Physical Properties and Structure of Fresh Cementitious Pastes

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•THE PHYSICAL properties, hydration and hardening of cementitious materials such as slag and pozzolanic cements and mixes of lime with slag or pozzolana, etc., are generally compared with those of portland cement. While the effects of the early structure of portland cement paste on the properties of hardened paste are now well recognized (1-6), this cannot be said of the pastes of the cementitious materials mentioned, even though some examples of improvement in the physical properties of the cementitious materials reported in the literature (7; 8) imply changes in the early structure of such pastes. It appears the latter have not been studied except for the recent work of Yamazaki (9). Since it was difficult to derive reliable information on the early structure of cementitious pastes from the published work because of the variable nature of materials and experimental conditions employed by different workers, an investigation was begun with a view to finding how important the differences in the structure of fresh pastes of the different cementitious materials are in comparison with portland cement and how these may be reflected in the properties of the hardened pastes.

EXPERIMENTAL

The bleeding characteristics and rheological behavior of fresh pastes were studied in order to elucidate information on the physical structure of pastes of pozzolanic and and slag cements and mixes of lime with slag or pozzolana. The experimental methods, in general, were similar to those employed by Powers and Steinour (10, 11) for studies on bleeding and by Shalom and Greenberg (4) on rheology of portland cement pastes.

Ordinary portland cement was prepared from a cement clinker with a potential compound composition (12) of 47, 27, 11 and 9 percent for C_3S, β-C_2S, C_3A and the ferrite phase, respectively. The two pozzolanas used were fly ash and surkhi, the latter a calcined clay. Both the pozzolanas satisfied the specific requirements (13). The fineness was determined by the Blaine and Wagner methods (14, 15). The fineness of fly ash was 2763 cm^2/g (Blaine) as determined by the modified method proposed by Chopra and Narain (16) and its loss on ignition at 700 C was 5.35 percent. The surkhi sample was ground to a fineness of $3200 \pm 50 cm^2/g$ (Blaine). The granulated slag used in the preparation of the portlandblast-furnace cements was obtained from the Tata Iron & Steel Works Ltd., Jamshedpur, and is known to be suitable for cement making (17). The slag was ground to the same fineness as surkhi.

The trial cements were prepared in the laboratory by mixing separately ground constituents homogeneously. The pozzolanic cements contained the pozzolana and ground cement clinker in the ratio of 25:75 by weight. The two portland blast-furnace cements contained the ground slag and clinker in the ratios of 35:65 (PBF) and 65:35 (FBP) by weight, respectively. Ordinary portland cement was prepared by mixing 4 percent by weight of ground gypsum with the ground clinker of fineness 3200 ± 50 cm^2/g (Blaine). The other cement samples also contained 4 percent gypsum by weight for retarding the setting times. The fineness of all cements, except the fly ash cement, was about 3200 cm^2/g (Blaine). The other cementitious mixes investigated were prepared from one part of hydrated lime (7025 cm^2/g Blaine) with two parts by weight of either fly ash or ground surkhi or slag. A 1:3 lime-fly ash mix (by weight) was also used.

The pastes were mixed in a Waring blendor under vacuum as suggested by Copeland (18). The mixing schedule for the cement pastes was a 2-3-2-minute cycle of mix-rest-mix following recommended practice (11). For lime-fines pastes a 3-1-2-minute cycle was adopted, as the volume of solids to be mixed was greater than for the cement. The mixing was done in a constant-temperature laboratory at 27 ± 2 C. The temperature of the paste after mixing was kept close to the laboratory temperature by using water whose temperature was so adjusted that the final temperature of the paste was close to 27 ± 2 C.

The bleeding characteristics were measured using Steinour's method (11). According to him the bleeding rate and bleeding capacity of a portland cement paste will conform to the following equations, respectively, if no channeling takes place during the bleeding test.

$$Q = \frac{0.2\,g\,(d_c - d_f)}{\sigma_w^2\,\eta} \cdot \frac{(W - W_i)^3}{C} \tag{1}$$

and

$$\Delta H' = k^2 c \left[(W/C) - (W/C)_m\right]^2 \tag{2}$$

where

Q = bleeding rate, cm/sec;
g = the gravitational acceleration, cm/sec^2;
C = absolute volume of cement per unit volume of mix;
d_c = density of cement, g/cm^3;
d_f = density of water, g/cm^3;
η = coefficient of viscosity of water, poises;
σ_w = specific surface of cement (on volume basis), cm^2/cm^3, determined by the Wagner turbidimeter method (15);
W = volume of water per unit volume of mix ($W + C = 1$);
W_i = a term which has a constant value for a given cement tested at a given temperature—it is a correction for water not involved in the flow but does not represent directly the quality of such water;
$\Delta H'$ = bleeding capacity, i.e., the ratio of the total decrease in paste height to the initial paste height;
k = the slope of the data line in a plot of $\sqrt{\Delta H'/C}$ vs W/C; and
$(W/C)_m$ = minimum water-cement ratio (by absolute volume) for pastes of a given cement, an empirical constant evaluated by extrapolation of plotted data in Eq. 2.

For determining W_i from the relationship between $(QC)^{1/3}$ vs W, theoretical slopes were calculated from

$$\sqrt[3]{\frac{0.2\,g\,(d_c - d_f)}{\sigma_w^2\,\eta}}$$

and the data lines were always drawn to the theoretical slope. The linear relationship between $\sqrt{\Delta H'/C}$ and W/C (by volume) was also determined after Steinour. The porosity of the sediment was calculated in terms of the final volume of the sediment, i.e., the settled paste. Powers' method (1, pp. 579-581) was used for calculating the mean pore-size, and average pore width was calculated as suggested by Powers and Brownyard (19).

For the determination of flow characteristics the MacMichael rotational viscometer was used and the measurements were made by the mulitiple point method. The speed of rotation of the cup was varied from 5 to 40 rpm. The internal diameters of the rotational cup and the bob were 3.00 cm and 2.25 cm, respectively. The bob was immersed to a depth of 4.50 cm in the sample under test and to reduce the end effects a recess was provided at the bottom of the bob. The instrument was calibrated with a standard oil sample using certified suspension wires. The measurements were carried out at a temperature of 25 ± 2 C. The method of making a flow curve in a rotational viscometer and the method of calculation of the apparent viscosity and yield value from the flow curve are well known and have been described by Green (20). Wire Nos. 26 and 30 with wire constant (K) of 82.0 and 13.9, respectively, were used in the present study.

RESULTS AND DISCUSSION

Flocculent State in Pastes

A fresh portland cement paste is considered to be in flocculent state; however, the term "flocculent state" is not to be construed to mean that the paste consists of a collection of more or less separate floccules. Instead, the whole body of paste constitutes a single floc, the floc structure being a rather uniform reticulum of cement particles (1).

The flocculent state of portland cement paste may or may not change when part of the portland cement particles in a paste are replaced by those of a pozzolana or slag. Strictly speaking, other things being equal, it will depend how such replacements affect the balance of attractive and repulsive forces. Information on the state of flocculation of pozzolanic or slag cement pastes can be deduced from the study of their bleeding characteristics.

The results of the bleeding tests on pastes of different cements are reported in Table 1. To test the validity of the rate equation for the pastes of two pozzolanic cements, bleeding tests were carried out at least at three different cement concentrations. A plot of $(QC)^{1/3}$ vs W showed that all the experimental points for the portland and pozzolanic cement containing fly ash fell on the data lines drawn to the theoretical slope. In the pozzolanic cement containing surkhi pozzolana, three of the four points were on the line. The agreement on the whole was good and it may be concluded that the rate equation also holds good for the pozzolanic cements. In view of this the slag cement was tested at one concentration only. Values of W_i for both the pozzolanic and slag cements were lower than that of the portland cement, the pozzolanic cements showing greater reductions.

The bleeding tests on the fresh pastes of mixes of lime with slag or pozzolanas are reported in Table 2. The rate equation was also found to hold good for this type of paste as the experimental points of a plot of $(QC)^{1/3}$ vs W for each of the pastes fell on the line having the theoretical slope of

$$\sqrt[3]{\frac{0.2g(d_c - d_f)}{\sigma_s^2 \eta}}$$

Here σ_s represents specific surface calculated from sedimentation analysis, assuming that the mean size of particles less than 7.5 microns is 3.75 microns; σ_s corresponds to σ_w in Eq. 1. The W_i values for 1:2 and 1:3 mixes ranged from 0.26 to 0.30 and are close to the value for the portland cement.

For a better understanding of the effect of the presence of slag and pozzolana powders in cement and lime-fines pastes on the magnitude of W_i, bleeding characteristics of the ground slag, surkhi and fly ash were studied separately (Table 3). A saturated solution of calcium hydroxide was used for flocculating these concentrated suspensions of powders. The slag and surkhi samples had a fineness of 3200 ± 50 cm^2/g (Blaine). While the values of specific surface as determined by the Wagner method were almost equal, the sedimentation method showed appreciable difference (Table 3). Fly ash, with a Blaine's surface of 2763 cm^2/g, showed correspondingly lower values of specific surface determined either by the Wagner or the sedimentation method. The particles of slag and surkhi were subangular to angular. The fly ash differed additionally in

TABLE 1

BLEEDING CHARACTERISTICS OF DIFFERENT CEMENT PASTES

Cement Designation	Specific Surface (Wagner)		Density in Kerosene (g/cc)	W/C Ratio		Cement Content (absolute volume)	Bleeding Rate ($Q \times 10^6$)	Bleeding Capacity ($\Delta H'$)	Porosity of Sediment (percent of settled volume)	W_i	$(W/C)_m$
	(cm²/g)	(cm³/cc)		Wt	Vol						
Portland cement (PC)	2144	6711	3.13	0.35	1.10	0.479	51.0	0.023	51.2	0.27	0.91
				0.40	1.25	0.444	93.0	0.028	55.4		
				0.50	1.56	0.390	146.0	0.065	58.9		
				0.55	1.72	0.367	221.0	0.109	59.8		
				0.60	1.87	0.347	325.0	0.160	59.4		
Portland-pozzolana cement (pozzolana-flyash)	1778	5736	2.96	0.35	1.10	0.479	122.0	0.047	49.9	0.23	0.76
				0.50	1.56	0.390	277.7	0.116	56.2		
				0.55	1.72	0.367	342.1	0.130	56.6		
Portland-pozzolana cement (pozzolana-surkhi)	2091	6317	3.02	0.28	0.86	0.537	70.9	0.023	45.0	0.15	0.58
				0.35	1.10	0.479	138.9	0.065	48.9		
				0.45	1.41	0.414	330.0	0.176	49.6		
				0.50	1.56	0.390	855.0	0.250	47.5		
Portland blast-furnace cement (PBF)	2044	6390	3.09	0.40	1.25	0.444	63.5	0.020	54.2	0.26	—

TABLE 2

BLEEDING CHARACTERISTICS OF LIME-SLAG/POZZOLANA PASTES

Paste Mix	Specific Surface σ_s		Density (g/cc)	W/C Ratio (vol)	Solid Content (absolute volume)	Bleeding Rate ($Q \times 10^6$)	Bleeding Capacity ($\Delta H'$)	Porosity of Sediment (percent of settled volume)	W_i	$(W/C)_m$
	(cm²/g)	(cm³/cc)[a]								
Hydrated lime	4060	9000	2.21	1.99	0.334	51.3	0.08	64.3	0.32	1.30
				2.55	0.282	100.0	0.16	66.4		
				3.12	0.242	194.4	0.20	67.7		
				3.41	0.227	277.7	0.27	68.5		
1:2 Lime-slag	—	6413	2.68	1.33	0.426	78.8	0.032	55.6	0.26	1.14
				1.67	0.374	116.6	0.048	60.7		
				1.88	0.347	158.3	0.066	62.8		
				2.22	0.310	222.3	0.127	64.4		
				2.36	0.298	244.4	0.113	66.4		
1:2 Lime-fly ash	—	5312	2.34	1.53	0.395	79.0	0.029	59.2	0.30	1.20
				1.65	0.377	106.0	0.040	60.5		
				1.77	0.361	117.0	0.042	62.2		
				1.89	0.346	196.0	0.077	62.4		
1:3 Lime-fly ash	—	4851	2.35	1.53	0.395	116.0	0.048	58.4	0.28	0.88
				1.65	0.377	153.0	0.067	59.4		
				1.77	0.361	206.0	0.104	59.7		
				1.88	0.347	213.0	0.123	60.4		
1:2 Lime-surkhi	—	6246	2.48	1.25	0.440	62.5	0.020	53.3	0.26	1.10
				1.62	0.380	105.5	0.026	60.8		
				1.87	0.348	196.0	0.051	63.2		
				2.12	0.320	225.0	0.075	65.3		
				2.25	0.308	262.0	0.096	66.0		

[a] The value for the hydrated lime was obtained from the sedimentation analysis; the values for the mixes were computed from the specific surface of the individual constituents.

TABLE 3

BLEEDING CHARACTERISTICS OF PASTES OF DIFFERENT POWDERS[a]

Powder Sample	Specific Surface			Density in Kerosene (g/cc)	W/C Ratio (vol)	Solid Content (absolute volume)	Bleeding Rate ($Q \times 10^6$)	Bleeding Capacity ($\Delta H'$)	Porosity of Sediment (percent of settled volume)	W_i	$(W/C)_m$
	Wagner	Sedimentation									
	(cm²/g)	(cm²/g)	(cm³/cc)								
Slag	1822	1743	5320	2.92	1.17	0.461	172.0	0.035	52.2	0.18	0.70
					1.45	0.408	297.0	0.055	56.8		
					1.75	0.363	333.0	0.087	60.2		
					1.89	0.346	394.0	0.094	61.9		
Fly ash 122C	1450	1520	3648	2.40	1.73	0.366	477.0	0.073	60.5	0.24	0.56
					1.80	0.357	539.0	0.088	60.8		
					1.92	0.343	584.0	0.091	62.3		
					2.04	0.329	788.0	0.113	62.9		
					2.28	0.305	1285.0	0.127	65.1		
Surkhi	1845	1851	4869	2.61	1.17	0.461	229.1	0.051	51.5	0.12	0.53
					1.30	0.435	416.6	0.096	51.8		
					1.52	0.396	488.2	0.174	51.9		
					1.83	0.353	990.9	0.219	54.7		
					2.08	0.324	1666.0	0.224	58.2		

[a] Flocculating agent—saturated lime water.

having spheriods of glass, and the particles appeared to be contaminated with unburnt fuel, as their color was black. The rate equation was also found to hold good for the pastes of the three powders. All the experimental points of a plot of $(QC)^{1/3}$ vs W for a slag paste fell on the line having the theoretical slope as mentioned earlier; four out of five experimental points were on the line in the case of pastes of both surkhi and fly ash. In short, Eq. 1 renders a good approximation.

Since contributions to W_i values in the pastes of chemically inert powders are considered to be wholly of physical origin (11), differences in W_i values of the different powders (Table 3) could be due to differences in particle size and shape, and state of flocculation. Since the fineness of slag and surkhi powders was nearly the same, and the shape of particles was also similar, the difference in W_i values is therefore primarily due to differences in the state of flocculation. On the other hand, a higher value of W_i for the comparatively coarser fly ash indicates both state of flocculation and particle shape to be responsible for the difference.

During the course of bleeding tests on lime-fines pastes the particles of pozzolana or slag remained in contact with a saturated solution of lime as against a changing concentration in the pastes of fines alone. Differences in state of flocculation on this account would thus be negligible in the former pastes. This is supported by the observation that 1:2 mix of lime with surkhi or slag showed the same value of W_i because the two powders had the same fineness and similar particle shape. But both 1:2 and 1:3 lime-fly ash mixes, though coarser, gave higher W_i values (Table 2). The difference in nature and shape of fly ash particles alone can explain it.

Steinour (11) considers the differences in W_i in portland cements of different compositions to be due to chemical reactions. According to him a significant amount of initial reaction takes place and the reaction products form as coatings on the cement particles, the latter increasing the immobile phase (W_i) at the expense of the mobile one. In view of this the pozzolanic and slag cement pastes are expected to show lower values of W_i, and actually this was found to be so (Table 1). But the data also show that reduction of W_i values for the pozzolanic and slag cements is not related in any way to the proportion of the active constituent, i.e., clinker. In view of this and the above discussion it may be inferred that the magnitude of W_i in the pozzolanic and slag cement pastes is a result of both the chemical and physical factors, particle shape of replacements playing an important role.

The degree of flocculation is known to influence the bleeding capacity strongly. The data on the bleeding capacity of the different pastes is reported in Tables 1-3 and the results are self-explanatory. The plots of $\sqrt{\Delta H'/C}$ vs W/C (by volume) for the pastes of cement, lime-pozzolana mixes and powders yielded straight-lime relationships, showing thereby that Eq. 2 holds good for all these pastes. The values of the constant $(W/C)_m$, which is the value of W/C where the straight line crosses the W/C axis, are reported in the last column of Tables 1-3. The $(W/C)_m$ values of lime-pozzolana pastes were generally higher than those of the portland cement, showing thereby an equal or a higher degree of flocculation. The values of $(W/C)_m$ for the two pozzolanic cements were 0.58 and 0.76, compared with 0.91 for the portland cement, indicating a lower degree of flocculation and a lower strength of the floc structure of the pozzolanic cement paste. In short, the physical structure of the different pastes differs significantly at early stages.

Rheological Behavior of Cement Pastes

According to Powers (1), solvated surfaces and electrostatic charge, size, shape and concentration of particles, and the viscosity of the fluid account for the rheological properties of a portland cement paste. Reiner (21) considers portland cement paste at W/C ratio of 0.40 and above as a first approximation to a Bingham body. Obviously, the rheological properties of a paste of slag or pozzolanic cement will be influenced by the physicochemical nature of the cement replacement.

According to Shalom and Greenberg (4), portland cement pastes show three types of rheological behavior: antithixotropic (A), reversible (R) and thixotropic (T). Antithixotropic behavior was characterized by a flow curve (rpm-torque) in which the

TABLE 4

RHEOLOGICAL DATA FOR PASTES OF DIFFERENT CEMENTS

Designation and Composition of Solids	W/S Ratio (vol)	Apparent Viscosity, CP[a]		Yield Values (dynes/cm^2)		Rheological Behavior		
		15 Min	45 Min	15 Min	45 Min	15 Min	45 Min	180 Min
Portland cement	1.89	76.0	85.5	40.3	66.5	A	R	T
Portland blast-furnace cement (PBF)	1.89	19.0	66.5	23.6	49.9	R	R	T
Portland blast-furnace cement (FBP)	1.89	57.0	76.0	27.1	47.3	R	R	—
Portland-pozzolana cement (fly ash)	1.89	19.0	28.5	51.6	57.8	T	T	T
Granulated slag	1.89	33.6	54.4	10.9	35.2	T	T	T

[a] The apparent viscosity was calculated from the deflection values corresponding to 25 RPM on the upcurve.

descending portion (decreasing rpm) is to the right of the upcurve (increasing rpm) and was noticeable 15 to 20 minutes after vigorous mixing. The reversible rpm-torque curves were obtained after 45 minutes of hydration. The predominant kind of flow was found to be thixotropic and was considered to be characteristic of the hydrogel formed by hydration of calcium silicates in cement.

In this study flow curves were obtained for the pastes of a portland cement, two slag cements (PBF and FBP) and a pozzolanic cement prepared at a water-cement ratio of 0.60 by weight. The results for the portland cement pastes were found to be similar to those obtained earlier by Shalom and Greenberg. The pozzolanic and slag cement pastes did not show antithixotropy—or dilatancy in the view of some (22). However, the reversible behavior was more commonly exhibited after 45 minutes by all the cement pastes except that of the pozzolanic cement. All the pastes showed thixotropy after 3 hours. The downcurve for the pozzolanic cement pastes was found to be on the left side of the ascending curve throughout the period of study. Similarly, a paste of the granulated slag prepared at an equivalent water-solid ratio (by volume) also showed thixotropic behavior throughout.

The apparent viscosity and yield values for the different cement pastes at early periods are reported in Table 4; values at 3 hours are not given, as they are not reliable. The viscosity was highest for the portland cement paste and lowest for the pozzolanic cement, the slag and slag cement pastes having intermediate values. Similarly, the yield values for the portland cement paste were highest. The yield values of the two slag cements were of the same order but lower than that of the pozzolanic cement paste.

Since a higher degree of flocculation generally implies comparatively higher apparent viscosity and yield value, the results of the portland cement paste in relation to other pastes were as expected. But the results of the other pastes, when compared among themselves, did not follow any definite pattern. For example, the apparent viscosity of the PBF cement was found to be lower than that of the FBP cement even though the content of clinker in the former cement was about two times as great. Because fineness of the two cements and water-solid ratio of the two pastes were the same, higher viscosities of the FBP cement would be due primarily to its higher gypsum/C_3A ratio. Since gypsum can alter the arrangement of hydration products considerably, its effects on the early structure of slag and pozzolanic cement pastes appear to be more important than on portland cement.

The study shows that replacement of portland cement particles in a paste by slag or pozzolana influences significantly the initial framework resulting from their interaction. Since the initial framework established on setting could determine the way in which the subsequent structure of hydration products is set up (2), a detailed investigation of the different factors influencing the rheological behavior of the slag and pozzolanic cement pastes is desirable for improving their properties.

Differences in Structure of the Pastes

While the total porosity of the sediment of a fresh paste can be calculated easily, it is difficult to know the pore-size distribution. However, the mean size of pores can be estimated from its hydraulic radius (1) and can be a useful guide for comparing the

TABLE 5

PORE SIZES OF FRESH PASTES OF CEMENT AND CEMENTITIOUS MATERIALS

Paste Composition	W/C Ratio		Fineness of Solids (cm^2/cc)	Water Content[a] W (abs. units)	Porosity of Sediment (percent)	Hydraulic Radius[b] (microns)			Estimated Average Width of Pore[c] (microns)
	Wt	Vol				A	B	C	
Portland cement (PC)	0.35	1.10	6860	0.521	51.2	1.586	0.764	1.558	3 - 6
	0.40	1.25	6860	0.556	55.4	1.826	0.939	1.686	3 - 6
	0.60	1.87	6860	0.653	59.4	2.740	1.610	1.807	3.5 - 7
Portland pozzolana cement (fly ash)	0.35	1.10	5736	0.521	49.9	1.897	1.059	1.816	3.5 - 7
Portland pozzolana cement (surkhi)	0.35	1.10	6317	0.521	48.9	1.721	1.226	1.616	3 - 6.5
Portland blast-furnace cement (PBF)	0.40	1.25	6860	0.556	54.2	1.959	1.067	1.910	3.5 - 7.5
Hydrated lime	0.875	1.99	9000	0.666	64.3	2.220	1.152	2.138	4 - 8.5
1:2 Lime-slag	0.60	1.67	6413	0.626	60.7	2.610	1.526	2.531	5 - 10
1:2 Lime-surkhi	0.65	1.62	6246	0.620	60.8	2.612	1.517	2.561	5 - 10
1:2 Lime-fly ash	0.70	1.65	5312	0.623	60.5	3.112	1.612	3.020	6 - 12
1:3 Lime-fly ash	0.70	1.65	4851	0.623	59.4	3.407	1.876	3.243	6.5 - 13

[a] W = 1-C where C is cement or solid content per unit volume of the original paste.

[b] A is the hydraulic radius calculated from $W/C\sigma$, considering W equal to the water content of the paste before bleeding; B is the hydraulic radius calculated from the formula $(W-W_i)/(C\sigma)$ where W_i is the immobile water (Tables 1-3); C is the hydraulic radius calculated from the formula $W/C\sigma$ where W is the water present in the sediment after bleeding and the volume of water corresponds to the porosity of sediment.

[c] Values of hydraulic radius under column C were used for calculating average width of pores.

TABLE 6

COMPARATIVE VALUES OF W_o/C FOR DIFFERENT CEMENTS

Cement Designation	W/C Ratio	W_t/C, 90 Days	W_o/C
Portland cement	0.400	0.456	0.400
	0.500	0.510	0.460
	0.550	0.556	0.504
	0.600	0.610	0.557
Portland blast-furnace cement (PBF)	0.400	0.422	0.375
	0.500	0.516	0.467
	0.550	0.550	0.483
	0.600	0.553	0.492
Portland blast-furnace cement (FBP)	0.400	0.403	0.373
	0.500	0.505	0.478
	0.550	0.504	0.478
Portland pozzolana cement (fly ash)	0.400	0.396	0.362
	0.500	0.472	0.426
	0.550	0.490	0.444

structure of different pastes. The hydraulic radius is a quotient of water content and wetted surface area. The estimated average width of pore was calculated on the assumption that the section of a typical pore resembles a rectangular slit (19).

The data for some typical pastes at the commonly employed W/C ratios show that the mean pore size in pozzolanic cement pastes was greater than in the portland cement paste even when the total porosity after bleeding was lower.

The mean pore size in the pastes was calculated under three conditions (Table 5): A, when W is equal to the water content of the paste before bleeding; B, when W is corrected by subtracting the immobile water, W_i; and C, when water content of the paste is considered equal to water present in the paste after bleeding, i.e., when volume of water corresponds to the porosity of the sediment of the paste. The data in Table 5 show that under conditions A and B the mean pore sizes of the pastes of lime and pozzolana or slag are comparable to that of the portland cement paste (W/C = 1.87), but under condition C, i.e., when the bleeding is over, the mean pore size is 1½ times that of the portland cement paste.

Since comparisons of the mean pore size are realistic only under condition C, it would be desirable that the mean size of pores in the fresh pozzolanic and slag cement pastes under condition C be very near or even smaller than the pore size in the portland cement paste because pore size is probably more important than the total porosity. Since at a given water content pore size decreases if the specific surface area of the powder increases, grinding of slag or pozzolana to a slightly greater fineness is suggested. Because finer grinding may lead to greater settled volume, it is difficult to say how much finer; broadly speaking, the fineness of the pozzolanic or slag cement could be made equal to that of a portland cement in terms of cm^2/cc instead of cm^2/g because of widely differing densities of the two cements. However, there may be other methods of reducing mean pore size, but they are outside the scope of this paper.

It was shown earlier that the important differences between the pastes of slag and pozzolanic cements and portland cement paste were degree of flocculation, strength of the floc structure and porosity of the sediment. The latter will affect the rate of hydration and strength characteristics of the hardened pastes. If strength is considered to be related to gel-space ratio (23), differences in porosity of the sediment after bleeding become important in any comparison of strength and other properties of clinker-based cements, among themselves or between them and ordinary portland cement. This is evident from the data on pastes of different cements prepared at equivalent W/C ratios (Table 6); W_0/C was calculated from Hayes and Copeland's formula (24). Very few workers have corrected W/C for bleeding in their interpretations of the strength data of the pozzolanic and slag cements. This is important for any realistic comparisons.

CONCLUSIONS

A study of the bleeding and rheological characteristics of the fresh pastes of pozzolanic and slag cements has shown important differences in their structure from that of portland cement paste. A comparison of the values of W_i, immobile water per unit volume of paste, and the minimum water-cement ratio, $(W/C)_m$, showed that cement replacements lowered the degree of flocculation, strength of the floc structure and porosity of the sediment. The apparent viscosity and yield values of the pastes were also lowered. The structure of the pozzolanic and slag cement pastes appeared to be influenced greatly by the physical characteristics of the replacements, the particle shape having a predominant influence. A similar conclusion was reached in respect to the structure of the fresh pastes of mixes of lime with either pozzolana or slag.

Though the values of the porosity of sediments of fresh pastes of pozzolanic and slag cements were considerably lower than that of portland cement paste, the mean pore size was greater. The mean pore size in the sediments of pastes of mixes of lime with pozzolana or slag was also greater—for example, the values was 1½ times greater for a 1:3 lime-fly ash mix of equivalent sediment porosity. The mean pore size, therefore, is considered more important than the porosity. For reducing pore size in the pastes of pozzolanic and slag cements, grinding of replacements to the specific surface of the portland cement on volume basis instead of weight basis is suggested.

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