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Modified water/cement ratio law for compressive strength of fly ash concretes

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Experimental data are presented which suggest that the development of compressive strength of fly ash concretes can be explained by superposition of two independent mechanical pore-filling mechanisms in the cement–fly ash paste. It is also suggested that the traditional water/cement ratio law for ordinary Portland cement concretes can be applied to fly ash concretes, provided that a slight modification is introduced. This will be of assistance in the design of fly ash concrete mixes for compressive strength.

1. INTRODUCTION

Design of normal Portland cement concrete mixes without fly ash is a simple matter. Although many different methods are used in practice, such as the procedures developed by ACI [1] in the United States and by DoE [2,3] in the United Kingdom, all concrete mix design methods are based on the same two well-established principles.

The first principle is the water/cement ratio law, which states that for given materials, age and curing conditions, the strength of hardened concrete is determined exclusively by the ratio, by weight or volume, between the content of free water and the content of cement in the concrete mix. Thus, the strength of hardened Portland cement concrete is independent of the absolute contents of free water and cement in the mix.

The second principle is the rule of constant water content, which states that for given materials, the consistency of fresh Portland cement concrete is determined exclusively by the free water content of the concrete mix. Thus, the consistency of fresh concrete is independent of the absolute cement content of the mix.

Although these two basic principles of concrete mix design are approximations rather than true physical laws, they remain valid and useful within wide limits of concrete mix proportions. However, when fly ash from coal-fired power plants is used as a mineral additive to normal Portland cement concrete, the mix design becomes more complex than for pure Portland cement concrete mixes. It is the purpose of this paper to demonstrate that a modified water/cement law applies to hardened fly ash concretes. In a further paper to be published shortly in this journal, it will also be shown that a modified rule of constant water content applies to the consistency of fresh fly ash concrete mixes.

2. THEORY

2.1 Mechanism of strength development in normal Portland cement concretes

In this paper we shall first deal with the mechanism of strength development of pure Portland cement concretes, which are produced without addition of any fly ash. Hansen [4] considered the simplest possible geometrical and mechanical model of the structure of hardened concrete. It consists of a single spherical capillary pore, located at the centre of a cube of solid cement gel. Assuming that the strength s of the cement paste is proportional to the cross-sectional area of solid matrix matter, here cement gel, in a plane through the centre of the pore, perpendicular to the direction of the applied uniaxial compressive load, Hansen [4] found that the following equation relates s to the free water/cement ratio w/c, the degree of hydration of cement m, where $0 < m < 1$, and the strength of hydrated Portland cement gel s_0:

$$s = \left[1 - 1.22\left(\frac{(w/c) - 0.36m}{(w/c) + 0.32}\right)^{0.66}\right]s_0 \qquad (1)$$

Hansen [4] then proceeded to show that Equation 2 is a linear and almost perfect approximation to Equation 1 within the geometrical limitations of the model:

$$s = A\frac{c}{w} + E \qquad (2)$$

where s = strength of concrete (MPa), c = cement content of concrete (kg m^{-3}), w = free water content of concrete (kg m^{-3}), and A, E = constants for given materials, age and curing conditions of concrete.

Equation 2 was first suggested on a purely empirical basis by Bolomey [5] in 1927, and it has successfully formed the basis of practical concrete mix design in many European countries for more than half a century. Incidentally, Bolomey's Equation 2 gives results very similar to Abrams' law, which should put American concrete engineers at ease.

It will follow from what is said above that Bolomey's law, as it is popularly called in Europe, and as it is expressed in Equation 2, involves nothing but an assumption of the simplest possible pore-filling model which can be imagined for any porous solid matter, whether metallic, organic or ceramic.

The exact mathematical expression for this pore-filling mechanism is a power function as shown in Equation 1, but Bolomey's Equation 2 is linear and therefore easier to use in practice. The fact that Equation 1 can be approximated by a linear function is purely accidental, and not based on any physical theory.

2.2 Mechanism of strength development in fly ash concretes

According to ACI, fly ash is defined as 'the finely divided residue resulting from the combustion of ground or powdered coal which is transported from the firebox in coal-fired power plants through the boiler by flue gases'. Fly ash is a pozzolanic material. According to ACI, a pozzolan is defined as 'a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.'

When Portland cement hydrates in concrete, crystalline calcium hydroxide is formed at the same time as colloidal cement gel. Eventually, this calcium hydroxide reacts with fly ash in concrete to form a colloidal gel which is similar in structure and properties to the gel which is formed when Portland cement hydrates. Therefore, it seems likely that the strength development of Portland cement concrete to which fly ash is added may be due to the superposition of two mechanically independent pore-filling mechanisms. One mechanism is probably due to pore-filling caused by hydration of Portland cement. The other mechanism is probably due to exactly the same kind of pore-filling, only caused by reaction between fly ash, water and calcium hydroxide.

If the mechanism of strength development of fly ash concrete is so simple, it should be possible to express the strength development of fly ash concrete in terms of a modified Bolomey equation:

$$s_f = A\frac{c}{w} + B\frac{f}{w} + E \tag{3}$$

where s_f = strength of fly ash concrete (MPa), c = cement content of concrete (kg m^{-3}), f = fly ash content of concrete (kg m^{-3}), w = free water content of concrete (kg m^{-3}) and A, B, E = constants for given materials, age and curing conditions of concrete.

Experience with many different fly ashes and concrete mixes indicates that the numerical value of E changes very little when fly ash is added to concrete. Therefore, we tentatively assumed that the numerical value of E is the same in Equations 2 and 3. Our experimental data later confirmed that this is a reasonable assumption.

From Equation 3 we obtain

$$s_f = A\left(\frac{c + k_s f}{w}\right) + E \tag{4}$$

The same nomenclature is used in Equation 4 as in Equations 2 and 3. However, in addition a so-called cementing efficiency index of fly ash k_s is introduced in Equation 4, which does not appear in Equation 2 or 3. The numerical value of k_s depends on given materials, as well as on the age and curing conditions of concrete. k_s takes into account the reactivity of fly ash with respect to strength compared to the reactivity of cement. Thus, if $k_s = 0.2$ it would take five times as much fly ash by weight to replace a certain amount of cement, in order to maintain the concrete strength. It will be seen that $k_s = B/A$.

On an empirical basis, Equation 4 was first suggested by Smith [6] in 1967 and it has formed the basis of most fly ash concrete mix design methods developed ever since. However, there has always been some doubt concerning the accuracy of predictions of fly ash concrete on the basis of Equation 4, and concerning the limits to fly ash content and concrete curing time within which Equation 4 can be safely applied.

It has been the purpose of this investigation to study how well experimental strength results for fly ash concretes correlate with the modified Bolomey Equation 4 for concretes made with different Portland cements and fly ashes of various origin. Fly ash contents and curing ages of concretes have also been varied systematically in this study.

3. EXPERIMENTAL PROCEDURE

3.1 Experimental design

Compressive strengths of five series of fly ash concretes were determined after 14, 28, 56 and 112 days of curing in water at 20°C (Table 1). In each of the series Nos 1 to 4, 27 different concrete mixes were produced with those combinations of c/w and f/w ratios which are shown by crosses in Fig. 1. In series No. 5, which was produced with white Portland cement and Asnæs fly ash, 67 different mixes were produced with the combinations of c/w and f/w ratios shown by circles in Fig. 2. Certain mixes were also produced with superplasticizers or water-thickeners, which will be apparent from Tables 4 and 5 below.

Table 1 Five series of fly ash concrete included in the investigation

Material	Series identification No.				
	1	2	3	4	5
Cement	SRPC	SRPC	OPC	OPC	White
Fly ash	Asnæs	Thy	Asnæs	Thy	Asnæs

SRPC = sulphate-resistant Portland cement, OPC = ordinary Portland cement.

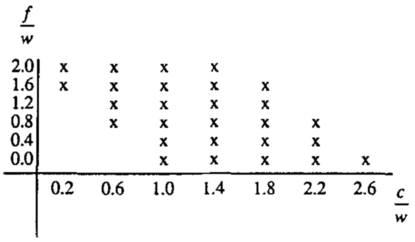

Fig. 1 In each of the series Nos 1–4, 27 different concrete mixes were produced with the combinations of c/w and f/w ratios shown by crosses. Complete concrete mix proportions for all mixes are presented in Table 4.

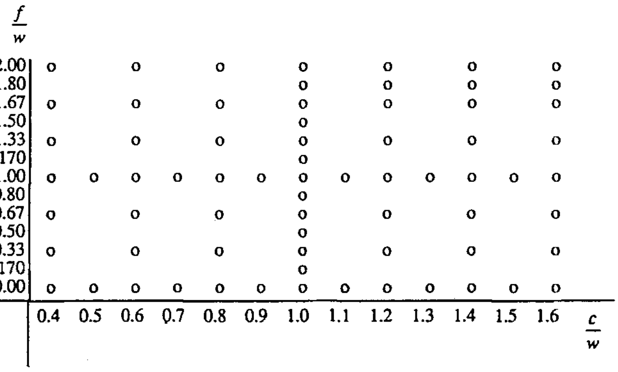

Fig. 2 In series No. 5, 49 different concrete mixes were produced with the combinations of c/w and f/w ratios shown by circles. Complete concrete mix proportions are shown for all mixes in Table 5.

3.2 Materials

Three different Portland cements were used. SRPC is a low-alkali sulphate-resistant Portland cement from Aalborg in Denmark. It is somewhat similar to ASTM type IV and V cements. OPC is an ordinary Portland cement from Slite in Sweden. It is somewhat similar to ASTM Type I and II cements. White cement is a white-coloured rapid-hardening Portland cement from Aalborg in Denmark. It has somewhat similar properties to an ASTM type III cement, but it is lower in alkalis and C_3A contents. None of the three cements contained any fly ash as received from the factory. Chemical compositions of the three cements are shown in Table 2.

Table 2 Chemical composition of cements

Item	SRPC cement (%)	OPC cement (%)	White cement (%)
SiO_2	24.43	19.84	24.25
Al_2O_3	2.33	2.08	1.78
Fe_2O_3	2.88	2.08	0.33
CaO	66.00	63.47	68.37
MgO	0.63	3.00	0.52
SO_3	2.08	2.88	2.05
Loss on ignition	0.80	2.42	1.86
Total	99.15	97.74	99.26
Total alkalis			
K_2O	0.18	1.25	0.03
Na_2O	0.16	0.21	0.09
$Na_2O_{eqv.}$	0.28	1.03	0.11
Water-soluble alkalis			
K_2O	0.04	1.10	0.008
Na_2O	0.02	0.13	0.023
$Na_2O_{eqv.}$	0.05	0.85	0.028

Table 3 Chemical composition of fly ashes

Item	Asnæs (%)	Thy (%)
SiO_2	54.92	63.58
Al_2O_3	30.26	21.18
Fe_2O_3	5.55	6.31
CaO	3.24	2.81
MgO	1.17	1.42
SO_3	0.22	0.51
Loss on ignition	2.23	2.75
Total	97.18	98.51
TiO_2	1.36	0.88
Total alkalis		
K_2O	1.45	2.00
Na_2O	0.37	0.70
$Na_2O_{eqv.}$	1.32	2.02
Water-soluble alkalis		
K_2O	0.35	0.56
Na_2O	0.09	0.18
$Na_2O_{eqv.}$	0.32	0.55

Two different fly ashes were used. Both are commercially available in Denmark. Chemical compositions of the fly ashes are shown in Table 3. Asnæs fly ash has a density of 2200 kg m^{-3} and contains 47 wt% of particles larger than 75 μm. Thy fly ash has a density of 2260 kg m^{-3} and contains 57 wt% of particles larger than 75 μm. Asnæs fly ash was derived from the burning of Polish coals. Thy fly ash was derived from the burning of Columbian coals.

Pure quartz sand from Voervadsbro was used as fine aggregate and 8 mm max. size crushed granite from Rønne was used as coarse aggregate for production of all concretes. Both Voervadsbro and Rønne are locations in Denmark and both aggregates were chosen because they are known to be innocuous regarding alkali–aggregate reactions.

3.3 Concrete mix proportions and testing programme

With fixed c/w and f/w ratios by weight as shown in Figs 1 and 2, all concrete mixes were designed according to DoE recommendations [2,3] with a slight modification as to the selection of optimum proportions of fine aggregate in fly ash concretes. Mix proportions of all concretes in the five series are presented in Tables 4 and 5. For some mixes in series Nos 1 to 5, which were particularly rich in cement or fly ash or both, it was necessary to add a diluted solution of the sodium salt of a naphthalene sulphonic acid–formaldehyde concentrate (Protex PSP-R) as a superplasticizer in order to achieve a fresh concrete slump of 30–90 mm, which was required for all mixes. For some mixes in series No. 5, which were particularly lean in cement or fly ash or both, it was necessary to add a water-thickener (Polyox WSR-301) in the form of polyethylene oxide in order to avoid excessive bleeding (see Tables 4 and 5). However, the main parameters in the investigations, which are the c/w and f/w ratios by weight, were carefully maintained on the basis of free water content even when additives were used.

Twenty-four 60 mm by 120 mm cylindrical test specimens were cast from each mix in series Nos 1 to 4, and five specimens were tested for compressive strength after 14, 28, 56 and 112 days of continuous curing in water at 20°C. From each individual mix in series No. 5, a total of 20 100 mm by 200 mm cylinders were cast, cured in water at 20°C, and five specimens from each mix were tested after 14, 28, 56 and 112 days. Because of the different specimen sizes used in series Nos 1 to 4 and in series No. 5, absolute values of compressive strength test results in the two sets of series cannot be directly compared.

4. RESULTS

Mean compressive strength test results and corresponding standard deviations from series Nos 1 to 5 are presented in Tables 6–10.

5. DISCUSSION

For all five series of concretes which were studied it has been tested statistically how accurate the experimental test results conform to predictions by Equation 3. A multi-linear regression analysis, based on the least-squares method, has been used to calculate the best linear model as well as the best estimates for the constants A, B and E in each case.

In the analysis each of the mean strength test results has been weighted according to the ratio between the mean strength and the standard deviation. By using this procedure it is assured that the strength for each concrete mix only counts in the analysis with a weight which depends on how accurately the mean strength is determined, independent of the level of strength. The statistical procedure employed, known as SAS-GLM-REG, is described by Sall [7].

Results of the regression analysis are presented in Table 11 concerning the best estimates of A, B and E in the modified Bolomey Equation 3. Resulting coefficients of correlation R^2 and cementing efficiency indices k_s for Equation 4 are also included in Table 11.

When dealing with concrete, which by nature is an extremely variable material, a coefficient of correlation R^2 above 0.95 in a statistical regression analysis usually indicates good correlation between a hypothetical model of concrete and corresponding experimental data. The maximum theoretically possible R^2 value of 1.00 would indicate perfect correlation between theory and experiments. Because of unavoidable experimental scatter, R^2 values above 0.95 are seldom obtained for any experimental tests on concrete.

Considering that all R^2 values except one in our experiments are at 0.95 or above, it may be concluded that there is very good correlation with Equation 3 and therefore between the predictions based on the proposed theory of strength development of fly ash concretes on the one hand, and experimental data on the other. Thus, it is suggested that the theory of strength development of fly ash concretes as presented in this paper, as well as the modified water cement ratio law, may be accepted as reasonable working hypotheses.

6. CONCLUSIONS AND SUMMARY

Experimental data are presented which suggest that development of strength in fly ash concretes may be due to two mechanically independent pore-filling mechanisms in the concretes. One mechanism is due to the hydration of Portland cement. The other mechanism is due to reaction of fly ash. Moreover, it is postulated that the traditional water/cement ratio for normal Portland cement concrete which is produced without fly ash can be modified in the following way for fly ash concretes:

> For given materials, age and curing conditions, the strength of hardened concrete is determined exclusively by the ratio between the content of free water and Portland cement in the concrete, jointly with the ratio between the content of free water and fly ash. Thus, the strength of fly ash concrete is independent of the absolute content of free water, Portland cement and fly ash in the concrete.

Experimental evidence is presented to support the hypothesis that the strength of fly ash concrete can be estimated by means of a modified Bolomey equation (Equation 3). The results of multilinear statistical

Table 4 Mix proportions of concretes in series Nos 1–4, with aggregate in a saturated and surface-dry condition. A superplasticizer, Protex PSP-R, was used. No water-thickener was used in these concretes

c/w	f/w	Cement (kg)	Ash (kg)	Water (kg)	Sand (kg)	Stone (kg)	Additive weight (‰)[a]	c/w	f/w	Cement (kg)	Ash (kg)	Water (kg)	Sand (kg)	Stone (kg)	Additive weight (‰)[a]
SRPC reference mixes without fly ash								*OPC reference mixes without fly ash*							
1.0	0.0	200	0	200	863	1054	0.0	1.0	0.0	200	0	200	846	1060	0.0
1.4	0.0	273	0	195	744	1156	0.0	1.4	0.0	273	0	195	732	1116	0.0
1.8	0.0	351	0	195	690	1126	0.0	1.8	0.0	351	0	195	670	1147	0.0
2.2	0.0	429	0	195	625	1112	0.0	2.2	0.0	425	0	193	607	1122	0.0
2.6	0.0	507	0	195	585	1086	2.3	2.6	0.0	507	0	195	565	1096	0.0
Series 1: SRPC mixes with Asnæs fly ash								*Series 3: OPC mixes with Asnæs fly ash*							
0.2	1.6	34	275	172	630	1169	0.0	0.2	1.6	35	282	176	606	1160	4.2
0.2	2.0	36	360	180	574	1113	4.2	0.2	2.0	36	360	180	547	1115	3.4
0.6	0.8	105	140	175	720	1174	0.0	0.6	0.8	106	141	176	696	1180	0.0
0.6	1.2	108	216	180	648	1152	0.0	0.6	1.2	106	211	176	624	1168	0.0
0.6	1.6	108	288	180	582	1131	0.0	0.6	1.6	108	288	180	562	1126	3.2
0.6	2.0	108	360	180	543	1083	3.9	0.6	2.0	106	352	176	524	1099	7.3
1.0	0.4	180	72	180	741	1159	0.0	1.0	0.4	180	72	180	721	1166	0.0
1.0	0.8	180	144	180	657	1169	0.0	1.0	0.8	176	141	176	650	1191	0.0
1.0	1.2	180	216	180	578	1137	0.0	1.0	1.2	180	216	180	577	1136	0.0
1.0	1.6	180	288	180	557	1082	2.8	1.0	1.6	180	288	180	531	1097	4.5
1.0	2.0	180	360	180	517	1049	6.6	1.0	2.0	180	360	180	490	1052	7.1
1.4	0.4	252	72	180	685	1167	0.0	1.4	0.4	246	70	176	660	1174	0.0
1.4	0.8	252	144	180	613	1139	0.0	1.4	0.8	252	144	180	593	1147	0.0
1.4	1.2	252	216	180	566	1099	3.2	1.4	1.2	252	216	180	544	1110	3.6
1.4	1.6	252	288	180	525	1066	7.0	1.4	1.6	246	282	176	509	1082	7.9
1.4	2.0	252	360	180	477	1014	12.1	1.4	2.0	252	360	180	465	1017	11.7
1.8	0.4	324	72	180	645	1147	0.0	1.8	0.4	324	72	180	611	1155	2.5
1.8	0.8	324	144	180	575	1116	2.0	1.8	0.8	324	144	180	558	1122	4.4
1.8	1.2	324	216	180	534	1084	7.4	1.8	1.2	317	211	176	520	1096	6.9
1.8	1.6	324	288	180	476	1035	11.5	1.8	1.6	317	282	176	484	1048	13.3
2.2	0.4	396	72	180	601	1117	3.0	2.2	0.4	396	72	180	572	1135	5.6
2.2	0.8	396	144	180	559	1985	5.4	2.2	0.8	387	141	176	534	1108	7.3
Series 2: SRPC mixes with Thy fly ash								*Series 4: OPC mixes with Thy fly ash*							
0.2	1.6	35	280	175	611	1170	0.0	0.2	1.6	34	270	169	621	1189	0.0
0.2	2.0	35	350	175	561	1138	0.0	0.2	2.0	33	330	165	579	1170	0.0
0.6	0.8	108	144	180	694	1172	0.0	0.6	0.8	108	144	180	696	1169	0.0
0.6	1.2	105	210	175	628	1176	0.0	0.6	1.2	106	211	176	628	1171	0.0
0.6	1.6	108	288	180	565	1132	0.0	0.6	1.6	106	282	176	573	1143	1.3
0.6	2.0	108	360	180	523	1091	3.3	0.6	2.0	106	352	176	679	1416	6.3
1.0	0.4	180	72	180	724	1167	0.0	1.0	0.4	176	70	176	725	1169	0.0
1.0	0.8	180	144	180	639	1167	0.0	1.0	0.8	176	141	176	645	1177	0.0
1.0	1.2	180	216	180	580	1146	0.0	1.0	1.2	180	216	180	582	1139	0.0
1.0	1.6	180	288	180	534	1104	2.0	1.0	1.6	176	282	176	542	1116	2.0
1.0	2.0	180	360	180	496	1059	5.0	1.0	2.0	176	352	176	503	1073	4.4
1.4	0.4	252	72	180	659	1172	0.0	1.4	0.4	252	72	180	658	1170	0.0
1.4	0.8	245	140	175	604	1167	0.0	1.4	0.8	246	141	176	603	1160	0.0
1.4	1.2	245	210	175	556	1133	3.0	1.4	1.2	246	211	176	553	1128	2.8
1.4	1.6	252	288	180	505	1074	5.0	1.4	1.6	246	282	176	513	1086	5.1
1.4	2.0	252	360	180	470	1026	7.9	1.4	2.0	246	352	176	478	1040	7.4
1.8	0.4	324	72	180	613	1159	0.0	1.8	0.4	317	70	176	618	1168	1.4
1.8	0.8	324	144	180	560	1127	1.5	1.8	0.8	317	141	176	563	1133	4.4
1.8	1.2	324	216	180	518	1086	4.4	1.8	1.2	317	211	176	524	1099	6.1
1.8	1.6	324	288	180	478	1035	12.0	1.8	1.6	317	282	176	487	1054	11.1
2.2	0.4	396	72	180	575	1137	3.0	2.2	0.4	387	70	176	581	1147	4.7
2.2	0.8	396	144	180	529	1099	4.0	2.2	0.8	387	141	176	535	1111	4.4

[a] Per 1000 by total weight of cement plus fly ash.

Table 5 Mix proportions of all concretes in series No. 5, with aggregate in a saturated and surface-dry condition

c/w–f/w by weight	Cement (kg m^{-3})	Ash (kg m^{-3})	Water (kg m^{-3})	Sand (kg m^{-3})	Stone (kg m^{-3})	Additives (wt%)
0.4–0.00	80	0	200	1320	635	0.1 WSR301
0.4–0.33	66	54	165	861	1147	0.05 WSR301
0.4–0.67	53	89	133	733	1331	0
0.4–1.00	55	138	138	640	1376	0
0.4–1.33	54	180	135	587	1376	0
0.4–1.67	55	231	138	541	1359	0
0.4–2.00	55	276	138	511	1340	0
0.5–0.00	93	0	185	1160	827	0.08 WSR301
0.5–1.00	67	133	133	632	1375	0
0.6–0.00	108	0	108	1040	949	0.07 WSR301
0.6–0.33	90	50	150	793	1240	0.03 WSR301
0.6–0.67	80	89	133	688	1355	0
0.6–1.00	82	136	136	615	1369	0
0.6–1.33	80	178	134	570	1375	0
0.6–1.67	83	231	138	527	1350	0
0.6–2.00	83	276	138	499	1329	0.39 Protex
0.7–0.00	155	0	164	972	1054	0.05 WSR301
0.7–1.00	95	136	136	604	1369	0
0.8–0.00	132	0	165	899	1112	0.03 WSR301
0.8–0.33	110	46	138	745	1307	0
0.8–0.67	110	93	138	649	1353	0
0.8–1.00	110	138	138	590	1364	0
0.8–1.33	109	181	136	549	1365	0
0.8–1.67	110	231	138	514	1340	0.22 Protex
0.8–2.00	110	276	138	487	1317	0.34 Protex
0.9–0.00	140	0	155	857	1174	0.01 WSR301
0.9–1.00	122	136	136	581	1370	0
1.0–0.00	153	0	153	814	1211	0
1.0–0.17	144	24	144	746	1287	0
1.0–0.33	138	46	138	696	1733	0
1.0–0.50	138	69	138	654	1351	0
1.0–0.67	135	91	135	625	1367	0
1.0–0.80	138	115	138	593	1363	0
1.0–1.00	136	136	136	572	1368	0
1.0–1.17	137	160	137	550	1361	0
1.0–1.33	138	184	138	532	1349	0
1.0–1.50	138	207	138	516	1340	0.16 Protex
1.0–1.67	138	230	138	502	1329	0.2 Protex
1.0–1.80	138	253	138	488	1318	0.7 Protex
1.0–2.00	140	280	140	474	1296	0.4 Protex
1.1–0.00	165	0	150	780	1245	0
1.1–1.00	152	138	138	560	1359	0
1.2–0.00	181	0	151	747	1262	0
1.2–0.33	166	46	138	661	1347	0
1.2–0.67	166	93	138	595	2362	0
1.2–1.00	166	138	138	551	1357	0
1.2–1.33	166	184	138	519	1340	0.34 Protex
1.2–1.67	166	231	138	490	1318	0.6 Protex
1.2–2.00	166	276	138	466	1292	0.76 Protex
1.3–0.00	192	0	148	723	1286	0
1.3–1.00	179	138	138	544	1353	0.35 Protex
1.4–0.00	209	0	149	698	1295	0
1.4–0.33	193	46	138	629	1356	0
1.4–0.67	193	93	138	575	1360	0
1.4–1.00	193	138	138	535	1350	0.27 Protex
1.4–1.33	193	184	138	505	1331	0.55 Protex
1.4–1.67	194	230	138	478	1307	0.81 Protex
1.4–2.00	193	276	138	456	1279	0.97 Protex
1.5–0.00	222	0	148	677	1308	0
1.5–1.00	207	138	138	528	1346	0
1.6–0.00	248	0	155	650	1296	0
1.6–0.33	221	46	138	605	1358	0
1.6–0.67	221	93	138	558	1354	0.18 Protex
1.6–1.00	221	138	138	522	1341	0.3 Protex
1.6–1.33	221	184	138	493	1320	0.7 Protex
1.6–1.67	221	231	138	469	1293	0.96 Protex
1.6–2.00	221	276	138	447	1265	1.2 Protex

regression analysis of 660 sets of data gives a coefficient of correlation R^2 for estimates of A, B and E in Equation 3 at 95% or above (with only a single exception). Therefore it seems justified to apply the modified Bolomey Equation 3 to fly ash concretes with as much confidence as the traditional water cement ratio law has been applied to ordinary Portland cement concretes for almost a century.

Use of Equation 3 has the advantage that values of the constants A and E are usually known to local contractors for local cements and local aggregates, and for different relevant standard curing conditions and times (typically 7, 14 and 28 days). Thus, in principle it would only require the testing at different curing ages of a single mix with an arbitrary content of a local fly ash in order to calculate an appropriate value of B in Equation 3, and thus to predict the strength of any standard cured fly ash concrete mix at any time of its strength development up to 112 days. The prudent contractor would probably produce several different fly ash concrete mixes in order to determine an accurate value of B.

However, concrete is accepted on the basis of compressive strength results obtained after 28 days of curing at 20°C. Therefore, if we assume that the values in Table 11 are reasonable, B_{28} would typically be 5.3 and an average value of A_{28} would be 29.0. Thus, a reasonable first estimate of the 28-day cementing efficiency index k_s of an average fly ash in concrete with an average modern Portland cement would be $k_s = 5.3/29.0 = 0.18$. This is probably the reason why DoE [3] suggests the general value of 0.20 to be applied as a reasonable first estimate of k_s in any desk-top mix design of fly ash concrete. It is then left up to the individual concrete engineer or contractor to determine a more accurate value of k_s for local materials and curing conditions, on the basis of results of trial mixes carried out on site.

The person in charge must obviously be aware that the value of k_s of any concrete will vary from close to zero at very early ages and up to perhaps 0.9 after 3–10 years, at which time it appears that the value of k_s reaches its maximum [8,9].

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Table 6 Mean strengths and standard deviations (in MPa) for series 1. The first figure in each pair is the mean compressive strength of five specimens in a series; the second figure is the standard deviation of the same test results

f/w	Curing time (days)	*c/w*						
		0.2	0.6	1.0	1.4	1.8	2.2	2.6
2.0	14	0.91/0.11	6.58/0.15	31.7/0.65	23.5/1.18			
	28	1.04/0.05	8.13/0.76	18.2/2.84	32.1/2.53			
	56	1.28/0.13	9.31/0.18	25.1/1.64	46.1/1.77			
	112	2.07/0.13	13.4/0.60	30.6/2.28	51.8/3.44			
1.6	14	0.78/0.02	5.03/0.23	13.2/1.29	19.4/0.88	35.6/2.40		
	28	0.87/0.09	6.82/0.53	16.9/1.66	26.7/3.44	43.2/4.59		
	56	1.23/0.11	8.09/0.63	26.1/1.02	41.5/4.05	59.3/1.75		
	112	2.20/0.10	12.3/0.32	32.9/2.40	43.9/5.90	69.3/5.86		
1.2	14	–	5.37/0.41	12.6/1.01	25.7/1.11	33.9/2.31		
	28	–	6.58/0.53	16.7/1.29	29.7/2.50	44.6/2.43		
	56	–	9.26/0.56	25.9/0.80	43.8/2.65	52.0/8.02		
	112	–	11.2/0.45	35.7/2.52	55.8/4.80	67.6/4.44		
0.8	14	–	4.16/0.35	11.7/0.76	25.9/0.91	29.1/1.97	45.2/6.39	
	28	–	5.26/0.42	14.7/1.08	31.1/1.55	38.0/3.96	50.5/4.54	
	56	–	8.09/0.42	22.8/1.09	39.0/3.56	49.4/2.56	61.7/5.40	
	112	–	12.0/0.64	30.2/1.56	48.6/3.37	61.5/5.70	75.7/3.38	
0.4	14	–	–	10.6/0.64	20.8/1.03	34.1/3.67	45.6/4.19	
	28	–	–	13.6/0.91	28.2/0.68	39.9/5.29	51.5/4.02	
	56	–	–	19.1/1.20	35.1/2.15	53.4/2.50	52.9/6.05	
	112	–	–	22.5/1.50	43.2/2.28	55.6/6.29	71.8/6.00	
0.0	14	–	–	10.6/0.39	16.4/0.49	30.4/3.12	39.7/2.65	46.3/2.31
	28	–	–	13.2/0.81	22.1/1.60	35.4/1.44	51.3/5.71	54.1/1.99
	56	–	–	16.4/1.21	25.4/1.21	41.7/5.20	53.1/1.63	58.4/7.13
	112	–	–	18.9/0.21	31.4/0.61	45.8/3.70	60.4/2.77	69.1/6.82

Table 7 Mean strengths and standard deviations (in MPa) for series 2 (see Table 6)

f/w	Curing time (days)	*c/w*						
		0.2	0.6	1.0	1.4	1.8	2.2	2.6
2.0	14	1.04/0.05	6.78/0.46	12.4/1.06	24.5/1.28			
	28	1.80/0.08	7.80/0.47	19.9/1.39	34.2/3.38			
	56	2.94/0.27	11.3/0.15	27.2/0.90	46.4/2.76			
	112	3.93/0.14	17.3/1.87	37.6/1.47	57.1/3.04			
1.6	14	1.22/0.05	4.05/0.69	13.2/0.83	26.1/1.46	37.9/1.52		
	28	1.62/0.16	7.36/0.22	19.4/1.01	34.5/2.28	45.1/2.49		
	56	2.45/0.12	10.1/0.45	27.2/1.92	44.6/3.58	61.0/3.53		
	112	3.28/0.07	16.1/0.82	37.6/2.88	52.5/6.11	72.2/1.56		
1.2	14	–	4.63/0.16	14.0/1.23	21.2/2.15	37.2/1.62		
	28	–	8.43/0.11	18.9/0.62	27.9/1.93	44.6/3.60		
	56	–	11.1/1.37	27.5/0.80	38.2/1.86	55.8/3.24		
	112	–	17.1/1.34	38.0/2.41	42.2/2.47	64.9/5.05		
0.8	14	–	4.40/0.08	11.8/1.11	22.7/3.67	37.4/2.60	43.5/3.20	
	28	–	4.46/0.18	16.9/1.27	31.2/1.29	44.8/1.53	54.5/2.43	
	56	–	9.44/0.48	25.0/0.83	39.7/1.42	57.5/5.45	68.9/2.42	
	112	–	14.3/1.28	35.4/1.66	48.0/2.16	70.2/3.38	78.9/5.78	
0.4	14	–	–	11.9/0.18	23.2/1.02	33.5/1.30	45.0/2.60	
	28	–	–	14.9/1.07	28.2/1.77	39.5/4.46	48.4/2.71	
	56	–	–	21.2/0.63	38.6/1.42	50.9/5.07	65.7/1.20	
	112	–	–	26.8/1.75	48.2/3.04	63.3/1.65	76.5/2.75	

Table 7 (*continued*)

f/w	Curing time (days)	*c/w*						
		0.2	0.6	1.0	1.4	1.8	2.2	2.6
0.0	14	–	–	10.6/0.39	16.4/0.49	30.4/3.12	39.7/2.65	46.3/2.31
	28	–	–	13.2/0.81	22.1/1.60	35.4/1.44	51.3/5.71	54.1/1.99
	56	–	–	16.4/1.21	25.4/1.21	41.7/5.20	53.1/1.63	58.4/7.13
	112	–	–	18.9/0.21	31.4/0.61	45.8/3.70	60.4/2.77	69.1/6.82

Table 8 Mean strengths and standard deviations (in MPa) for series 3 (see Table 6)

f/w	Curing time (days)	*c/w*						
		0.2	0.6	1.0	1.4	1.8	2.2	2.6
2.0	14	1.79/0.03	7.82/1.40	19.4/0.24	34.0/0.82			
	28	2.37/0.04	9.30/1.48	25.5/0.96	40.6/1.49			
	56	2.98/0.13	13.9/0.45	30.2/1.76	48.7/3.15			
	112	3.88/0.18	18.0/0.70	39.2/1.64	54.1/8.28			
1.6	14	0.91/0.04	8.80/0.32	17.9/0.82	24.5/2.19	42.0/1.71		
	28	1.42/0.10	11.1/0.54	21.8/0.82	28.3/2.44	46.5/2.78		
	56	1.90/0.35	13.6/0.43	23.8/1.57	35.9/5.16	58.2/1.83		
	112	2.87/0.24	19.3/1.03	34.8/0.59	43.2/5.08	66.6/3.71		
1.2	14	–	7.03/0.48	18.0/0.84	27.0/1.10	50.1/0.84		
	28	–	8.40/0.33	23.3/0.91	32.4/1.62	54.0/1.11		
	56	–	10.0/0.59	29.2/0.81	38.1/1.09	60.0/4.90		
	112	–	13.5/1.93	34.9/0.73	46.5/1.71	73.7/1.95		
0.8	14	–	6.59/0.39	18.6/0.61	24.1/1.69	38.0/0.35	40.0/2.15	
	28	–	7.65/0.34	22.0/0.74	29.2/1.82	41.3/2.43	49.3/2.15	
	56	–	9.04/0.44	25.6/1.15	35.0/3.23	48.5/1.49	55.4/5.27	
	112	–	12.7/0.15	32.1/1.38	46.1/1.81	54.8/7.00	63.3/3.56	
0.4	14	–	–	13.4/0.14	26.7/0.43	36.1/0.45	44.2/0.97	
	28	–	–	15.9/0.11	30.0/1.12	44.0/0.77	48.9/2.26	
	56	–	–	18.0/0.76	34.3/1.54	48.6/0.82	52.3/4.37	
	112	–	–	22.0/0.41	41.0/1.17	56.3/1.54	61.9/2.12	
0.0	14	–	–	10.6/0.55	22.7/0.71	30.5/1.22	41.9/0.21	53.8/1.96
	28	–	–	12.2/0.56	24.7/1.36	35.5/0.64	45.0/2.10	56.4/1.01
	56	–	–	12.6/0.39	28.5/0.97	36.4/1.62	49.2/1.68	63.3/3.21
	112	–	–	12.8/0.66	30.1/0.43	39.7/1.19	51.2/3.12	65.9/5.00

Table 9 Mean strengths and standard deviations (in MPa) for series 4 (see Table 6)

f/w	Curing time (days)	*c/w*						
		0.2	0.6	1.0	1.4	1.8	2.2	2.6
2.0	14	2.10/0.06	9.91/0.74	18.5/0.31	29.7/1.84			
	28	3.52/0.11	13.4/0.43	24.3/0.91	37.5/1.69			
	56	4.59/0.46	17.9/0.83	29.9/1.88	44.9/2.86			
	112	6.13/0.34	25.5/0.45	39.6/0.89	52.9/3.58			
1.6	14	1.60/0.07	7.89/0.43	19.2/0.65	27.5/1.90	42.1/2.01		
	28	2.52/0.18	10.5/0.47	23.3/1.75	34.1/2.16	50.7/4.38		
	56	3.51/0.30	14.9/0.70	29.2/0.95	41.1/3.03	56.9/3.19		
	112	4.10/0.18	22.3/0.67	38.5/1.28	48.3/2.49	72.0/4.74		

Table 9 (*continued*)

f/*w*	Curing time (days)	*c*/*w*						
		0.2	0.6	1.0	1.4	1.8	2.2	2.6
1.2	14	–	8.18/0.19	16.9/0.43	26.1/1.22	38.3/1.68		
	28	–	10.5/0.35	22.5/0.51	33.8/0.87	45.4/1.34		
	56	–	13.9/0.86	26.8/2.10	42.0/0.70	53.9/2.17		
	112	–	20.8/0.58	36.4/0.72	49.1/1.10	59.8/2.56		
0.8	14	–	5.35/0.27	14.2/0.71	26.0/1.67	38.9/1.47	46.5/2.62	
	28	–	6.91/0.18	18.2/0.40	29.9/1.39	42.3/1.85	48.6/1.83	
	56	–	8.98/0.23	21.4/0.98	37.6/2.49	51.6/1.51	59.3/4.78	
	112	–	13.1/0.17	28.4/1.10	38.3/6.23	60.0/0.67	72.9/1.42	
0.4	14	–	–	16.7/0.77	27.8/0.56	35.4/0.91	42.1/3.46	
	28	–	–	20.7/0.39	31.1/0.97	39.8/1.67	48.6/2.06	
	56	–	–	25.5/0.49	33.6/1.54	45.9/1.11	57.4/0.58	
	112	–	–	29.0/1.01	39.3/0.55	49.9/0.76	64.5/0.99	
0.0	14	–	–	10.6/0.55	22.7/0.71	30.5/1.22	41.9/0.21	53.8/1.96
	28	–	–	12.2/0.56	24.7/1.36	35.5/0.64	45.0/2.10	56.4/1.01
	56	–	–	12.6/0.39	28.5/0.97	36.4/1.62	49.2/1.68	63.3/3.21
	112	–	–	12.8/0.66	30.1/0.43	39.7/1.19	51.2/3.12	65.9/5.00

Table 10 Mean strengths and standard deviations (in MPa) for series 5 (see Table 6)

f/*w*	Curing time (days)	*c*/*w*												
		0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
2.00	14	04.93/0.24		10.53/0.61		15.41/0.35		25.30/0.71		28.25/0.36		33.24/0.71		37.85/1.01
	28	06.54/0.41		13.14/0.22		19.39/0.52		29.80/0.90		34.64/1.30		38.74/1.59		43.53/1.29
	56	10.31/0.59		17.11/0.96		23.39/0.87		34.20/0.46		39.93/1.43		44.30/1.70		48.75/3.36
	112	15.10/0.63		25.03/0.55		29.80/1.00		41.00/0.95		44.68/2.04		51.35/1.46		57.50/2.22
1.80	14							25.00/0.93						
	28							28.05/0.75						
	56							32.14/0.95						
	112							39.83/0.77						
1.67	14	04.56/0.17		09.93/0.55		16.24/0.56		23.70/0.56		26.40/0.36		32.48/1.05		38.35/1.05
	28	05.95/0.26		12.15/0.46		18.84/0.62		29.40/0.86		32.54/0.35		39.10/1.59		45.60/1.07
	56	09.26/0.46		16.09/0.65		23.68/0.92		33.88/1.30		39.15/0.26		45.74/1.48		49.08/1.87
	112	14.44/0.81		22.58/1.00		30.03/0.91		39.30/0.90		43.75/1.75		50.88/0.67		54.90/2.29
1.50	14							23.49/0.97						
	28							28.15/1.14						
	56							32.64/0.60						
	112							37.43/0.55						
1.33	14	03.59/0.08		08.23/0.49		15.31/0.44		20.90/0.45		27.34/0.41		33.43/1.16		37.11/1.43
	28	04.89/0.11		10.53/0.51		19.48/0.23		26.80/0.52		33.28/1.38		38.95/1.47		42.93/0.88
	56	07.23/0.33		13.65/0.55		21.94/1.04		29.56/1.30		39.18/1.30		42.28/2.43		50.38/3.43
	112	12.63/0.30		19.09/0.51		28.63/1.10		35.80/0.80		43.41/1.62		49.53/2.93		54.33/1.30
1.17	14							22.40/0.61						
	28							25.56/0.94						
	56							29.89/1.39						
	112							36.36/0.42						
1.00	14	03.55/0.21	05.42/0.16	08.20/0.23	11.60/0.75	14.43/0.60	17.13/1.00	20.15/0.62	21.41/2.12	25.43/0.60	27.95/0.25	33.21/0.54	33.88/1.54	35.45/1.50
	28	04.74/0.17	06.48/0.21	09.80/0.37	14.50/0.80	17.54/0.43	20.53/0.59	24.57/0.69	28.30/1.20	29.70/2.12	33.50/1.62	38.69/0.89	39.74/1.16	40.00/2.72
	56	06.46/0.17	08.76/0.30	12.50/0.23	17.05/0.74	20.80/0.61	25.49/1.50	29.03/0.87	32.99/0.54	36.73/1.53	39.46/2.60	44.50/2.10	44.13/1.10	48.90/0.88
	112	11.33/0.54	14.35/0.46	17.41/0.74	22.19/1.32	25.89/0.97	30.66/0.71	34.00/0.91	38.38/0.83	41.53/0.98	46.03/0.83	48.63/2.30	49.30/1.60	51.18/2.99
0.80	14							21.85/0.42						
	28							26.40/1.10						
	56							31.10/0.77						
	112							36.10/0.83						
0.67	14	02.95/0.17		06.56/0.50		11.90/0.96		19.40/0.60		23.52/0.67		28.91/1.06		35.18/1.34
	28	03.63/0.38		08.75/0.50		15.49/0.72		24.30/1.05		27.60/1.36		34.26/0.78		38.90/1.77
	56	05.05/0.19		09.89/0.42		18.34/0.67		28.70/0.81		33.80/0.60		40.79/1.17		45.68/2.02
	112	08.08/0.35		13.23/0.60		21.73/0.35		35.40/0.80		38.15/1.14		46.23/1.12		54.18/2.44

Table 10 (*continued*)

f/w	Curing time (days)	c/w												
		0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
0.50	14							18.68/1.01						
	28							22.14/0.47						
	56							26.60/1.32						
	112							31.70/0.67						
0.33	14	02.43/0.12		05.34/0.38		10.11/0.36		17.04/0.40		21.70/0.70		28.36/0.92		39.13/1.07
	28	03.11/0.16		06.94/0.10		12.75/0.46		20.10/0.55		25.03/1.13		31.85/1.02		37.00/1.23
	56	03.94/0.12		08.75/0.31		16.09/0.40		25.48/0.58		30.33/0.82		36.98/1.72		41.70/1.72
	112	05.49/0.28		10.85/0.56		19.38/0.45		30.40/1.40		36.15/1.51		44.40/1.06		47.23/1.38
0.17	14							16.23/0.56						
	28							18.96/0.90						
	56							22.71/0.30						
	112							27.65/0.48						
0.0	14	01.95/0.07	02.95/0.18	05.11/0.13	06.35/0.37	09.33/0.14	11.72/0.34	15.08/0.66	17.36/0.63	20.90/0.40	22.20/1.30	28.83/0.70	29.35/1.40	32.43/0.73
	28	02.27/0.09	03.29/0.12	05.96/0.16	06.96/0.19	10.50/0.40	13.15/0.39	17.40/0.50	20.39/1.04	23.20/0.93	26.50/1.10	33.20/2.40	32.48/0.92	36.59/1.12
	56	02.86/0.09	04.43/0.30	07.54/0.06	08.63/0.35	12.55/0.24	15.20/0.36	20.40/0.30	23.25/0.72	26.44/0.58	28.46/0.84	36.68/1.37	36.93/0.73	40.83/0.71
	112	03.55/0.19	04.45/0.25	08.96/0.23	10.15/0.41	15.38/1.51	18.59/0.76	23.14/0.33	25.15/1.14	30.28/0.98	32.85/1.53	42.13/1.56	39.05/1.22	44.36/1.36

Table 11 Results of the multi-linear regression analysis of all experimental data, assuming the mechanical model presented by Equations 3 and 4. Calculated values of coefficients of correlation R^2 and cementing efficiency indices k_s are also included

Cement type	Fly ash type	Curing age (days)	A	B	E	R^2	$k_s = B/A$
SRPC (Aalborg)	Asnæs (series 1)	14	23.59	3.00	−12.55	0.96	0.13
		28	28.40	4.20	−15.13	0.98	0.15
		56	35.97	6.46	−19.97	0.95	0.18
		112	41.21	8.33	−22.10	0.96	0.20
	Thy (series 2)	14	23.59	3.42	−12.55	0.97	0.14
		28	28.40	4.96	−15.13	0.98	0.17
		56	35.97	7.21	−19.97	0.96	0.20
		112	41.21	11.06	−22.10	0.96	0.27
OPC (Slite)	Asnæs (series 3)	14	25.92	5.09	−13.52	0.95	0.20
		28	28.50	6.33	−14.33	0.96	0.22
		56	32.62	7.67	−16.63	0.96	0.24
		112	36.81	11.27	−19.14	0.92	0.31
	Thy (series 4)	14	25.92	4.22	−13.52	0.98	0.16
		28	28.50	5.97	−14.33	0.98	0.21
		56	32.62	8.56	−16.63	0.97	0.26
		112	36.81	12.14	−19.14	0.96	0.33
White (Aalborg)	Asnæs (series 5)	14	27.51	3.81	−11.50	0.97	0.14
		28	31.42	5.06	−13.02	0.98	0.16
		56	34.57	6.35	−13.33	0.99	0.18
		112	36.00	7.72	−10.94	0.96	0.21

the requirements for obtaining a PhD degree at the Technical University of Denmark. A complete version of the report [10] is available in Danish.

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RESUME

Une modification du principe du rapport e/c appliqué à la résistance en compression des bétons aux cendres volantes

Les résultats expérimentaux présentés suggèrent que le développement de la résistance à la compression des bétons aux cendres volantes peut s'expliquer par la superposition de deux mécanismes indépendants l'un de l'autre qui déterminent le remplissage des pores dans la pâte de ciment. L'un des mécanismes est dû à l'hydratation du ciment Portland, et l'autre à l'hydratation de la cendre volante et de l'hydroxyde de calcium libéré par l'hydratation du ciment Portland.

Le rapport eau/ciment pour les bétons à ciment Portland ordinaire peut s'appliquer aux bétons aux cendres volantes, à condition d'introduire une légère modification qui tienne compte de l'effet pouzzolanique supplémentaire dû aux cendres volantes sur le développement de la résistance du béton. Cet article aidera les ingénieurs à doser les mélanges de bétons aux cendres volantes pour la résistance à la compression.