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Seven-Year Study on the Effect of Silica Fume in Concrete

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An experimental and numerical study of the long-term interaction between silica fume and Portland cement in concrete subjected to air, water, or sealed curing is outlined. About 250 kg of eight qualities of each concrete were studied at four different ages each over a period of 7 years between 1989 and 1996. Parallel studies of strength, hydration, and internal relative humidity were performed. Half of the concretes contained silica fume. New and original results and analyses of the interaction between Portland cement and silica fume related to compressive strength, split tensile strength, hydration, and internal relative humidity are presented. The specimens are available for future measurements. Advanced Cement Based Materials 1998, 7, 139–155. *© 1998 Elsevier Science Ltd.*
KEY WORDS: Efficiency factor, High-performance concrete, Hydration, Internal relative humidity, Pozzolanic effect, Silica fume, Strength

In recent years, silica fume has been used to obtain high strength, high fluidity, and other high qualities in concrete. However, the efficiency factor of silica fume related to strength, hydration, and self-desiccation has not yet been sufficiently analyzed, particularly with regard to the effect of time t and the water-to-cement ratio (w/c). Reports dealing with the decrease of strength of concrete over time due to the presence of silica fume have been presented over the last few years [1]. The decrease was related to the amount of microcracking that occurred in silica fume concrete. Some of the observations have been explained by different moisture conditions in the concrete when the compressive tests were performed [2]. The decrease of split tensile strength compared to compressive strength in silica fume concretes has been related to the autogenous shrinkage [3]. The development of hydration differs substantially between concretes with and without silica fume [4]. During the pozzolanic interaction between silica fume and Portland cement, some calcium hydroxide was transformed into silicate hydrates, which increased the strength. It was observed that the amount of silica fume required to consume all the calcium hydroxide was dependent on w/c [5]. At w/c = 0.48, about 15% silica fume was required to consume all the calcium hydroxide but only 10% silica fume at w/c = 0.28 [5]. These results were confirmed indirectly by studies on carbonation shrinkage [6]. In concrete with 10% silica fume, no carbonation shrinkage was observed, provided w/c = 0.25 [6]. Since the presence of calcium hydroxide was fundamental for carbonation shrinkage to occur, correlations were calculated between age, w/c, and the amount of silica fume required to eliminate calcium hydroxide [6]. Theoretically, about 16% silica fume was required of the cement content, provided that sufficient water was available for pozzolanic reaction to occur [7]:

$$3\ Ca(OH)_2 + 2\ SiO_2 = 3\ CaO.2\ SiO_2.3\ H_2O. \qquad (1)$$

The C/S ratio was dependent mainly on the content of the silica fume calculated on the basis of the cement content but also on the amount of alkalis. Figure 1 shows the C/S ratio vs. the silica fume content in the concrete at varying combinations of alkalis, K_2O, and Na_2O [7–14]. A C/S ratio of 1.5 seemed to be relevant in concrete with 10% silica fume. The effect of silica fume, on the interfacial zone of cement paste, and aggregate was investigated [15]. The cement paste had w/c = 0.35 (control paste). The different matrices are given in Table 1. Figure 2 shows the porosity of the interfacial zone vs. the distance from the aggregate in concrete of 1 month's age [15]. The porosity was correlated to the distance from the aggregate:

$$P_{ifz} = a \cdot d^b \qquad (5 < d < 100\ \mu m) \qquad (2)$$

where P_{ifz} = porosity of the interfacial zone (in %), a, b = constants given in Table 2, and d = distance from the aggregate (μm).

The matrix with silica fume showed the lowest porosity at a distance of 5 μm from the aggregate, followed by the porosity of the matrix with latex + antifoaming agent and the sand matrix. Close to the aggregate, the reference cement paste exhibited twice as

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Received January 6, 1997; Accepted January 6, 1998

655 Avenue of the Americas, New York, NY 10010

ISSN 1065-7355/98/$19.00
PII S1065-7355(98)00003-0

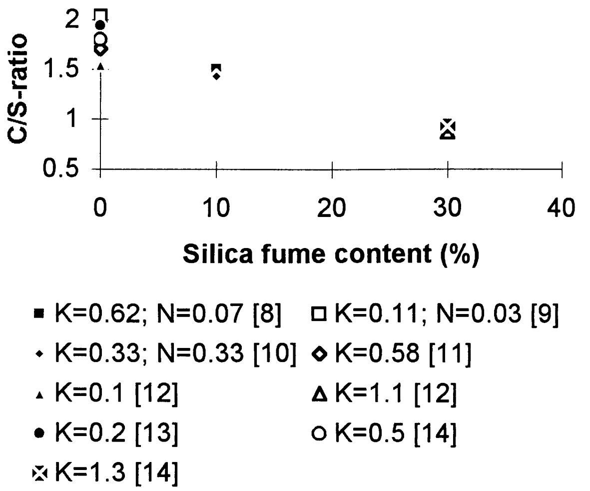

FIGURE 1. C/S ratio vs. silica fume content with varying combinations of alkalis. K = K_2O; N = Na_2O [7–14].

much porosity as the matrix with 10% silica fume replacement. The silica fume mainly improved the interfacial zone due to the pozzolanic reaction, cp. eq 1, but also due to a filler effect of the silica fume grains. The effect of silica fume on the porosity of the interfacial zone was studied for concrete with w/c = 0.45 and 50% by mass river gravel [16]. Figure 3 shows the pore area in the interfacial zone and in the bulk paste [16]. It was concluded that the porosity decreased in the interfacial zone at early ages with the silica fume content but increased with the silica fume content in mature concrete. This observation perhaps was due to the pronounced self-desiccation in low w/c concretes with silica fume. The self-desiccation in turn caused air-filled volume in the concrete and autogenous shrinkage [3]. Initial cracking in the interfacial zone perhaps explained the increase of porosity in mature concrete [16]. However, in the bulk paste at a distance from the aggregate, no aggregate influenced the shrinkage and thus no initial cracking occurred. According to Larsen et al. [1], cracking of the cement paste in high performance concrete (HPC) and decrease of strength were clearly related to the silica fume content.

Since silica fume concrete was introduced on a large

TABLE 1. Properties of matrixes [15]

Matrix	Replacement of Cement (by mass)
Silica fume	10%
Latex copolymer (emulsion) + antifoaming agent	33%
	1%
Sand maximum size 3 mm	60%

TABLE 2. Constants of eq 2

Matrix	Constant a	Constant b
Silica fume	49	−0.64
Latex + antifoaming agent	35	−0.28
Sand	28	−0.26
Control paste	55	−0.28

scale, it has been well known that strength is rapidly improved. Concrete with w/c = 0.35 and 470 kg/m^3 of cement + silica fume was studied [17]. Curing in water at temperatures of 20°C and 50°C was studied. Figure 4 shows the development of strength over 3 months for concrete with <20% silica fume at temperatures of 20°C and 50°C.

The effect of silica fume on the elastic modulus of the interfacial zone was shown for mortar mixes with w/c = 0.52 and varying specific surface of the sand [18]. Figure 5 shows the dynamic elastic modulus vs. the specific surface of the sand [18]. Above a certain specific area of the aggregate, no bulk paste seemed to exist in the silica fume mortar (only transition zone paste). The elastic modulus E was expressed by two equations (in GPa):

$$E = [20.6 + 5.1 \cdot ln(t)] \cdot (su)^{-0.11} \quad (3)$$

$$E_s = 17.4 + 4.7 \cdot ln(t) \quad (4)$$

where $ln(t)$ = natural logarithm of age ($1 < t < 28$ days), su = specific surface of the sand ($0.6 < s < 10$ m^2/kg), E = dynamic modulus of elasticity for mortar without silica fume, and E_S = dynamic modulus of elasticity for mortar with 10% silica fume.

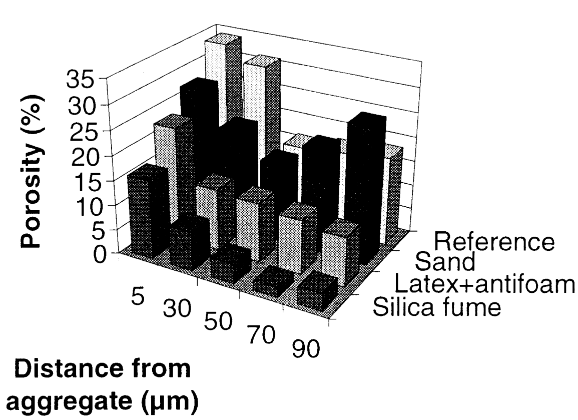

FIGURE 2. Porosity of the interfacial zone obtained by scanning electron micrographs vs. the distance from the aggregate [15].

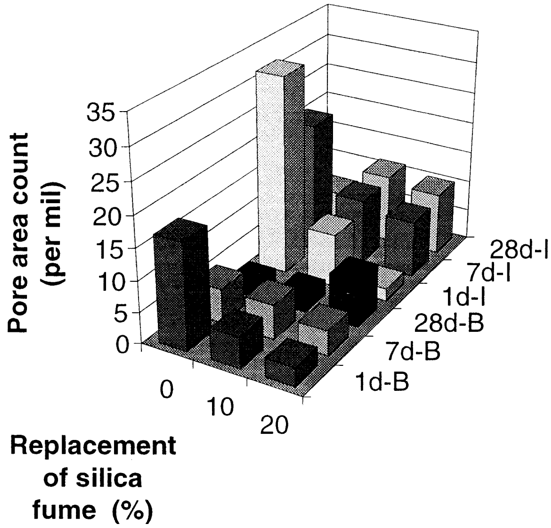

FIGURE 3. Pore area in the interfacial zone (I) and in the bulk paste (B) [16]. d = days.

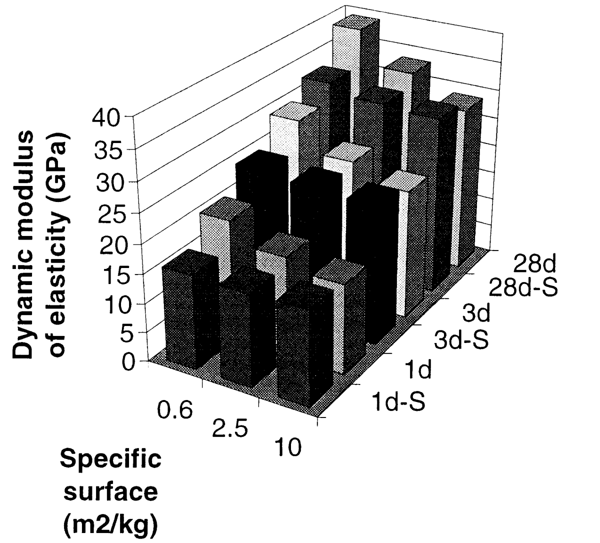

FIGURE 5. Elastic modulus vs. specific surface of sand [18]. d = days' age; S = 10% silica fume.

Objectives of the Study

The main objective of the work was to compare, over at least 7 years, the compressive and the split tensile strengths of mass concrete with 10% silica fume with the same properties of concrete without silica fume. The w/c varied between 0.22 and 0.58. Sealed, air, and water curing were studied. The concrete was poured in a way that avoided influences of the pouring. Parallel studies were performed on strength, internal relative humidity, and the development of hydration.

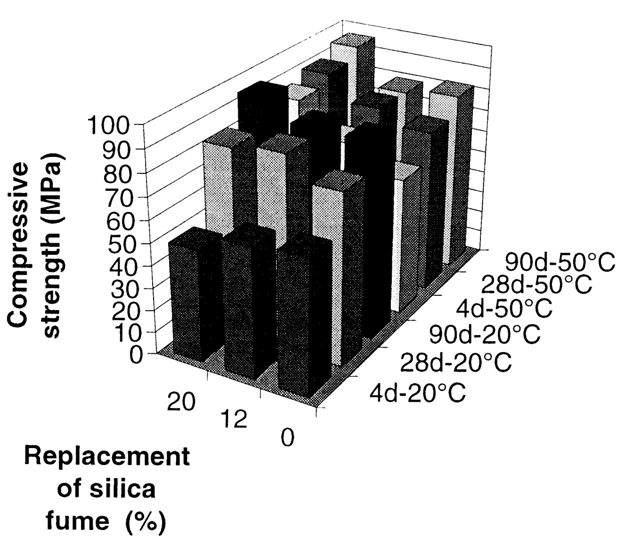

FIGURE 4. Strength at 3 months of concrete with ≤20% silica fume [17]. d = days.

Experimental

Material Studied

Table 3 shows the chemical composition of the low alkali cement used [4]. Eight types of concrete were studied in all 24 large specimens. The aggregate consisted of crushed quartzite sandstone 8 to 12 mm (compressive strength: 333 MPa, split tensile strength: 15 MPa, Young's modulus: 60 GPa [19], and ignition losses: 0.25% [20]) together with natural gravel 0 to 8 mm (granite, ignition losses: 0.85% [20]). The silica fume was granulated powder. The superplasticizer

TABLE 3. Chemical composition of the cement

Analyzed properties (%)	
CaO	64.6
SiO_2	21.8
Al_2O_3	3.34
Fe_2O_3	4.39
MgO	0.84
K_2O	0.62
Na_2O	0.07
Alkali	0.48
SO_3	2.23
CO_2	0.14
Free CaO	1.13
Mineralogical properties (%)	
C_2S	22.5
C_3S	53.0
C_3A	1.42
C_4AF	13.4
Physical properties	
Ignition losses	0.63%
Fineness (Blaine)	325 m^2/kg
Density	3180 kg/m^3

TABLE 4. Composition (kg/m^3 dry material) and properties of the concretes [20]

Concrete Type/Material	1	2	3	4	5	6	7	8
Quartzite (8 to 12 mm)	1358	1306	1306	1214	1158	1150	1153	1145
Gravel (0 to 8 mm)	525	630	549	723	730	846	825	812
Cement (low alkaline)	484	456	476	400	389	303	298	299
Silica fume (granulated powder)	48	—	48	—	39	—	30	—
Superplasticizer (dry material)	13.32	8.84	7.78	3.35	3.07	3.01	2.13	—
Density	2533	2513	2500	2469	2456	2441	2451	2424
Water/cement ratio	0.222	0.251	0.243	0.326	0.358	0.465	0.483	0.577
Aggregate content	0.712	0.738	0.753	0.746	0.731	0.712	0.731	0.700
Air content (%)	0.95	1.5	0.8	1.4	1.1	1.1	0.95	0.75
Workability (vebe)	29	34	13	25	12	9	12	15
1-month strength (cylinder, MPa)	111	93	112	77	93	58	65	38
3-month strength (cylinder, MPa)	128	104	128	91	100	70	76	45
15-month strength (cylinder, MPa)	142	121	139	105	104	78	81	51
90-month strength (cylinder, MPa)	139	121	131	106	106	74	79	49

(naphthalene sulphonate) was added 30 s after all the other materials during the mixing (mixing time: 240 s). The mix proportions, the properties in the fresh state, and the strengths are given in Table 4 [20].

Specimen

Compressive strength f_c, split tensile strength f_{sp}, and hydration were studied on cores, 80 mm long and 40 mm in diameter, drilled out of the concrete specimens described below (250 kg each). The concrete was poured in the shape of a disc, 1 m in diameter and 0.1 m thick. To simulate a long column, the flat sides of the disc were sealed by thick layers of epoxy resin, at least 2 mm. The circular surface of one third of the specimens was sealed by a minimum of 2 mm of epoxy resin. The diffusion of moisture through the epoxy resin was negligible compared to the diffusion through the porous concrete. One third of the specimens were subjected to a climate with an ambient relative humidity between 23% and 48% [21]. The remaining third of the specimens were submerged and cured in water. About 1850 measurements were performed, as outlined in Table 5.

Experimental Methods

To measure internal relative humidity, cast-in plastic tubes were placed at different distances (50, 150, and 350 mm) from the exposed circular surface of the specimen. Thermocouples were placed in the concrete close to the cast-in items [21]. The measurement points were protected by a cover made of expanded plastic insulation to minimize the effects of variations in the ambient climate in the laboratory. The measurement period was 22 hours. The probes were carefully calibrated [22]. Figure 6 shows the different stages in the measurement of the internal relative humidity. A total of 936 cylinder cores were taken in equal shares at distances of 50, 150, or 350 mm from the exposed surface to study strength and hydration. During the testing of strength, interlayers of hardboard were used. A total of 642 ignition tests were performed to obtain the hydration in the specimens [4,23]. Compensation was made for the ignition losses of cement and aggregate [4,23].

TABLE 5. Number of measurements

Parameter	1 m	3 m	5 m	15 m	90 m
f_c	144	144	72	144	144
f_{sp}	72	72	—	72	72
Hydration	144	144	72	144	144
Ø	72	72	36	72	18
Total	432	432	180	432	378

Note: m = month.

Results

Compressive Strength

Figures 7–9 show the development of strength with sealed, air, and water curing, respectively (filled marks = 10% silica fume). Figure 10 shows strength of all the cores studied. The moisture condition of the specimen

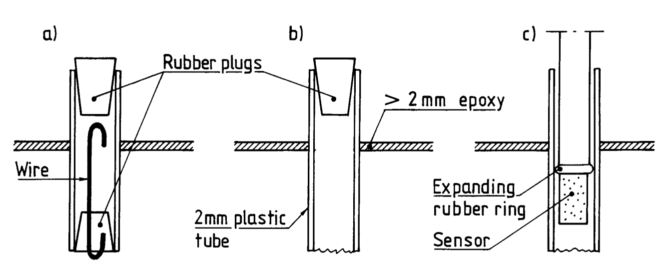

FIGURE 6. Different stages in the measurement of the internal relative humidity in concrete: (a) before measurement; (b) between measurements; (c) during measurement [20].

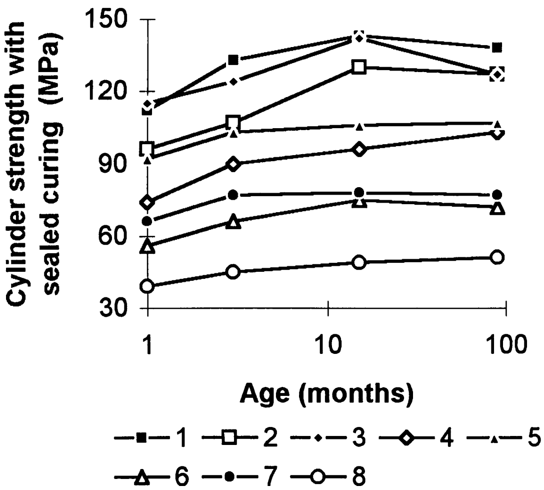

FIGURE 7. Strength vs. age with sealed curing (average of six tests). Mix number is given in Table 4.

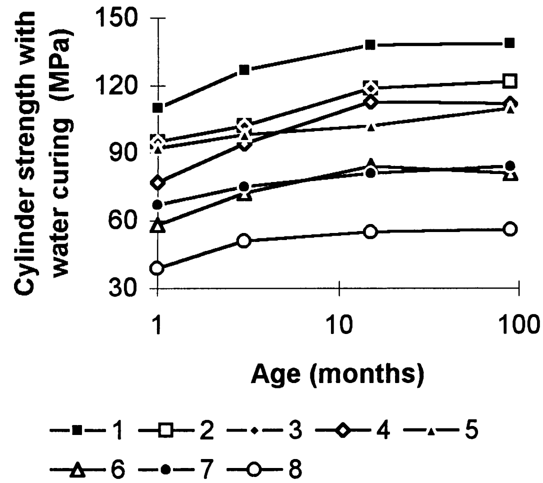

FIGURE 9. Strength vs. age with water curing (average of six tests). Mix number is given in Table 4.

had some influence on the measured strength, which was investigated at 5 months' age. Figure 11 shows strength of cores with interlayers f_c during testing vs. strength of cores without interlayers f_{cc}. The following influence was obtained (in MPa, R^2 = accuracy factor):

$$f_c = 0.94 \cdot f_{cc} \qquad (R^2 = 0.97). \tag{5}$$

The moisture conditions in the core during the testing also had an influence on the result. Figure 12 shows the strength at 5 months' age with 1 month of intensive drying of cores at 55°C f_{cd} and the strength with the mentioned drying period followed by water curing f_{cw} for another month. Figure 11 refers to strength with sealed curing f_c. The following equations were obtained:

$$f_{cd} = 1.19 \cdot f_c \qquad (R^2 = 0.91) \tag{6}$$

$$f_{cw} = 0.87 \cdot f_c \qquad (R^2 = 0.96). \tag{7}$$

Moisture stresses were avoided by studies with sealed conditions. Figures 13–16 show the strength vs. w/c for sealed, air, water, and all three kinds of curing, respectively (filled marks = 10% silica fume). The age (in months) is indicated. The following equation was used to describe the compressive strength $f_c(w/c)$ (in MPa):

$$f_c(w/c) = A \cdot (w/c) + B \tag{8}$$

where A, B = constants given in Table 6.

The curing conditions of the large specimens had a minor effect on the long-term strength. However, the

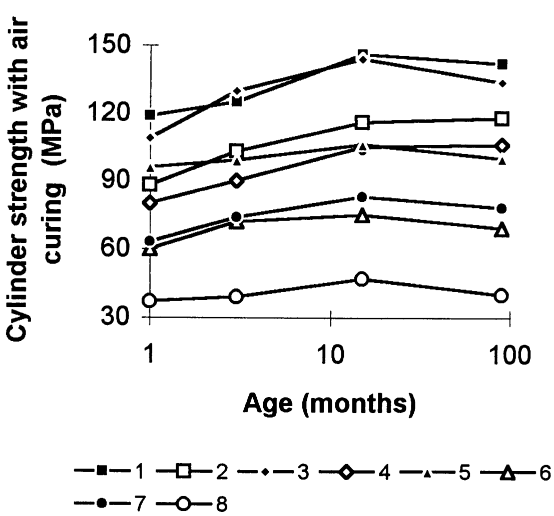

FIGURE 8. Strength vs. age with air curing (average of six tests). Mix number is given in Table 4.

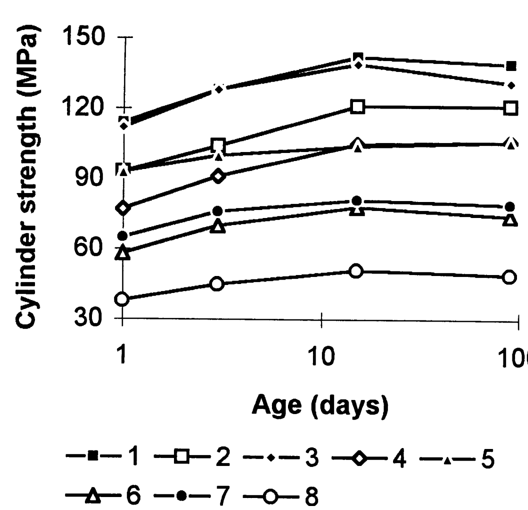

FIGURE 10. Strength vs. age of all cores (average of 18 specimens). Mix number is given in Table 4.

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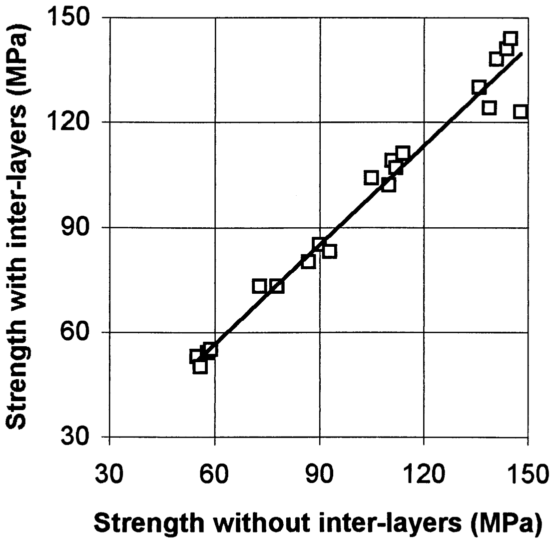

FIGURE 11. Strength with interlayers during testing vs. strength without interlayers.

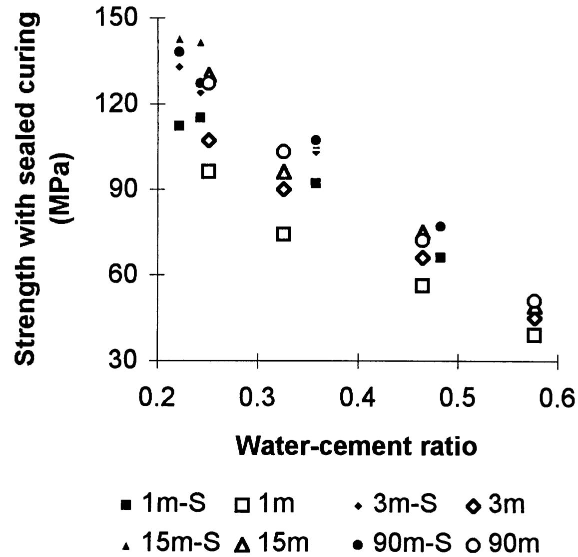

FIGURE 13. Strength vs. water-cement ratio with sealed curing. m = months; S = 10% silica fume.

influence of silica fume was more significant. At 1 month's age, concrete with 10% silica fume obtained about 15 MPa greater strength than concrete without silica fume (with the w/c held constant). Based on eq 8, the time dependence of strength was found to be:

$$(\delta f_c/\delta t)_s \approx 10 \cdot [0.7 - (w/c)]/t \qquad \text{(10\% silica fume, } R^2 = 0.94) \tag{9}$$

$$\delta f_c/\delta t \approx 15 \cdot [0.73 - (w/c)]/t \qquad \text{(No silica fume, } R^2 = 0.96) \tag{10}$$

where t = age (in months).

As an average, the long-term development of the strength growth rate was about 55% larger in concrete without silica fume than in concrete with 10% silica fume.

Split Tensile Strength

Figures 17–19 show the development of split tensile strength with sealed, air, and water curing, respectively (filled marks = 10% silica fume). Figure 20 shows the split tensile with sealed curing vs. w/c.

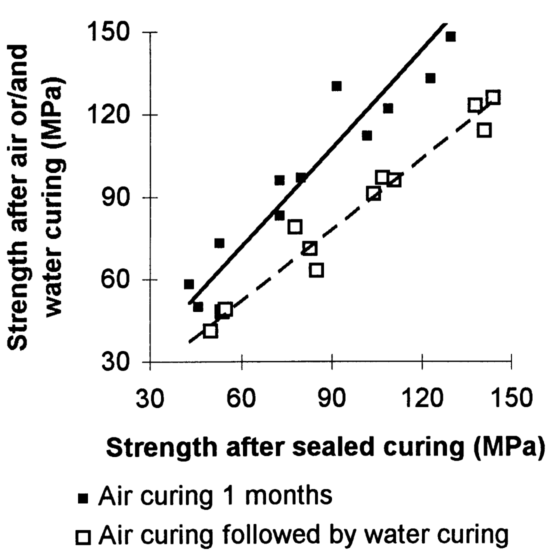

FIGURE 12. Strength with drying and strength with drying followed by water curing.

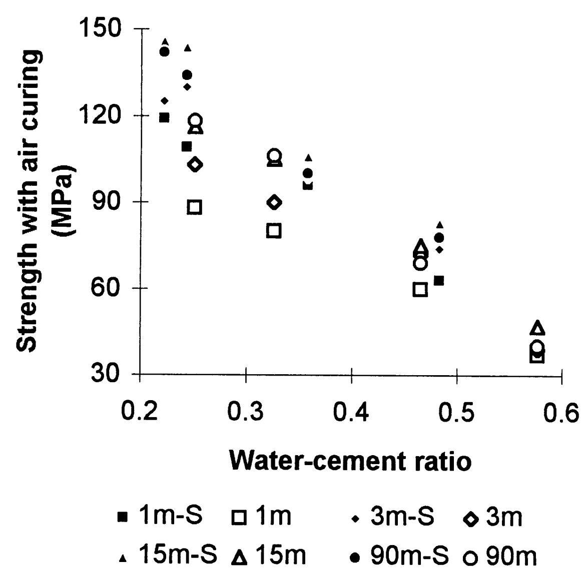

FIGURE 14. Strength vs. water-cement ratio with air curing. m = months; S = 10% silica fume.

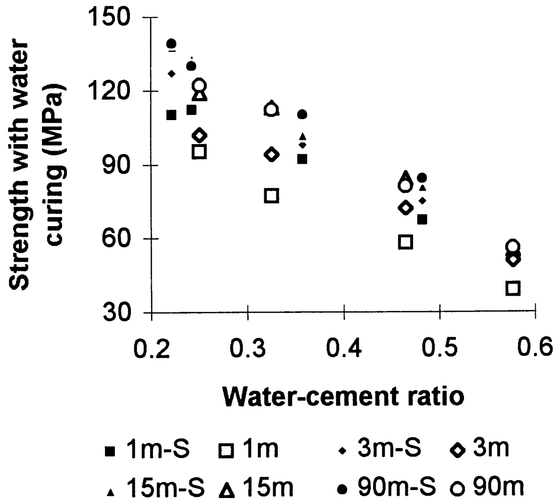

FIGURE 15. Strength with water curing vs. water-cement ratio. m = months; S = 10% silica fume.

The following equation was used to describe split tensile strength vs. w/c:

$$f_{sp}(w/c) = C \cdot (w/c) + D \tag{11}$$

where $f_{sp}(w/c)$ = split tensile strength in (MPa), and C, D = constants given in Table 6.

Hydration

In concretes without silica fume, the maximum degree of hydration α_{max} can only be obtained with w/c > 0.39 [24]. For w/c < 0.39, α_{max} is linearly dependent on w/c [4,23]:

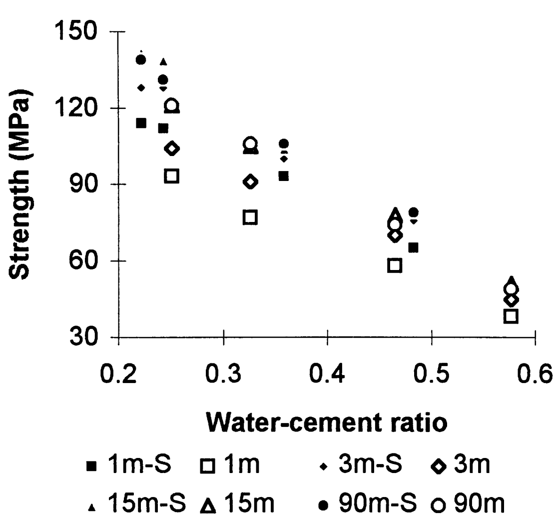

FIGURE 16. Strength of all cores studied vs. w/c. m = months; S = 10% silica fume.

TABLE 6. Constants of eq 8 and 9 (in MPa)

Age (months)	Silica Fume	A	B	C	D
1	10%	−186.26	167.06	−10.831	11.936
1	—	−166.23	133.53	−12.423	11.053
3	10%	−206.5	176.67	−15.524	14.119
3	—	−187.06	152.71	−15.25	13.197
15	10%	−259.46	201.96	−14.057	13.665
15	—	−231.05	181.02	−16.894	14.138
90	10%	−221.42	184.54	−13.142	13.766
90	—	−229.88	181.29	−15.419	13.591

$$\alpha_{max} = w/(0.39 \cdot c). \tag{12}$$

Figures 21–23 give the hydration (nonevaporable water to cement w_n/c) with sealed, air, and water curing, respectively [4]. The procedure according to Byfors [23] was applied. Compensation was made for the self-losses of the different materials during the ignition. In concrete without silica fume, the degree of hydration α can also be expressed as:

$$\alpha = w_n/(0.25 \cdot c). \tag{13}$$

Dividing eq 12 by eq 13 gave the maximum value of the relative hydration w_n/w:

$$(w_n/w)_{max} = 0.64 \qquad (0 < w/c < 0.39) \tag{14}$$

$$(w_n/w)_{max} = 0.25 \cdot c/w \qquad (w/c > 0.39). \tag{15}$$

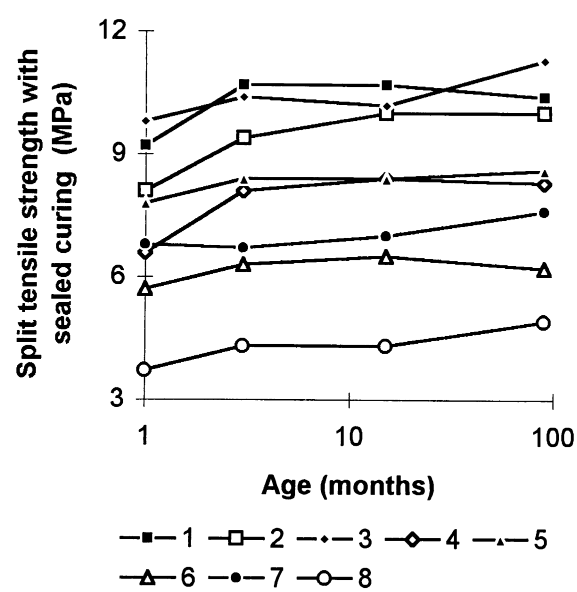

FIGURE 17. Split tensile strength with sealed curing vs. age (average of three tests). Mix number is given in Table 4.

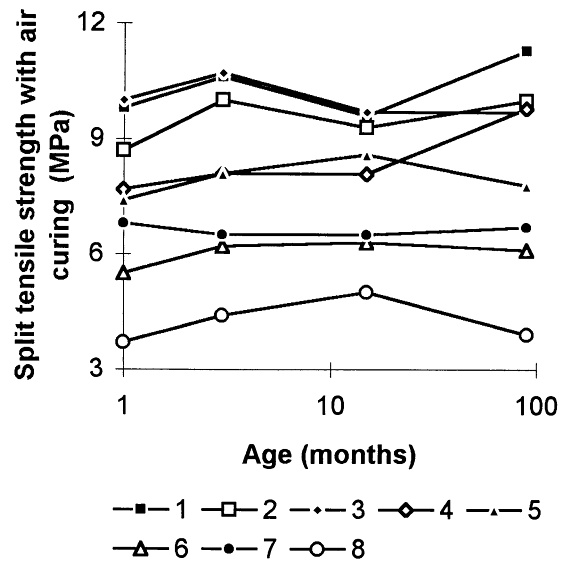

FIGURE 18. Split tensile strength with air curing vs. age (average of three tests). Mix number is given in Table 4.

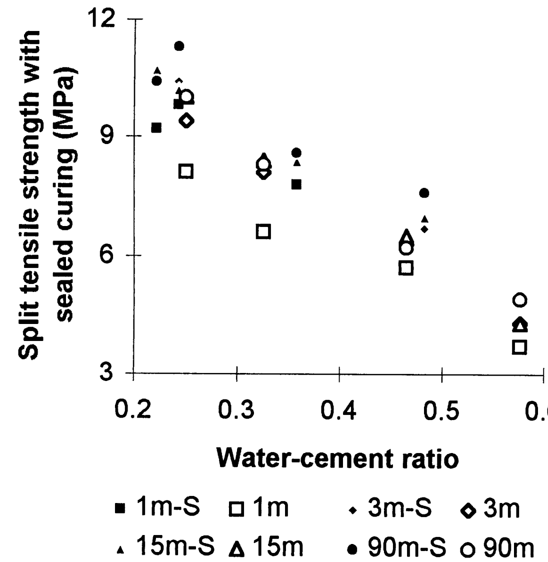

FIGURE 20. Split tensile strength with sealed curing vs. water-cement ratio (average of three tests). Mix number is given in Table 4.

For silica fume concretes, the pozzolanic effect had to be taken in account when calculating the degree of hydration [5]. Silica fume consumed a substantial part of the calcium hydroxide. The compensation for the silica fume was dependent on age, w/c, and amount of silica fume [5]. Thus, it was more convenient to utilize w_n/w [24]. Figure 24 shows the hydration in all the cores studied. In Figure 25 the relative hydration (nonevaporable water to mixing water) w_n/w in concrete with sealed curing is given vs. w/c. From Figure 25 the following equation was calculated:

$$(w_n/w)_S(t, w/c) = 0.0113 \cdot [ln(t) + 20)] \cdot (w/c)^{0.006 \cdot t \cdot (1 - 0.01 \cdot t) - 0.5} \quad (10\%\ silica\ fume, \quad R^2 = 0.93) \tag{16}$$

$$(w_n/w)(t, w/c) = 0.0117 \cdot [ln(t) + 20)] \cdot (w/c)^{0.006 \cdot t \cdot (1 - 0.01 \cdot t) - 0.6}$$

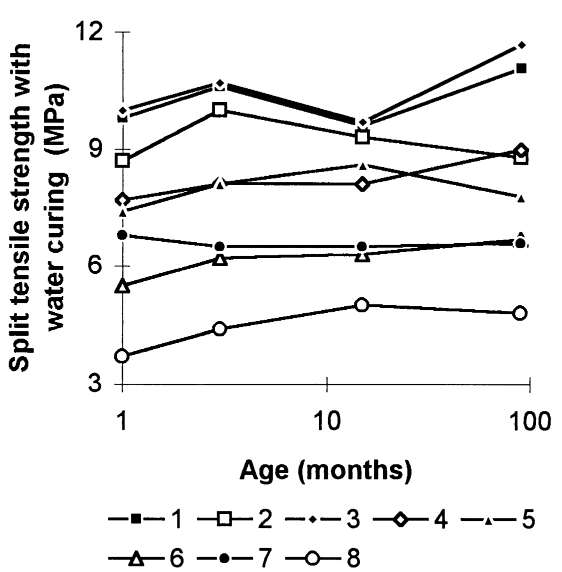

FIGURE 19. Split tensile strength vs. age with water curing (average of three tests). Mix number is given in Table 4.

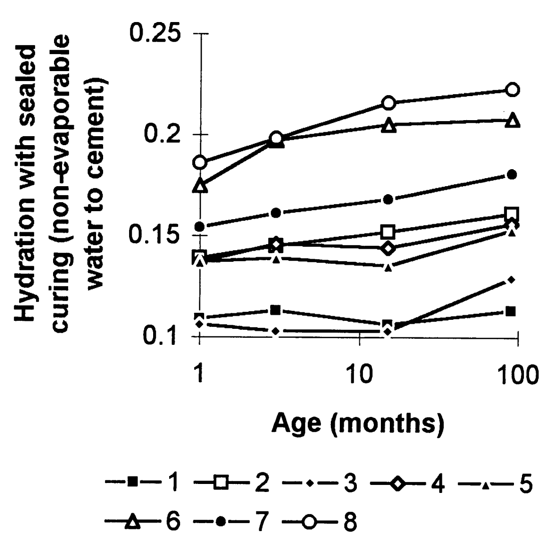

FIGURE 21. Hydration with sealed curing vs. age (average of six tests). Mix number is given in Table 4.

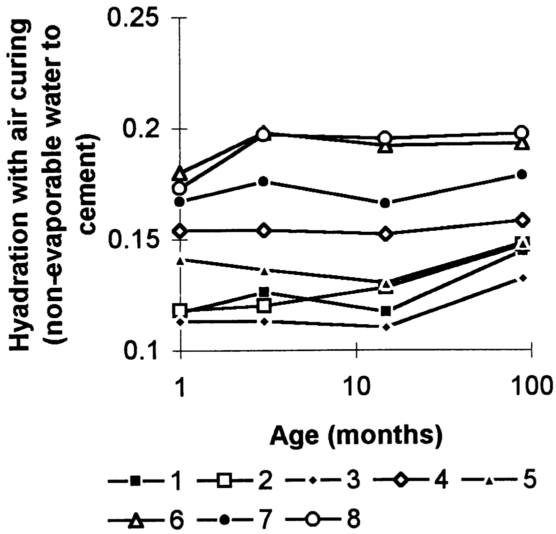

FIGURE 22. Hydration with air curing vs. age (average of six tests). Mix number is given in Table 4.

$$\text{(No silica fume,} \qquad R^2 = 0.90) \tag{17}$$

where $ln(t)$ = natural logarithm of age t (in months).

Internal Relative Humidity

The internal relative humidity Ø of the concrete was of great importance in explaining the development of hydration [25]. However, after 15 months the measurement program on Ø in the present study was limited due to leakage through or missing rubber plugs in the plastic tubes used (Figure 6). The 90-month measurements of Ø with sealed curing were only performed in concretes that were parallel cast in glass flasks. Figures 26–28 give the development of Ø with sealed, air, and water curing, respectively (filled marks = 10% silica fume). After 15 months' age, Ø remained more or less

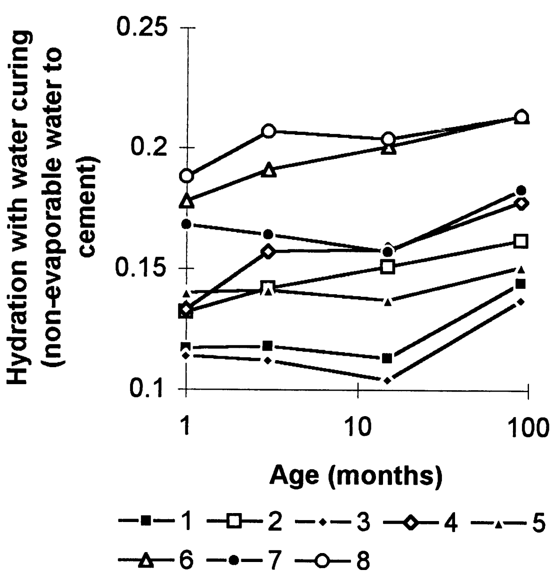

FIGURE 23. Hydration with water curing vs. age (average of six tests). Mix number is given in Table 4.

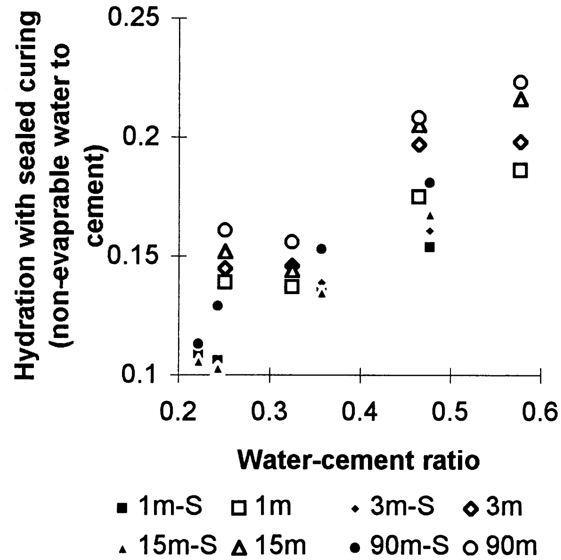

FIGURE 24. Hydration with sealed curing vs. water-cement ratio (average of six tests). Mix number is given in Table 4.

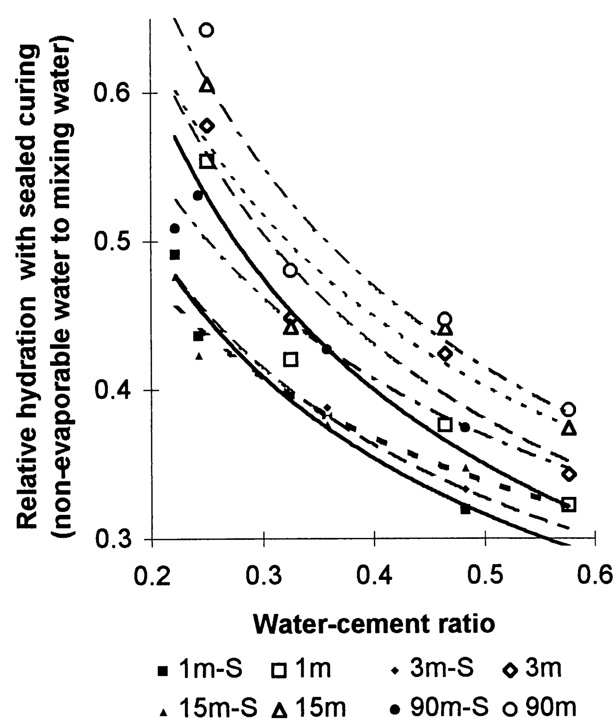

FIGURE 25. Relative hydration (non-evaporable water to mixing water) in concrete with sealed curing. m = months; S = 10% silica fume.

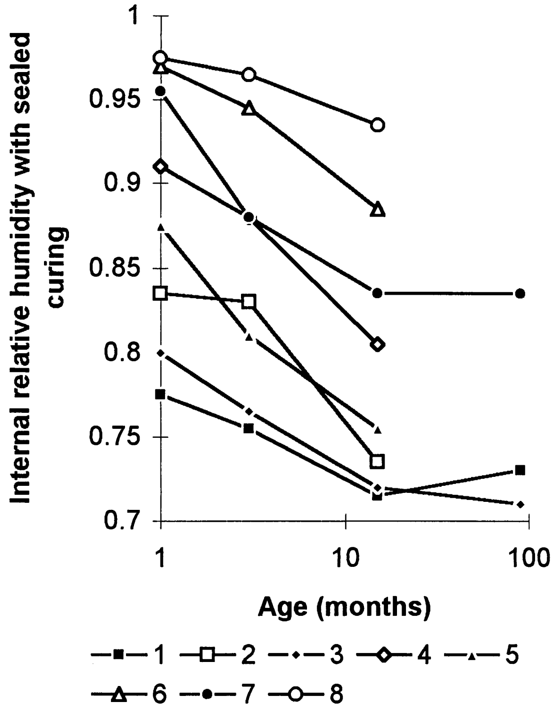

FIGURE 26. Internal relative humidity in concrete with sealed curing (average of six measurements). Mix number is given in Table 4.

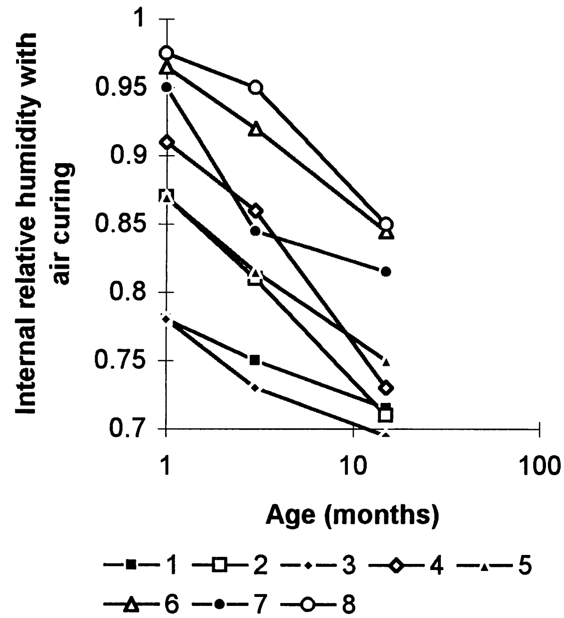

FIGURE 27. Internal relative humidity with air curing 50 mm from the exposed surface (average of two measurements). Mix number is given in Table 4.

constant with sealed curing according to the few measurements that were available, (Figures 26 and 28). Figure 29 shows Ø vs. w/c. From Figure 29 two different equations of Ø (with 10% silica fume *S*, or without silica fume) were obtained related to age and w/c [21]:

$$\varnothing_S(t, w/c) = 1.13 \cdot [1 - 0.065 \cdot ln(t)] \cdot (w/c)^{0.24 \cdot [1 - 0.1 \cdot ln(t)]} \quad (1 < t < 15 \text{ months}; \; 0.22 < w/c < 0.48, R^2 = 0.88) \tag{18}$$

$$\varnothing(t, w/c) = 1.09 \cdot (w/c)^{0.17 \cdot (1 + 0.0451 \cdot t)} \quad (1 < t < 15 \text{ months}; \; 0.25 < w/c < 0.58; R^2 = 0.65). \tag{19}$$

Accuracy

To judge the accuracy of the study, the standard deviation was calculated for all measurements. Tables 7–10 give the coefficient of variation of the measurements related to compressive strength, split tensile strength, hydration, and internal relative humidity with sealed curing, respectively. The coefficient of variation χ was defined according to the following equation:

$$\chi = \xi / av \tag{20}$$

where χ = coefficient of variation, ξ = standard deviation, and av = average.

Generally the coefficient of variation was reasonably low, taking into account that the study was performed long-term. However, an advantage was that the operator and the equipment were the same over the whole study. The measurements related to both compressive and split tensile strengths on concretes with w/c < 0.39 obtained a variation coefficient $\leq$5%, which was acceptable since drilled cores were studied. However, measurement of normal concretes with w/c ≥ 0.39 had a slightly larger variation coefficient. The reason for this rise in the variation coefficient is not known. Especially when related to the measurements of split strength, the coefficient of variation increased with the age, which may also be an effect of autogenous shrinkage that continuously extended in concretes due to self-desiccation [3]. Measurements of hydration and internal relative humidity exhibited low coefficients of variation (4.4% and 2.3%, respectively).

Analysis and Discussion

General

Only the one type of correlation that gave the highest coefficient of correlation is presented hereafter. The pozzolanic effect of silica fume *k* was defined according to the following equation:

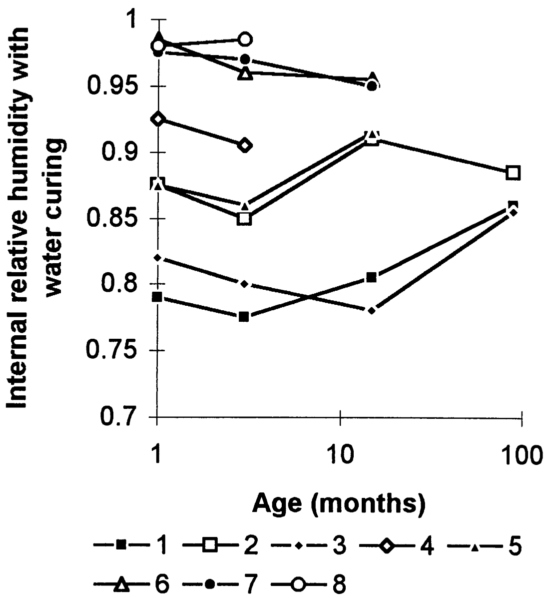

FIGURE 28. Internal relative humidity with water curing 50 mm from the exposed surface (average of two measurements). Mix number is given in Table 4.

$$(w/c)_{eff} = w/(c + k \cdot s) \tag{21}$$

where c = cement content (in kg/m^3), k = efficiency factor of silica fume, s = content of silica fume (10% for mixed proportions 1, 3, 5, and 7, Table 4), w = all the mixing water (in kg/m^3), and $(w/c)_{eff}$ effective (eff) w/c, i.e., the w/c that was used in concrete without silica fume to obtain identical properties (compressive strength, split tensile strength, hydration, or internal relative humidity) to concrete with 10% silica fume, with the w/c held constant.

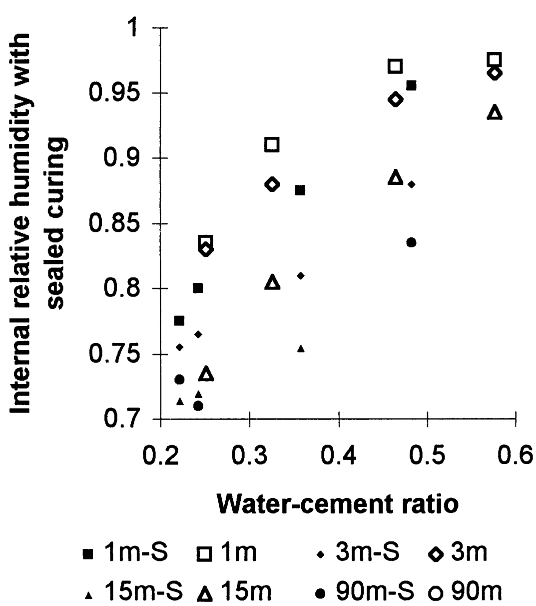

FIGURE 29. Internal relative humidity with sealed curing. m = months; S = 10% silica fume.

TABLE 7. Coefficient of variation related to compressive strength with sealed curing

	Age				
Concrete	**1 m**	**3 m**	**15 m**	**90 m**	**Av**
1	0.092	0.032	0.029	0.035	0.047
2	0.040	0.046	0.041	0.042	0.042
3	0.021	0.046	0.042	0.050	0.040
4	0.036	0.037	0.041	0.096	0.053
5	0.119	0.042	0.030	0.029	0.058
6	0.047	0.073	0.052	0.029	0.050
7	0.090	0.057	0.100	0.115	0.093
8	0.098	0.106	0.098	0.117	0.105
Av	0.069	0.055	0.054	0.065	0.061

Note: Av = average; m = month.

The definition of the efficiency factor of silica fume k could be discussed. For w/c $\geq$ 0.39, about 60% of the amount of silica fume (10% calculated on the basis of the cement content) was available for the reaction with Portland cement to come to an end [7]. After 90 months of hydration, the ratio of nonevaporable water to cement w_n/c in concretes without silica fume varied between 0.16 and 0.22, *i.e.*, $<$ 0.25. However, until 15 months' age, w_n/c was $<0.6 \cdot 0.25 = 0.15$ for concretes with w/c $<$ 0.39, which theoretically implied that a sufficient amount of silica fume still remained in concretes with w/c $<$ 0.39 for the long-term interaction between Portland cement and silica fume to continue. For concretes with w/c $\geq$ 0.39, the pozzolanic reaction between Portland cement and silica fume took place mainly before 1 month's age, but for concretes with w/c $<$ 0.39 the pozzolanic interaction was still observed during the studies at 15 months' age. These results coincide well with observations according to Yogendran et al. [5]. From the practical point of view, it was essential to use an amount of silica fume in the concrete

TABLE 8. Coefficient of variation related to split tensile strength with sealed curing

	Age				
Concrete	**1 m**	**3 m**	**15 m**	**90 m**	**Av**
1	0.060	0.068	0.053	0.177	0.090
2	0.057	0.033	0.047	0.067	0.051
3	0.012	0.034	0.049	0.041	0.034
4	0.084	0.037	0.036	0.018	0.044
5	0.030	0.018	0.036	0.040	0.031
6	0.035	0.033	0.081	0.145	0.074
7	0.043	0.046	0.041	0.112	0.061
8	0.016	0.024	0.098	0.109	0.062
Av	0.042	0.037	0.055	0.089	0.056

Note: Av = average; m = month.

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TABLE 9. Coefficient of variation related to hydration with sealed curing

	Age				
Concrete	**1 m**	**3 m**	**15 m**	**90 m**	**Av**
1	0.032	0.037	0.036	0.041	0.036
2	0.020	0.035	0.072	0.027	0.039
3	0.073	0.052	0.118	0.024	0.067
4	0.044	0.045	0.024	0.038	0.038
5	0.068	0.051	0.030	0.032	0.045
6	0.028	0.038	0.030	0.051	0.037
7	0.035	0.041	0.065	0.022	0.041
8	0.052	0.054	0.066	0.046	0.054
Av	0.044	0.042	0.055	0.035	0.044

Note: Av = average; m = month.

that did not exceed the present limitations in the national regulations: 10% calculated on the basis of the cement content. However, from the theoretical point it would have been of interest to study concrete with >16% silica fume [7–14]. The main objective of the work, however, was to compare properties of mass concrete with 10% silica fume with the same properties of concrete without silica fume. At low w/c, less silica fume was required to consume all the calcium hydroxide. The following expression for the required amount of silica fume to consume all calcium hydroxide s_{rq} was obtained theoretically [6,7]:

$$s_{rq} \approx [(w/c)/0.39] \cdot 0.16 \approx 0.4 \cdot (w/c). \quad (w/c < 0.39) \qquad (22)$$

From parallel studies on carbonation shrinkage ε_C, the following results for concrete with 10% silica fume were obtained [6]:

$$\varepsilon_C = 0.85 \cdot [(w/c) - 0.25] \qquad (0.25 < w/c < 0.39, \; R^2 = 0.49). \qquad (23)$$

TABLE 10. Coefficient of variation for internal relative humidity with sealed curing

	Age				
Concrete	**1 m**	**3 m**	**15 m**	**90 m**	**Av**
1	0.021	0.017	0.020	0.068	0.032
2	0.004	0.012	0.037	—	0.018
3	0.018	0.02	0.038	0.046	0.031
4	0.023	0.016	0.046	—	0.028
5	0.021	0.019	0.057	—	0.032
6	0.008	0.013	0.026	—	0.016
7	0.008	0.022	0.043	0.006	0.020
8	0.003	0.007	0.020	—	0.010
Av	0.013	0.016	0.036	0.040	0.023

Note: Av = average; m = month.

Both these results [5–7] and the present study showed that 10% silica fume calculated on the basis of the cement content was sufficient to consume all calcium hydroxide at w/c ≈ 0.28.

Internal Relative Humidity

The internal relative humidity Ø was of the utmost importance for describing the hydration in the concrete. Reaction products, i.e., hydroxides, from the hydration were required for the pozzolanic reaction to take place [7–14]. When the internal relative humidity decreased, the pozzolanic reaction also decreased and finally stopped [25]. Self-desiccation of concrete also was of great importance [3]. Autogenous shrinkage was more pronounced in concretes with silica fume than in concretes without silica fume. The autogenous shrinkage was clearly related to the self-desiccation [3] of the concrete. It also was observed that the self-desiccation was caused by depression in the pore water [26], which also more obvious in concretes with silica fume. The autogenous shrinkage caused tensile stresses in the cement paste but compression in the aggregate of the concrete [26]. This was of great importance in explaining the mechanical properties of the concrete, such as compressive strength and split tensile strength. Due to the compression of the aggregate of the concrete with low w/c (which increased continuously due to the autogenous shrinkage), the total compressive capacity of the concrete decreased slightly in concretes of low w/c with silica fume. When the autogenous shrinkage exceeded the tensile strain of the cement paste, which often occurred in concretes with low w/c and containing silica fume [26], cracks arose.

The amount of cracking in the concrete was clearly related to a decreasing compressive strength of the concrete [1]. To evaluate the efficiency factor related to self-desiccation k_{se}, eqs 18 and 19 were used, i.e., w/c in eq 19 was replaced by $(w/c)_{eff}$ according to eq 21. After this substitute of w/c in eq 19, eqs 18 and 19 were equalized and the efficiency factor k_{se} easily calculated. Figure 30 shows the efficiency factor related to self-desiccation. The efficiency factor k_{se} was described by the following equation:

$$k_{se}(t, w/c) = 2 \cdot (t - 8.33) \cdot (w/c) - 0.77 \cdot t + 9.2 \quad (1 < t < 15 \text{ months}; 0.25 < w/c < 0.50; R^2 = 0.77) \qquad (24)$$

where t = age of the concrete (in months).

At w/c ≈ 0.39, the efficiency factor k_{se} = 2.7 was observed to be fairly independent of age. However, at lower w/c, k_{se} was larger at 1 and 3 months' age and smaller at 15 months' age since the hydration then

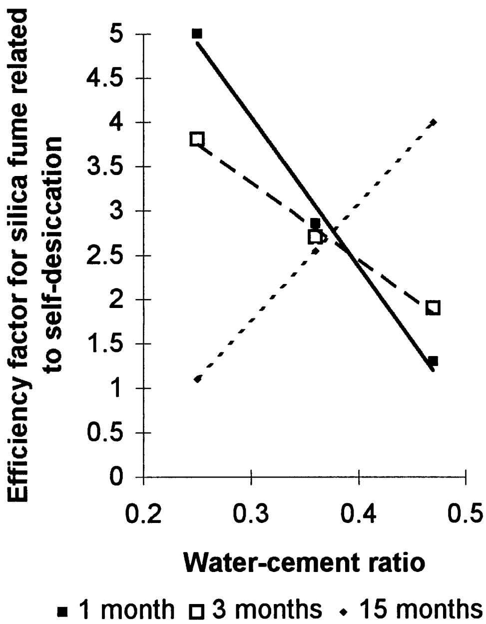

FIGURE 30. Efficiency factor of 10% silica fume related to internal relative humidity with sealed curing (self-desiccation).

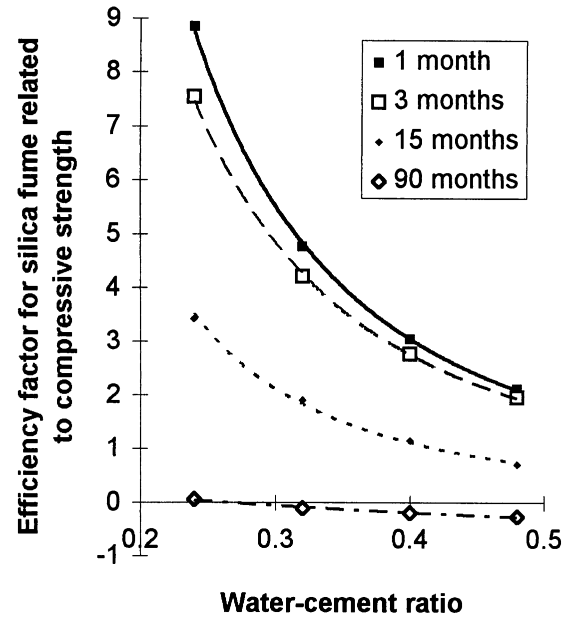

FIGURE 31. Efficiency factor of silica fume related to compressive strength with sealed curing.

ceased and also the pozzolanic reaction. The contrary was observed at higher w/c where the hydration continued and obviously also the pozzolanic reaction in contrast to the relations stated in the general discussion. The pozzolanic reaction caused smaller average pore diameter in the gel and thus lower Ø according to the well-known Kelvin equation [27]. The small size of the silica fume particles most probably affected the pore size distribution in the concrete.

Compressive Strength

Compressive strength is one of the most important and discussed properties of concrete. Especially related to HPC, the possible retrogression of the strength in silica fume concretes is of utmost importance [1,2]. In the present study, no significant decrease over 90 months was observed. Initially, the effect of silica fume on compressive strength was pronounced, especially in concrete with low w/c. Early pozzolanic reaction created reaction products such as calcium silicate hydrates instead of calcium hydrates with about 15 MPa larger compressive strength. However, due to the noticeable self-desiccation in concretes with silica fume, especially in concretes with low w/c, the hydration stopped and thus the hydration, the pozzolanic reaction, and also the strength growth, cp. eqs 9 and 10.

The rate of long-term strength growth was about 55% larger in concretes without silica fume than in concretes with 10% silica fume. Only sealed curing was studied regarding the efficiency factor related to strength k_{sc}. To evaluate the efficiency factor, eq 8 was used, i.e., w/c in the equation for concrete without silica fume was replaced by $(w/c)_{eff}$ according to eq 21. After this replacement of w/c in eq 8, the equations valid for concrete with and without silica fume were equalized and the efficiency factor k_{sc} estimated. Figure 31 shows the efficiency factor of silica fume related to compressive strength and outlined by the equation:

$$k_{sc}(t, w/c) = 0.113 \cdot [4.44 - ln(t)] \cdot (w/c)^{-0.056 \cdot [ln(t) + 35]}$$
$$(1 < t < 90 \text{ months}; 0.25 < w/c < 0.50; R^2 = 0.85) \quad (25)$$

where $ln(t)$ = natural logarithm of the age of the concrete t (in months).

Figure 32 mainly confirms the present results in the experimental study performed [28]. The importance of the long-term effect of the silica fume may be related to the application. If long-term strength growth is demanded for design reasons, the silica fume may be avoided in the concrete.

Split Tensile Strength

Only sealed curing was studied regarding the efficiency factor related to split tensile strength k_{sp}. To evaluate the efficiency factor, eq 11 was used, i.e., w/c in the equation valid for concrete without silica fume was replaced by $(w/c)_{eff}$ according to eq 21. After this replacement of w/c in eq 11, the equations valid for

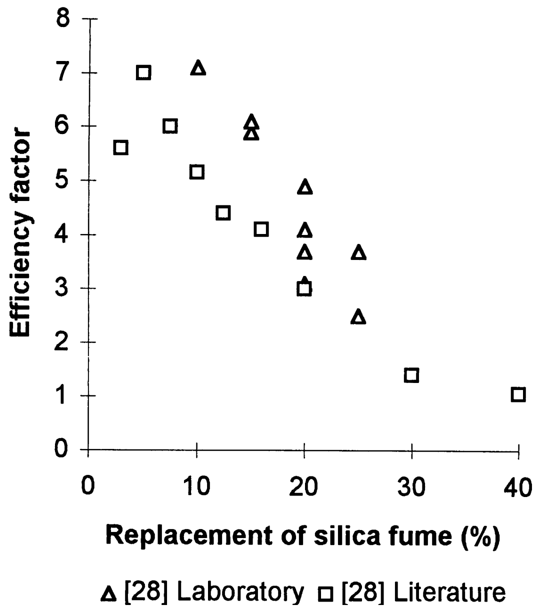

FIGURE 32. Efficiency factor for concrete vs. the replacement of cement by silica fume [28].

concrete with and without silica fume were equalized and the efficiency factor k_{sp} estimated. Figure 33 shows the efficiency factor related to split tensile strength k_{sp} described by the following equations:

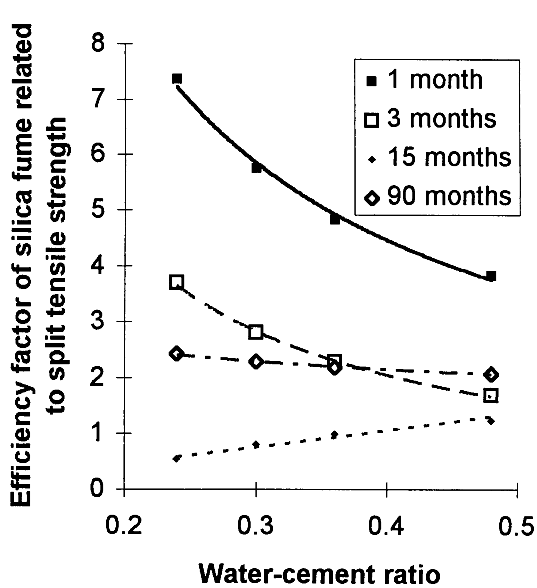

FIGURE 33. Efficiency factor of silica fume related to split tensile strength with sealed curing.

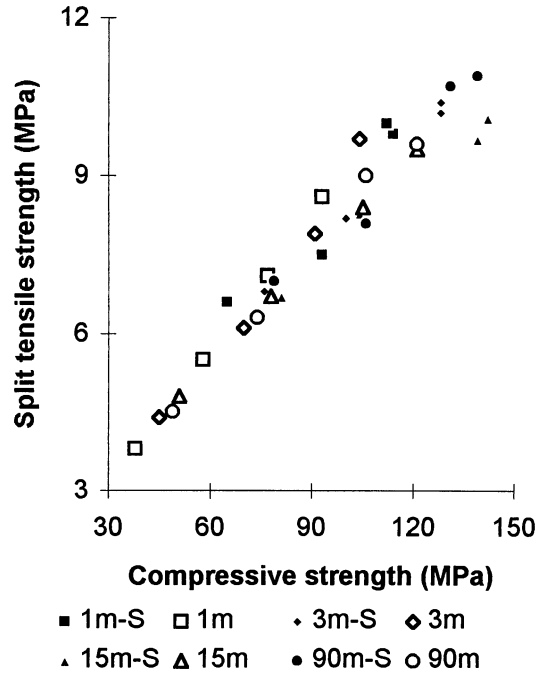

FIGURE 34. Split tensile strength vs. the compressive strength in concrete at different ages. m = months; S = 10% silica fume.

$$k_{sp}(t, w/c) = 0.58 \cdot (4.3 - t) \cdot (w/c)^{-0.095 \cdot (9 + t)}$$
$$(1 < t < 3 \text{ months}; 0.25 < w/c < 0.50; R^2 = 0.96) \quad (26)$$

$$k_{sp}(t, w/c) = 0.018 \cdot (185 - t) \cdot (w/c)^{0.019 \cdot (76 - t)}$$
$$(15 < t < 90 \text{ months}; 0.25 < w/c < 0.50; R^2 = 0.89) \quad (27)$$

where $ln(t)$ = natural logarithm of the age of the concrete t (in months).

Between 3 and 15 months' age, a substantial decrease of k_{sp} was observed, probably due to the pronounced autogenous shrinkage and microcracking that occurred in concretes with silica fume [1]; cp. the previous discussion on the importance of self-desiccation [3]. Thus, the factor k_{sp} has to be expressed by two equations due to the discontinuous behavior after 3 months' age.

Split Tensile Strength and Compressive Strength

The ratio between compressive strength and split tensile strength became lower with higher strength [4]. One explanation for this observation was the limitations due to the split tensile strength of the aggregate ($f_{sp,max} \approx 0.75 \cdot 15 = 12$ MPa). Another possible explanation for the development of the ratio between compressive and tensile strength was the pozzolanic interaction between Portland cement and silica fume. Silica fume often was used in concrete with higher strength. As mentioned previously, the pozzolanic effect of silica fume caused microcracking in the cement paste and thus lower tensile strength in comparison to the compressive strength. Figure 34 shows the split tensile strength vs. the compressive strength for a total of 864 specimens. The relationship between split tensile strength and compressive strength decreased with higher strength and age in concrete with 10% silica fume compared with concrete without silica fume. The following equations were obtained:

$$f_{sp,S} = [0.281 - 0.0144 \cdot ln(t)] \cdot (f_c)^{0.744 + 0.0109 \cdot ln(t)}$$
$$(30 < f_c < 150\, MPa; 1 < t < 90 \text{ months}$$
$$R^2 = 0.78) \tag{28}$$

$$f_{sp} = [0.144 + 0.0084 \cdot ln(t)] \cdot (f_c)^{0.902 - 0.0165 \cdot ln(t)}$$
$$(30 < f_c < 150\, MPa; 1$$
$$< t < 90 \text{ months}; R^2 = 0.83) \tag{29}$$

where f_c = compressive strength (in MPa), f_{sp} = split tensile strength (in MPa), $ln(t)$ = natural logarithm of age t (in months), R^2 = accuracy factor, and S = 10% calculated on the basis of the cement content.

After 90 months, the relationship between compressive strength and split tensile strength was not affected by the addition of silica fume. This observation confirms that the effect of silica fume related to both compressive and split tensile strengths in concrete vanished over time.

Hydration

Only sealed curing was studied regarding the efficiency factor k_{wn} related to the relative hydration w_n/w (Figure 25). To evaluate the efficiency factor, eqs 16 and 17 were used, i.e., w/c in eq 17 valid for concrete without silica fume was replaced by $(w/c)_{eff}$ according to eq 21. After this replacement of w/c in eq 17, the equations valid for concrete with and without silica fume, eqs 16 and 17, respectively, were equalized and the efficiency factor k_{sc} estimated. Figure 35 shows the efficiency factor k_{wn} related to the relative hydration w_n/w described by the following equation ($1 < t < 90$ months; $0.25 < w/c < 0.50$):

$$k_{wn}(t, w/c) = 0.043 \cdot (ln(t) + 30) \cdot ln(w/c)$$
$$- 0.006 \cdot t \cdot (1 - 0.01 \cdot t) - 0.71$$
$$(R^2 = 0.99) \tag{30}$$

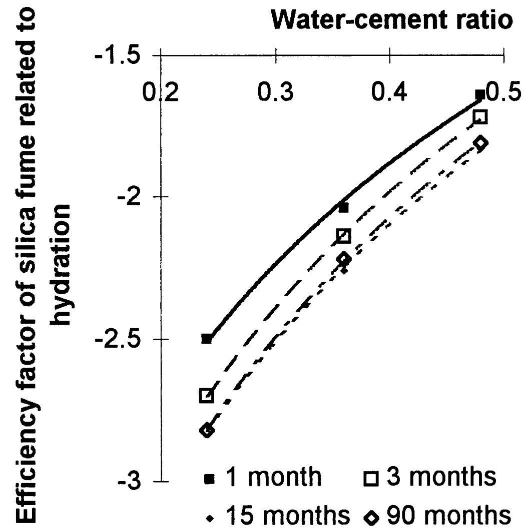

FIGURE 35. Efficiency factor of silica fume related to the relative hydration vs. water-cement ratio with sealed curing.

where $ln(t)$ = natural logarithm of the age of the concrete t (in months), and $ln(w/c)$ = natural logarithm of the age of w/c.

Naturally, the efficiency factor of 10% silica fume related to hydration became negative since the calcium hydroxide was partly or completely consumed in the pozzolanic reaction [5]. These studies confirm this well-known behavior of silica fume in concrete.

Hydration and Compressive Strength

According to Powers and Brownyard [24], a good correlation exists between relative hydration and strength.

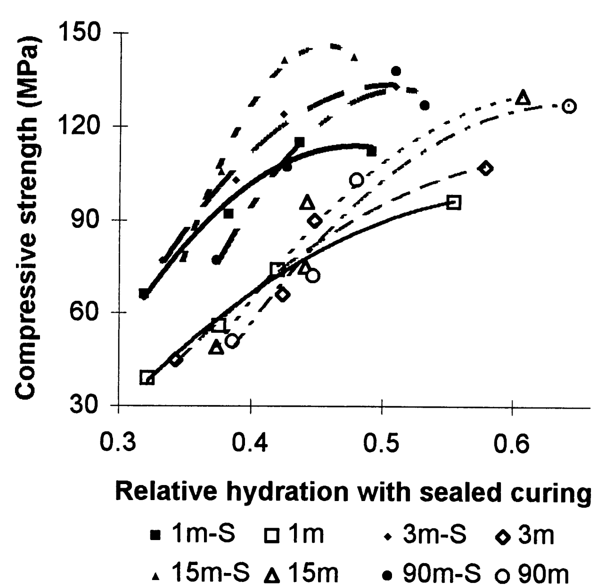

FIGURE 36. Compressive strength vs. relative hydration w_n/w with sealed curing.

The relative hydration was a substitute for the porosity. The higher the relative hydration, the lower the porosity. Thus, it was essential to carry out analysis of the relative hydration vs. strength of concretes with and without silica fume. Figure 36 shows that the interaction of Portland cement and silica fume clearly affected the relationship between relative hydration w_n/w and strength. In concrete with 10% silica fume, the maximum strength was obtained at $w_n/w \approx 0.45$ but was increasing to $w_n/w \approx 0.60$ in concrete without silica fume.

Summary and Conclusions

Large concrete specimens, about 250 kg of concrete each, were used in long-term studies of the effect of silica fume on the properties of concrete related to strength, hydration, and internal relative humidity. Half of the concretes contained 10% silica fume calculated in relation to the cement content. More than 900 cores were studied to determine their strength. More than 1850 observations were performed over 90 months. The efficiency factors of silica fume related to strength, hydration, and internal relative humidity generally showed continuous decline over time. The following conclusions were drawn.

One and 3 Months' Age

Initially, within 3 months' age, silica fume had a positive effect on all the properties of concrete (compressive and split tensile strengths and internal relative humidity) studied with the exception of hydration. The effect was pronounced on concretes with low w/c. Silica fume had larger specific effect (kg/kg) on compressive strength, split tensile strength, and internal relative humidity than cement had. The efficiency factor varied between 1.2 and 8.8 with the exception of the effect on hydration, which varied between -2.5 and -1.7 due to the pozzolanic reaction.

Fifteen Months' Age

Due to the low internal relative humidity and subsequently the slow hydration in concretes with low w/c < 0.39, silica fume still remained available for the pozzolanic interaction with the Portland cement, at least until 15 months' age. In concrete with higher w/c, the pozzolanic effect stopped before 1 month's age due to the insufficient amount of silica fume available in the mix proportions.

Ninety Months' Age

After long time periods, 90 months, the effect of silica fume on the strength development was negligible. Between 15 and 90 months' age, the efficiency factor of silica fume related to compressive strength became slightly negative compared to a concrete in which only Portland cement was used. This phenomenon was most probably explained by the pronounced self-desiccation, which consequently stopped the hydration in concretes with low w/c. In concretes with higher w/c, no more silica fume remained for the pozzolanic interaction to continue after 1 month's age. The importance of the long-term effect of the silica fume may be related to the utilization. If long-term strength growth was demanded for design reasons, the silica fume may be avoided in the concrete.

Split Tensile Strength

The pozzolanic interaction between silica fume and Portland cement also affected the autogenous shrinkage of the concrete, which most probably was the explanation for the unfavorable development of the split tensile strength in concretes with silica fume compared to concretes without silica fume. The tensile strain most probably was exceeded in concretes with silica fume and low w/c, causing early microcracking in the cement paste. As a consequence of the autogenous shrinkage in concrete of low w/c and with 10% silica in the mix proportions, the efficiency factor of silica fume related to split tensile strength declined to about 1 before 15 months' age. After 15 months' age, a rise of the efficiency factor to about 2 related to split tensile strength was observed. The rise probably was due to the healing effect of hydration in the cement occurring after 15 months' age (after the pozzolanic reaction had stopped).

Acknowledgment

Financial support of the Swedish Council for Technical Development is gratefully acknowledged.

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