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SENSITIVITY OF CONCRETE PROPERTIES TO THE PORE STRUCTURE OF HARDENED CEMENT PASTE

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ABSTRACT:

Coefficients and degrees of sensitivity are introduced to define quantitatively the sensitivity of concrete properties to the pore structure of cement paste. Proposed parameters have been applied to experimental data obtained from 60 different concrete mixtures, measuring eight properties for each mix and the results obtained have been discussed and evaluated. *Copyright © 1996 Elsevier*

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Introduction

It is known that concrete can be considered as a three-phase composite material consisting of hardened cement paste, aggregate and the interfacial region between cement paste and aggregate (1-5). Mechanical behavior, especially deformation and fracture of concrete generally exhibit the most important and complex dependence on the structure of cement paste (6,7). But, the microstructure of cement paste and the mechanical properties of concrete have generally been studied separately in the past years (8-10). It is obvious that this traditional approach has limitations and new research concepts must therefore be used (6).

There have been some attempts to apply a material science approach to study the dependence of the mechanical behavior of concrete on the structure of cement paste (9). Properties of concrete sensitive or insensitive to cement paste pore structure, which have been proposed (10,11) and a quantification of the degree of sensitivity will be emphasized here. Another paper (12) will discuss whether the coefficients of correlation between the concrete properties are affected by such degrees of sensitivity.

Coefficient of Sensitivity

Sensitive and Insensitive Properties of Concrete to the Pore Structure of Cement Paste. If a specific property of concrete is affected by the amount, but not by the type of pores (whether capillary or entrapped air) in cement paste, this property is said to be insensitive to the cement paste pore structure; if the property is affected by both the amount and type of pores it is said to be sensitive to the paste pore structure.

The Structure of Hardened Concrete. Within the limits of this paper, the structure of hardened concrete can be considered as a simplified model given in Figure 1.



FIG. 1.

The schematic representation of the structure of hardened concrete.

Gel formation has occurred starting from the surfaces of cement particles. Each 1 cm^3 of unhydrated cement has caused the formation of 2.06 cm^3 of cement gel (13,14). Capillary pores between the cement particles which were originally filled with water have been reduced due to gel formation (These pores now may be dry or filled fully or partially with water).

Now, let us calculate the decreased volume of capillary pores. The original volume of capillary pores in 1 m^3 of fresh concrete was equal to the volume of mixing water (w). Suppose that α ($0 \leq \alpha \leq 1$) is the fraction of the total absolute volume of cement particles which have been hydrated, where α is defined as the hydration degree (13,14) and that the total absolute volume of unhydrated cement in 1 m^3 of compacted concrete is c , then a gel volume of $2.06\alpha c$ forms. Thus, the decrease in capillary pore volume will be $2.06\alpha c - \alpha c = 1.06\alpha c$, from which the volume of capillary pores is $w - 1.06\alpha c$.

On the other hand, the gel volume $2.06\alpha c$ is reduced by the effects of chemical shrinkage and the shrinkage caused by the movement of gel water to the capillaries. If we call (s) the fraction decrease in gel volume from these effects, then the amount of the decrease in gel volume is $2.06\alpha cs$. This also causes the same reduction in the decrease of the volume of the capillary pores. Thus, the volume of capillary pores is

$$w - 1.06\alpha c + 2.06\alpha cs = [1 - (1.06 - 2.06s)\frac{\alpha c}{w}]w \quad (1)$$

If we call (a) the volume of entrapped air in 1 m^3 of compacted concrete, then the total volume of pores in the cement paste phase may be expressed as:

$$v = [1 - (1.06 - 2.06s)\frac{\alpha c}{w}]w + a \quad (2)$$

Coefficient of Sensitivity. Let P_{hi} be a hardened concrete property and n_i a parameter, and let us consider the values taken by P_{hi} in a sample large enough to be representative of the concrete in relation to the variable $n_i [1 - (1.06 - 2.06s)\frac{\alpha c}{w}]w + a$ by giving several values to n_i . Suppose that for $n_i = n_i^*$ the highest coefficient of correlation $[R(n_i)]_{\max}$ is obtained. By obtaining this it can be thought that the variable used is the best representation of the influence of the pore structure of cement paste on the property. Thus if $n_i^* = 1$, this means that the

volume of capillary pores and the volume of entrapped air affect the property equally. Hence, the property is insensitive to the pore structure of cement paste. If $n_i^* \neq 1$, then the volume of pores and their type affect the property, which is said to be sensitive to the pore structure of cement paste. How far n_i^* takes a value different from 1 is an indication of the different effects of the two types of pores on the property. According to this, n_i^* may be called "the coefficient of sensitivity to the pore structure of cement paste" of the property envisaged.

Determination of Sensitivity by Comparison with Unit Weight

Generally it is difficult to determine the coefficient of sensitivity defined above since α and s are probably not known exactly. But even so it is possible to determine the sensitivity of a property to the pore structure of cement paste, by using an approximate method which will be explained below.

Let us call the unit weight of concrete as Δ , which is measured when the capillary pores are dried out completely. It is obvious that Δ must be an insensitive property to the cement paste pore structure, because the decrease in unit weight caused by pores is dependent only on their total volume and not on their shapes and dimensions.

In this case if we apply the method explained above to the unit weight (Δ), the result of $n_i^* = 1$ should be obtained, in other words if we take the variable on the horizontal axis as $[1 - (1.06 - 2.06s)\frac{\alpha c}{w}]w + a$ we must obtain the greatest coefficient of correlation.

In the last variable, the multiplier $[1 - (1.06 - 2.06s)\frac{\alpha c}{w}]$ in front of w has a different value for each concrete in the series. In spite of this, let us investigate the variation of Δ 's in the concrete series in relation to the variable $(kw + a)$ by giving several values to k , where k is a parameter. Suppose that the highest value of correlation coefficient is obtained for a specific value of $k = k_0$. This k_0 value can be considered as a kind of parameter of central tendency of the $[1 - (1.06 - 2.06s)\frac{\alpha c}{w}]$ values. An approximate verification of this idea will be given later.

Now let us investigate the variation of another property P_{hi} other than Δ , with respect to the $(kw + a)$ variable. Suppose the highest coefficient of correlation is obtained for $k = k_i^*$. Here, thinking as above, this k_i^* value can be considered as a parameter of central tendency of $n_i^* [1 - (1.06 - 2.06s)\frac{\alpha c}{w}]$ values (on the other hand, it can be said that $k_i^* / k_0 \approx n_i^*$, see the next paragraph). If $k_i^* = k_0$ (then $n_i^* \approx 1$), this means that P_{hi} is insensitive to the cement paste pore structure. If $k_i^* \neq k_0$ (then $n_i^* \neq 1$), P_{hi} is said to be sensitive to the cement paste pore structure.

Degrees of Sensitivity

Type 1 Sensitivity Degree of a Property to the Pore Structure of Cement Paste. For any (P_{hi}) concrete property, let us call $k_i^* / k_0 = (SD1)_i = \text{Type 1 sensitivity degree of this } (P_{hi}) \text{ property}$. It was mentioned above that k_0 is a parameter of central tendency of $[1 - (1.06 - 2.06s)\frac{\alpha c}{w}]$ values and k_i^* is of $n_i^* [1 - (1.06 - 2.06s)\frac{\alpha c}{w}]$ values; (n_i^*) the coefficient of sensitivity, was constant for a certain concrete property.

Let \bar{x} be a parameter of central tendency of x variables in a group, λ being a constant coefficient; if $\lambda\bar{x}$ is the same parameter of central tendency of (λx) 's, we write $\lambda\bar{x} = \lambda \bar{x}$. Similarly here between k_o and k_i^* , we can write $k_i^* = n_i^* \cdot k_o$. However, here the parameters of central tendencies k_o and k_i^* have not been calculated completely by the same manner. In the calculation of k_o , the vertical axis is Δ while in that of k_i^* , the vertical axis is (P_{hi}) .

Therefore, it can be seen that there is an approximation in the above equality which can be written $k_i^* \approx n_i^* \cdot k_o$. Thus, we have

$$(SD1)_i = \frac{k_i^*}{k_o} \approx n_i^* \quad (3)$$

Thus it can be seen that $(SD1)_i$ Type 1 sensitivity degree of a concrete property P_{hi} is approximately equal to n_i^* sensitivity coefficient of the same property defined above.

Type 2 Sensitivity Degree of Properties to the Pore Structure of Cement Paste. For any P_{hi} concrete property, the Type 2 sensitivity degree $(SD2)_i$ is defined as:

$$(SD2)_i = \frac{R(k_i^*)}{R_i(k_o)} \quad (4)$$

where, $R(k_i^*)$ = the highest coefficient of correlation when the variation of the concrete property P_{hi} is calculated with respect to $(kw + a)$ by allocating different values to the k parameter. $R_i(k_o)$ = the correlation coefficient obtained by allocating the value k_o to parameter k in the same investigation of the P_{hi} concrete property (k_o gives the maximum correlation coefficient for unit weight).

According to this, $(SD2)_i$ indicates how much the correlation of the P_{hi} property degenerates with respect to the $(kw + a)$ variable when the sensitivity of P_{hi} is not taken account of and P_{hi} is considered as insensitive.

$(SD2)_i$ can be defined in terms of n coefficients as:

$$(SD2)_i = \frac{R(n_i^*)}{R(n_i = 1)} \quad (5)$$

Here; $R(n_i^*)$ = the highest correlation coefficient obtained when the variation of the P_{hi} property is calculated with respect to the $n_i[w - (1.06 - 2.06s)\alpha c] + a$ variable, by giving several values to the parameter n_i . $R(n_i = 1)$ = the correlation coefficient obtained in the same manner by allocating the value of 1 to the parameter n_i .

Experimental Work

To verify the concepts proposed in this paper experimental work has been performed, where 60 concrete mixtures, whose compositions vary randomly within practical limits of application, have been prepared. The origins of coarse aggregates and sands in batches have been randomly changed, all being normal density aggregates. The sources of cements and their production dates have also been randomly changed, all being ordinary Portland cements (Type I) or Portland-Pozzolana blended cements (Type IP).

Cylindrical specimens with a diameter of 150 mm and height of 300 mm and cubic specimens of 200 mm size were cast. These were demoulded after 24 hours, and then moist-

cured for 7 days under polyethylene sheets and wet burlap. After that, they were kept in air at temperatures between 10°C and 25°C for different mixtures. Specimens used in unit weight determination were dried at 105°C in the oven before the measurements.

The following properties have been measured for each mixture on the 28th day:

- Unit weight (Δ)
- Ultrasonic pulse velocity perpendicular to the casting direction, measured on cubes (V_c)
- Ultrasonic pulse velocity on cylinders measured in the direction of the axis (V_s).
- Rebound number by Schmidt's Hammer measured on cubes (S)
- Splitting tensile strength measured on cylinders (T_s)
- Cube compressive strength (fcc)
- Cylinder compressive strength (fcs)
- Modulus of elasticity (E) under compressive loading measured on cylindrical specimens.

Cement contents (C), amounts of mixing water (w), air volumes (a) and fineness modulus of aggregate mixtures (m) in 1m³ of concretes produced are given in Table 1 with the measured values of 8 properties mentioned above. Fineness moduli are calculated according to the sieve series with circular openings described in the previous DIN 1045 specification. The maximum particle size in all concretes is 30 mm.

Sensitivity Degrees Obtained According to Various Functions of (kw+a). Linear regression analysis has been done between the variables (kw+a) and the properties P_{hi} in the form

$$P_{hi} = A(kw+a) + B \quad (6)$$

where A and B are regression constants. In these calculations the k parameter has been changed by increments of 0.05; the k value giving the highest coefficient of correlation for unit weight has been called k_0 and the k value which gives the highest coefficient of correlation for any other P_{hi} property has been called k_i^* . The value k_0 has been found as 0.45.

To verify the idea that the value k_0 can be considered as a kind of parameter of central tendency of $[1-(1.06-2.06s) \alpha c/w]$ values, neglecting the effect of shrinkage and taking α values from reference (15), the arithmetic mean of $(1-1.06 \alpha c/w)$ values of all mixtures has been calculated as 0.48, which is close to the 0.45 value calculated above for k_0 .

Using eq.(6), k_i^* values and (SD1)'s (Eq.(3)), $R(k_i^*)$'s, $R_i(k_0)$'s and (SD2)_i's (Eq.(4)) were also calculated. Further calculations used the following more developed functions of (kw + a):

$$P_{hi} = A \left(\frac{c}{kw+a} \right) + B \quad (7)$$

$$P_{hi} = A (c + w + a) + B \left(\frac{c}{kw+a} \right) + C \quad (8)$$

$$P_{hi} = A (c + w + a) + B \left(\frac{c}{kw+a} \right) + C m + D \quad (9)$$

m being the fineness modulus of aggregate mixture and A,B,C and D being constants.

TABLE 1

Data Related to the Composition and Properties of Mixtures

Mix No	C (kg/m ³)	W (dm ³ /m ³)	a (dm ³ /m ³)	m	Δ (kg/m ³)	V _c (km/sec)	V _a (km/sec)	S	f _α (N/mm ²)	f _α (N/mm ²)	T _a (N/mm ²)	E (N/mm ²)
1	349	212	5	3.24	2360	4.97	4.76	34.5	30.4	28.6	2.99	31800
2	393	214	16	3.24	2350	4.89	4.82	34.9	32.8	28.4	2.59	30100
3	347	216	1	3.24	2317	4.68	4.64	29.9	26.5	24.9	2.45	28900
4	300	173	18	3.24	2369	4.85	4.84	30.3	26.5	22.3	2.37	31400
5	352	186	9	3.24	2342	4.94	4.90	31.9	26.8	27.3	2.47	32100
6	350	178	12	3.24	2396	5.11	5.07	34.0	30.5	32.3	2.62	37000
7	347	162	14	3.24	2396	5.51	5.31	36.8	42.2	42.7	3.36	42300
8	297	175	16	3.24	2276	4.55	4.65	35.6	36.7	32.1	3.11	25700
9	299	170	12	3.24	2345	5.05	4.89	32.5	29.9	25.5	2.46	34500
10	323	142	19	3.33	2332	4.84	4.60	36.0	35.0	31.5	3.09	27800
11	318	182	11	3.24	2352	4.61	4.72	35.0	29.0	24.1	2.03	32300
12	391	231	13	3.24	2360	4.80	4.69	31.4	23.2	20.8	2.30	33700
13	300	150	10	3.24	2310	5.04	4.87	32.1	25.6	23.5	2.39	35100
14	300	180	12	3.24	2237	4.65	4.76	24.9	21.4	20.5	1.94	36600
15	350	160	8	3.24	2323	5.04	4.85	31.4	36.1	28.1	2.96	36300
16	401	181	13	2.82	2289	4.66	4.58	33.1	33.3	27.8	2.17	31400
17	349	230	10	2.82	2254	4.40	4.44	26.0	15.1	13.1	1.13	25800
18	342	137	79	2.82	2252	5.00	4.75	34.3	33.3	28.0	2.34	34300
19	304	146	39	2.82	2298	4.92	4.72	33.2	29.3	25.6	2.14	32500
20	315	151	79	2.82	2188	4.71	4.71	28.4	28.6	23.5	2.17	35700
21	336	145	23	2.82	2362	5.06	5.01	38.0	40.6	41.0	3.13	44000
22	289	182	50	2.82	2274	4.54	4.58	26.9	17.1	17.0	1.74	34600
23	291	198	30	2.82	2243	4.28	4.36	33.9	17.1	16.7	1.58	27500
24	399	160	36	2.82	2297	4.76	4.68	42.8	35.9	25.5	2.58	29100
25	309	164	26	2.82	2340	4.74	4.59	34.6	26.9	23.9	2.60	28900
26	298	158	36	2.82	2258	4.67	4.68	31.2	19.0	16.6	1.85	34200
27	304	197	5	2.82	2314	4.43	4.37	32.2	25.3	19.5	2.34	26000
28	300	195	26	2.82	2230	4.41	4.32	30.1	21.8	18.6	1.89	24300
29	590	265	0	2.82	2352	4.88	4.79	38.4	32.9	27.5	2.89	33900
30	301	181	27	2.82	2336	4.42	4.40	25.2	22.0	19.2	1.94	25500
31	339	169	34	2.48	2244	4.46	4.22	35.3	28.1	22.9	2.40	24400
32	312	187	28	2.46	2230	4.34	4.27	30.6	16.9	15.4	1.48	25400
33	307	169	33	2.40	2298	4.64	4.59	33.4	23.3	20.3	2.32	29100
34	304	198	38	2.46	2198	4.33	4.16	30.8	18.4	16.7	1.81	21900
35	298	211	38	2.45	2164	4.26	4.28	29.2	13.1	12.7	1.31	27300
36	293	220	56	2.28	2100	3.84	3.54	25.8	12.8	12.2	1.49	15800
37	284	193	57	2.31	2084	3.88	3.72	29.6	16.3	14.2	1.54	17400
38	322	200	12	2.22	2233	4.34	4.23	30.4	24.3	22.4	2.13	23600
39	338	180	37	2.62	2226	4.30	4.10	31.4	24.5	22.3	2.28	21900
40	268	134	82	2.43	2170	4.29	3.98	24.8	17.9	14.7	1.50	20400
41	320	240	17	2.62	2200	3.82	3.62	22.2	14.2	13.8	1.34	17400
42	307	190	7	2.57	2304	4.44	4.38	29.4	24.7	18.3	2.05	29200
43	323	217	22	2.56	2250	4.02	4.08	28.4	15.5	15.8	1.90	22300
44	268	146	33	2.45	2257	4.48	4.36	33.1	22.8	19.5	2.07	26300
45	269	178	37	2.45	2251	4.09	4.03	26.7	18.1	16.0	1.77	23000
46	343	240	55	1.85	2040	3.64	3.60	22.2	13.2	12.4	1.40	15100
47	285	157	97	1.85	2102	4.18	4.00	26.9	16.9	13.8	1.67	23200
48	312	203	68	1.85	2081	4.07	3.86	27.2	17.7	14.7	1.79	19800
49	338	203	68	1.85	2128	4.21	4.04	28.4	21.7	19.2	1.95	21500
50	307	231	17	1.85	2130	4.16	4.28	28.0	18.2	18.6	1.97	23300
51	321	200	61	1.85	2095	4.28	4.24	29.2	23.7	20.2	2.04	23600
52	352	193	35	1.85	2193	4.56	4.46	32.7	32.7	28.7	2.45	26100
53	305	207	46	1.85	2184	4.25	4.30	29.4	21.4	19.7	2.43	21400
54	319	207	57	1.85	2115	3.98	4.16	29.5	18.8	16.4	1.96	26500
55	354	265	19	1.85	2152	3.75	3.86	29.2	14.3	15.8	1.31	22300
56	316	196	54	1.85	2196	3.98	3.96	27.5	13.9	11.4	1.47	20400
57	340	197	57	1.85	2174	4.10	4.22	29.0	21.6	19.4	1.97	26700
58	336	229	55	1.85	2130	3.82	3.83	27.2	15.7	12.9	1.54	19800
59	330	235	22	1.85	2178	4.07	4.01	29.2	17.6	15.8	1.53	22800
60	305	274	35	1.85	2146	3.68	3.62	14.4	7.5	7.1	0.82	14500

The results obtained are given in Table 2; however the (SD1)'s are not mentioned in this Table because they did not have stable values with the different functions. It has also been found that (12), the (SD1)'s are not successful in clarifying correlations between properties. For these reasons only the (SD2)'s are given in Table 2.

Comparison of Functions Used for Expressing the Properties. When $R(k_i^*)$ values given by different functions are compared (see Table 2) it can be seen that those using Eq.(9) are the highest. Only for compressive and splitting-tensile strengths are the values given by Eq.(8) equal to them. All $R(k_i^*)$ correlation coefficients given by Eqs.(6) and (7) are smaller. According to this, higher correlation coefficients have been obtained using functions containing more variables, which is an expected result.

The relations between properties and composition with highest correlation coefficients are given in Table 3. Although it is possible to obtain higher correlation coefficients with non-

TABLE 2
Type 2 Sensitivity Degree of Properties

Properties	Function (6)				Function (7)			
	k_i^*	$R(k_i^*)$	$R_i(k_{oi})$	$(SD2)_i$	k_i^*	$R(k_i^*)$	$R_i(k_{oi})$	$(SD2)_i$
Δ	0.45	0.859	0.859	1.00	0.55	0.822	0.822	1.00
V_c	0.85	0.795	0.738	1.08	1.50	0.842	0.781	1.08
V_s	0.70	0.775	0.747	1.04	1.10	0.800	0.770	1.04
S	0.85	0.611	0.568	1.08	1.80	0.772	0.682	1.13
f_{cc}	0.90	0.702	0.643	1.09	1.85	0.878	0.785	1.12
f_{cs}	0.75	0.686	0.652	1.05	1.45	0.827	0.768	1.08
T_s	0.75	0.669	0.637	1.05	1.30	0.794	0.748	1.06
E	0.80	0.702	0.657	1.07	1.45	0.752	0.702	1.07
Δ	0.35	0.873	0.873	1.00	0.45	0.908	0.908	1.00
V_c	1.40	0.875	0.821	1.07	2.75	0.908	0.858	1.06
V_s	0.95	0.835	0.808	1.03	1.50	0.865	0.841	1.03
S	1.80	0.773	0.644	1.20	1.65	0.775	0.678	1.14
f_{cc}	1.85	0.882	0.759	1.16	1.90	0.882	0.786	1.12
f_{cs}	1.40	0.834	0.752	1.11	1.45	0.834	0.774	1.08
T_s	1.25	0.801	0.737	1.09	1.25	0.801	0.756	1.06
E	1.30	0.778	0.731	1.06	2.45	0.807	0.765	1.06

TABLE 3

Relations Between Properties and Composition with Highest Correlation Coefficients

Property	Relation	Correlation coefficient
Δ (kg/m ³)	$\Delta = -0.328(c+w+a) + 177 \text{ c}/(0.45w+a) + 75.9m + 1990$	0.908
V_c (km/sec)	$V_c = -0.00115(c+w+a) + 6.61 \text{ c}/(2.75w+a) + 0.318m + 2.73$	0.908
V_s (km/sec)	$V_s = -0.00118(c+w+a) + 3.24 \text{ c}/(1.50w+a) + 0.293m + 2.92$	0.865
S	$S = -0.00871(c+w+a) + 63.9 \text{ c}/(1.65w+a) - 0.788m + 15.5$	0.775
f_{cc} (N/mm ²)	$f_{cc} = -0.0153(c+w+a) + 132 \text{ c}/(1.90w+a) + 0.339m - 8.49$	0.882
f_{cs} (N/mm ²)	$f_{cs} = -0.0170(c+w+a) + 82.5 \text{ c}/(1.45w+a) + 0.601m - 3.98$	0.834
T_s (N/mm ²)	$T_s = -0.00154(c+w+a) + 5.34 \text{ c}/(1.25w+a) + 0.0175m + 0.407$	0.801
E (N/mm ²)	$E = -13.6(c+w+a) + 83600 \text{ c}/(2.45w+a) + 4430m + 2130$	0.807

linear multiple regression analysis, in this paper and in Ref. (12) only the linear ones have been used.

In the previous paragraph, it has been shown that with functions containing more variables, properties can be better correlated to the internal structure of concrete. On the other hand, the following questions may rise: What is the situation regarding sensitivity degrees? Through which type of functions can more significant sensitivity degrees be obtained? We believe that in answering these questions it will be necessary to consider the relations between the properties and to compare the correlation coefficients of these relations with the closeness of sensitivity degrees of properties. This topic will be investigated in Ref. (12).

Conclusions

In this paper, it has been shown that sensitivity of concrete properties to the pore structure of cement paste can be quantitatively defined by sensitivity degrees. The second of the sensitivity degrees defined here, takes more stable values than the first for different functions, which relate the properties of concrete to its internal structure, and thus it is more significant.

To understand from which function the degree of sensitivity obtained is more significant, it is necessary to investigate the correlations between the concrete properties. This investigation is the subject of our next paper (12).

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