Hardened Hydraulic-Cement Concrete.

[4]Methods for Analysis of Hardened Concrete, BS 1881, Part 124, *Testing Concrete,* British Standards Institute, London, 1988.

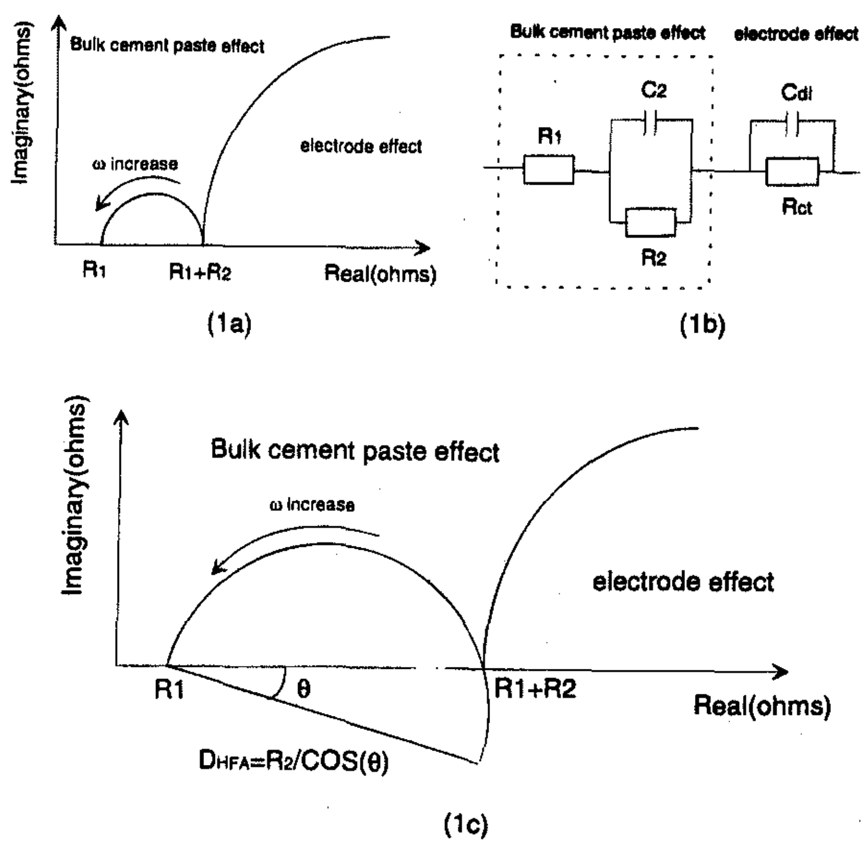

FIG. 1—(a) *Schematic plot of a high-frequency arc in the impedance complex plane obtained for cement paste or concrete systems;* (b) *the corresponding electrical equivalent circuit; and* (c) *an inclined semicircle whose center is depressed below the real axis by an angle* θ.

in the pore solution; (2) the high frequency arc diameter D_{HFA} or R_2 is an inverse function of porosity, mean pore size and ionic concentration of the pore solution. An increase of R_2 or D_{HFA} value is due to the change of porosity and mean pore size as the hydration time increases if the concentration term remains unchanged; (3) both R_1 and R_2 or D_{HFA} are affected by ionic additives. Increase of additive concentration leads to lower R_1 and R_2 or D_{HFA} values. R_2 or D_{HFA} is more sensitive to the microstructure and concentration changes and is relatively easy to obtain experimentally. In this paper, it will be used as a descriptor to characterize the silica-fume content in concrete.

Experimental

Materials

Type 10 portland cement was used. The chemical composition (wt%) is as follows: 19.83% SiO_2, 61.21% CaO, 3.20% Fe_2O_3, 4.18% Al_2O_3, 4.09% MgO, 3.93% SO_3, 0.45% Na_2O, and 0.82% K_2O. Silica fume was supplied by the SKW Company, Montreal Quebec. Its composition is as follows: 95.17% SiO_2, 0.23% CaO, 0.13% Fe_2O_3, 0.21% Al_2O_3, 0.15% MgO, 0.12% SO_3, 0.10% Na_2O, and 0.27% K_2O.

Specimen Preparation

Twenty different concretes were prepared. Four different cement:sand:aggregate weight ratios (1:1:1, 1:1.5:1.5, 1:2:2, and 1:2.5:2.5) and five different silica-fume contents (0, 5, 10, 15, and 20% cement replacement) were made. Fresh concrete mixtures were mixed in a conventional mixer at a *W-C* ratio—0.50 and cast in cylindrical molds 76 cm diameter by 75 cm. The samples were cured in a 100% relative humidity environment for 24 h and subsequently immersed in saturated lime solution.

Instrumentation and Data Extraction

A 1260 Impedance Gain-Phase Analyzer from Schlumberger Technologies was used for impedance measurements. A two-point measurement set-up was applied by connecting the I_H (high current lead) with V_H (high voltage lead) and I_L (low current lead) with V_L (low voltage lead). However, to eliminate the electrode effects a four-point measurement set-up is recommended (Method for Field Measurement of Soil Resistivity Using the Wenner Four-Electrode Method, ASTM G 57). Data was collected using a frequency scan from 20 MHz to 1 Hz with 10 readings per decade. D_{HFA} is extracted by fitting the experimental data with the equivalent circuit (Fig. 1*b*) until the best fit is obtained.

Results and Discussion

High Frequency Arc Diameter-Hydration Time

Figures 2*a* through 2*d* are plots of HFA diameter D_{HFA} versus hydration time for plain concrete and concrete containing silica fume at the early hydration ages. The inserted figures are those for more advanced hydration times ranging from 71 to 81 days. The cement-sand-aggregate ratios are indicated in the Figs. 2 through 5. Silica fume changes the impedance behavior of the hydrating concrete significantly.

At the early hydration times, the HFA diameter D_{HFA} increases with time. This is the result of the hydration process in which

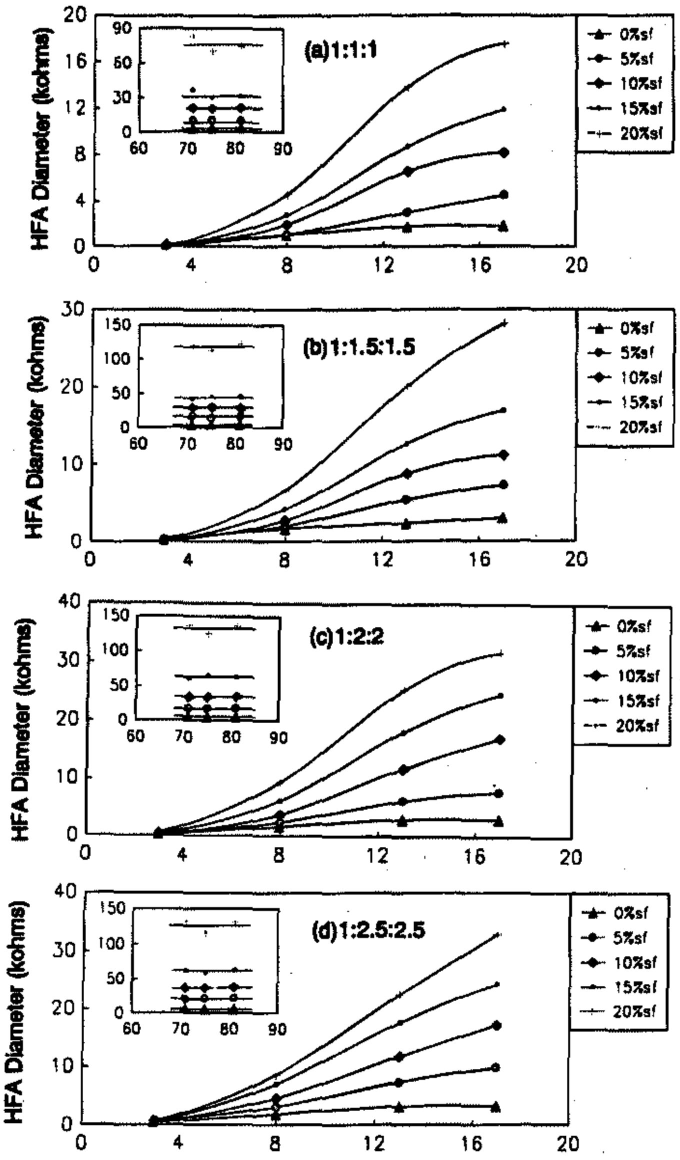

FIG. 2—*Plots of HFA diameter versus hydration time for plain concrete and concrete containing silica fume at early hydration. The inserted figures correspond to more advanced hydration times. The cement-sand-aggregate ratios are indicated in Figs.* (a) *through* (d). (a) *1:1:1,* (b) *1:1.5:1.5,* (c) *1:2:2, and* (d) *1:2.5:2.5.*

consumption of free water and reduction of capillary porosity are taking place. However, the rate of hydration decreases significantly as about 85% of the cement is hydrated after 28 days. The HFA diameter appears to reach a relatively constant value at advanced hydration times as indicated in Fig. 2. High silica-fume contents result in a large increase of the HFA diameter. This indicates formation of a denser matrix. Rapid hydration, better particle packing, and lower calcium ion concentration in the pore solution are factors attributed to the increase of HFA diameter.

Concretes made with high cement-sand-aggregate ratio have large HFA diameters when other conditions remain the same. The difference due to the aggregate volume fraction is small compared to that of silica fume.

High Frequency Arc Diameter-Silica Fume Content

Examination of the relation between HFA diameter and silica fume content was carried out at two different hydration periods.

Early Hydration Times—Figures 3*a* through 3*d* are plots of HFA diameter (kΩ) versus percentage of silica fume at various hydration times from 3 to 17 days, respectively. There is no clear relation between HFA diameter and silica fume content at 3 days. Linear relationships are obtained at 8, 13, and 17 days. The empirical relationships for concrete binders at early hydration times can be generally expressed as

$$D_{HFA} = K_o\beta_{sf} + C \tag{3}$$

where D_{HFA} is the HFA diameter, β_{sf} is the silica fume content in percentage, K_o, and C are constants related to hydration rate and *W-C* ratio, and so forth. The correlation coefficients are in the range 0.94 to 1.0. It is also noted that the constants K_o and C change with hydration time. A list of the regression constants K_o and C is given in Table 1 for comparison.

The values of constants K_o and C increase as the hydration time increases. This suggests that determination of the silica-fume content in young concrete would be more difficult as both cement: aggregate ratio and the hydration time have to be known.

Advanced Hydration Times—At advanced hydration times, the HFA diameter reaches a relatively constant value as indicated in Fig. 2. The HFA diameter is then affected mainly by the silica-fume content. The effect of hydration time becomes insignificant (assuming the ionic concentration of the pore solution is relatively constant). The plots of HFA diameter (kΩ) versus silica-fume content at advanced hydration times (71 to 81 days) are given in Figs. 4*a* through 4*c*, respectively. An exponential relation is obtained. The correlation coefficients range from 0.97 to 0.99. The empirical equation has the general form

$$D_{HFA} = C'(K'_o)\beta_{sf} \tag{4}$$

or

$$\log D_{HFA} = \log C' + \log(K'_o)\beta_{sf} \tag{5}$$

A straight line is obtained in a plot of log D_{HFA} versus β_{sf} (Fig. 5). The regression constants K'_o and C' are listed in Table 2.

TABLE 1—*Regression constants* K_o *and* C *in Eq 3 for various hydration times.*

	K_o				C			
Days	1:1:1[a]	1:1.5:1.5	1:2:2	1:2.5:2.5	1:1:1	1:1.5:1.5	1:2:2	1:2.5:2.5
8	0.177	0.245	0.381	0.346	0.543	1.07	0.914	1.59
13	0.598	0.855	1.13	0.981	0.813	1.36	1.59	2.67
17	0.776	1.20	1.49	1.47	1.01	1.34	1.71	2.75

[a]Cement-sand-aggregate ratio.

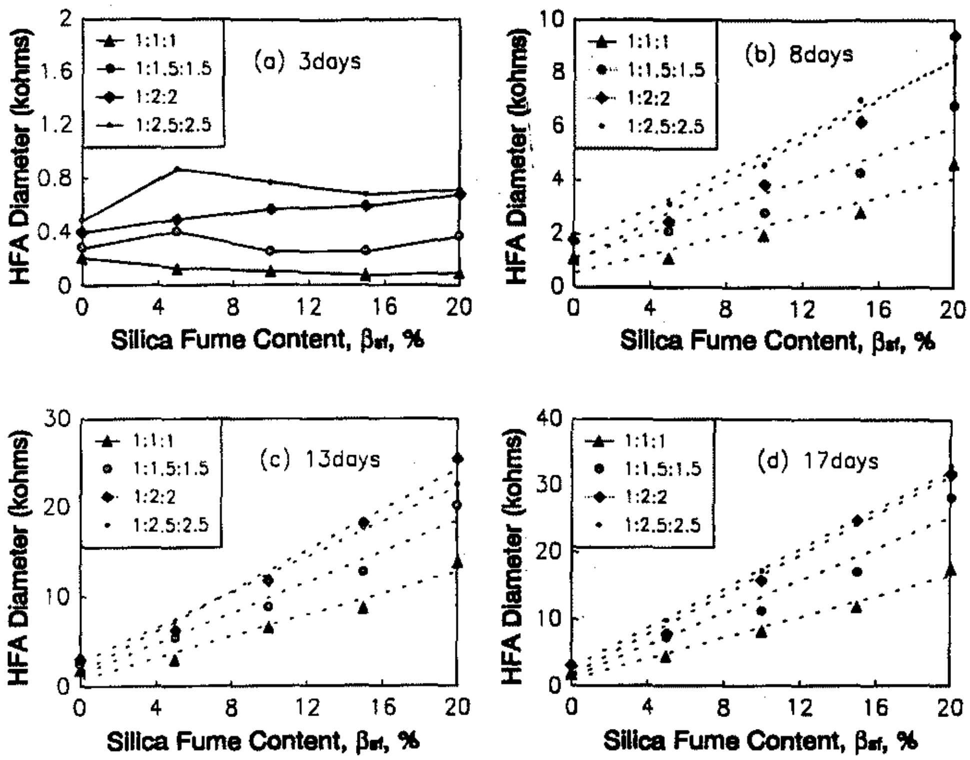

FIG. 3—*Plots of HFA diameter (kΩ) versus silica-fume content at early hydration times.* (a) *3,* (b) *8,* (c) *13, and* (d) *17 days.*

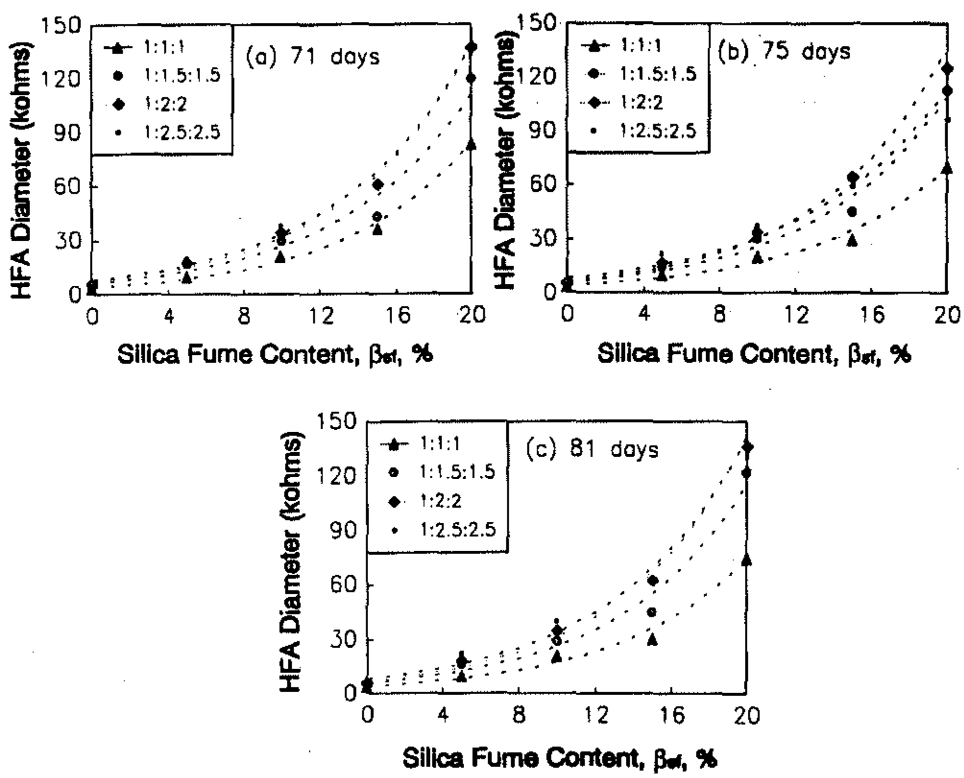

FIG. 4—*Plots of HFA diameter (kΩ) versus silica-fume content at advanced hydration times.* (a) *71,* (b) *75, and* (c) *81 days.*

TABLE 2—*Regression constants* K'_o *and* C' *of Eq 4 for various hydration times.*

	K'_o				C'			
Days	1:1:1	1:1.5:1.5	1:2:2	1:2.5:2.5	1:1:1	1:1.5:1.5	1:2:2	1:2.5:2.5
71	1.163	1.153	1.159	1.153	4.160	6.432	7.261	8.057
75	1.149	1.155	1.163	1.140	4.349	6.151	6.738	8.337
81	1.157	1.160	1.164	1.154	4.066	5.993	6.892	8.047

[a]Cement-sand-aggregate ratio.

A comparison of the values of K'_o and C' indicates that there are no significant changes of these constants with hydration time. This means that the silica fume content in an old concrete can be quite easily determined by using the AC impedance technique if the cement-aggregate ratio is known.

Effect of Aggregate Volume on High Frequency Arc Diameter

Plots of HFA diameter (kΩ) versus aggregate volume fraction are made to illustrate the effect of aggregate volume on HFA diameter. Figures 6*a* through 6*b* are typical plots at 17 and 71 days hydration, respectively. Sets of straight lines are obtained. The HFA diameter increases linearly with increasing aggregate volume. It is clear that the slope of the straight line increases with (1) hydration time and (2) silica-fume content. The conductive path would be mainly attributed to the volume fraction of cement paste since aggregate has a very high resistivity. High aggregate volume fraction or low cement paste volume fraction yields high resistivity values for concrete. Change of slope is a result of the change of cement paste conductivity that is affected by hydration time and silica-fume content. Therefore, the effect due to the aggregate volume fraction can be taken into account in the determination of silica-fume content in a concrete.

D_{HFA} as previously stated is a function of pore ion concentration, porosity, and mean pore size. Factors that have an impact on these three parameters such as batching errors, *W-C* ratio, mineral and chemical additives, air content, and so forth, will significantly affect the results. Application of the AC impedance technique to determine the content of various chemical or mineral additives, although potentially very difficult, is possible if the influencing factors are isolated. AC impedance spectroscopy appears to be a potential tool for determining silica-fume content in concrete. This method also has potential for the determination of the content of other mineral and chemical additives in well hydrated concrete. However, it is apparent that caution must be taken to consider the effect of ionic concentration of pore solution, hydration time, aggregate volume, *W-C* ratio, and other porosity-related factors.

Conclusions

The HFA diameter increases with hydration time, aggregate volume, and silica-fume content at the early hydration times. The HFA diameter varies directly with silica-fume content at constant time and aggregate volume.

The HFA diameter increases with aggregate volume and silica-fume content at advanced hydration times. The effect of hydration time becomes insignificant. An exponential relation between the HFA diameter and silica-fume content is obtained at a constant aggregate volume.

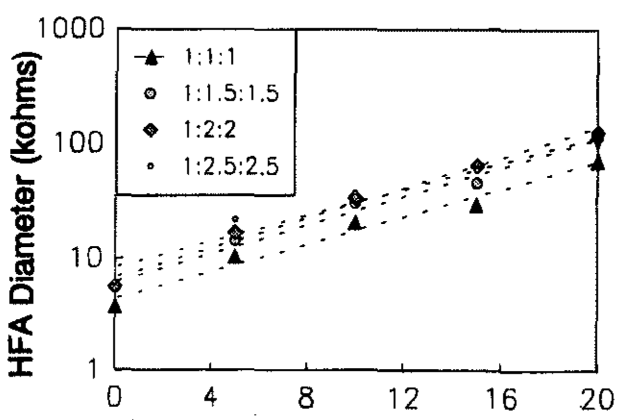

FIG. 5—*A sample plot of log D_{HFA} versus β_{sf} for hydrated concrete containing silica fume at 71 days hydration.*

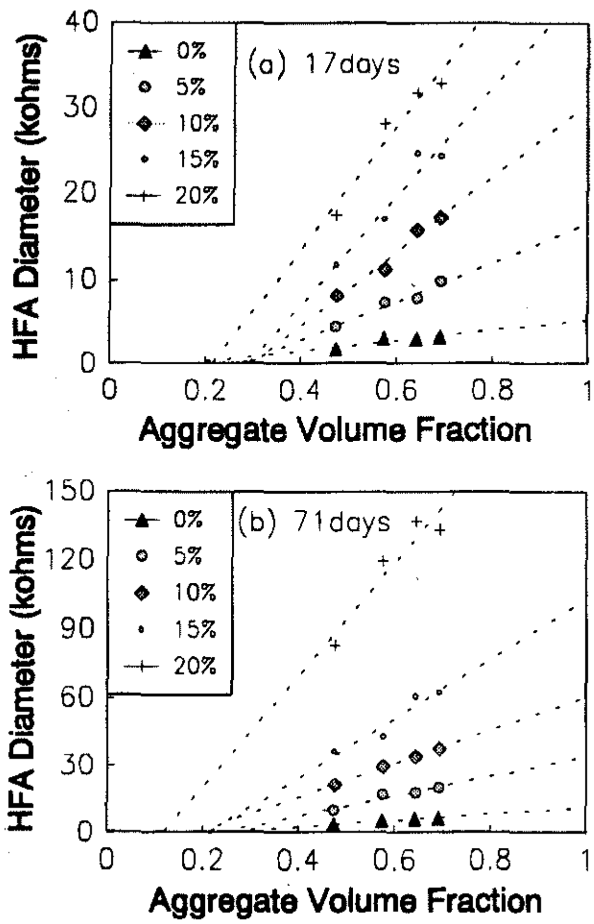

FIG. 6—*Plots of HFA diameter (kΩ) versus aggregate volume fraction for hydrated concrete containing silica fume at hydration times.* (a) *17 and* (b) *71 days.*

Larger values of HFA diameter are obtained at high-aggregate volume. The HFA diameter increases linearly with increasing aggregate volume in the range studied. The slope increases rapidly as the silica-fume content increases. The difference due to the aggregate volume is relatively small compared with the effect of silica fume.

AC impedance spectroscopy appears to be a potential tool for the determination of mineral and chemical additive content in a hydrated concrete.

Acknowledgments

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References

Gu, P., Xie, P., Beaudoin, J. J., and Brousseau, R., 1992, "A.C. Impedance Spectroscopy (I): A New Equivalent Circuit Model for Hydrated Portland Cement Paste," *Cement Concrete Research,* Vol. 22, No. 5, pp. 833–840.

Gu, P., Xie, P., Beaudoin, J. J., and Brousseau, R., 1993a, "A.C. Impedance Spectroscopy (II): Microstructural Characterization of Hydrated Cement-Silica Fume Systems," *Cement Concrete Research,* Vol. 23, No. 1, pp. 157–168.

Gu, P., Xie, P., and Beaudoin, J. J., 1993, "Microstructural Characterization of the Transition Zone in Cement Systems by Means of A.C. Impedance Spectroscopy," *Cement Concrete Research,* Vol. 23, No. 3, pp. 581–591.

Gu, P., Xu, Z., Xie, P., and Beaudoin, J. J., 1993c, "Application of A.C. Impedance Techniques in Studies of Porous Cementitious Materials (I): Influence of Solid Phase and Pore Solution on High Frequency Resistance," *Cement Concrete Research,* Vol. 23, No. 3, pp. 531–540.

Xie, P., Gu, P., Xu, Z., and Beaudoin, J. J., 1993, "A Rationalized A.C. Impedance Model for Microstructural Characterization of Hydrating Cement Systems," *Cement Concrete Research,* Vol. 23, No. 2, pp. 359–367.

Xu, Z., Gu, P., Xie, P., and Beaudoin, J. J., 1993, "Application of A.C. Impedance Techniques in Studies of Porous Cementitious Materials (I): Relationship Between ACIS Behaviour and Porous Microstructure," *Cement Concrete Research,* Vol. 23, No. 4, pp. 853–862.