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STUDIES ON VISCOSITY EQUATION OF PORTLAND CEMENT PASTE

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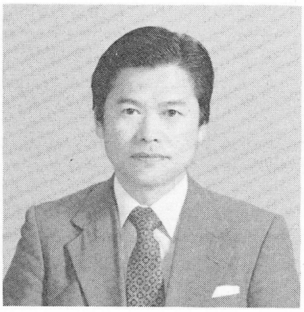


Jiro MURATA

Hiroji KIKUKAWA

SYNOPSIS

As basic research to establish a viscosity equation for mortar and concrete, the authors investigate the viscosity equation of cement paste. Various kind of cement are used to make cement pastes of water-cement ratios from 0.40 to 1.00 to measure rheological constants. For experiments, the authors change Roscoe's viscosity equation on suspensions of high concentrations to adapt it to portland cement paste. As a result of the experiments the authors propose a viscosity equation on cement paste with solid volume percentage,volumetric concentration, and Blaine specific surface as factors. Furthermore, corrections for thermal conditions, influence of time-dependent change, and influences of many kinds of admixtures are discussed.

J. Murata is a professor of civil engineering at Tokyo Metropolitan University, Tokyo,Japan.His research includes rheology of fresh concrete and rationalization of concrete construction. He is a member of JSCE,JCI,ACI and RILEM. He received the Yoshida Medal from JSCE in 1961 for "Studies on Permeability of Concrete," the JCI Medal in 1978 for " Fundamental Studies on the Rheology of Fresh Concrete," and the JCA Medal in 1985 for "Rheological Analysis of Pipe Flow of Cement Mixtures and Application Thereof."

H. Kikukawa is an associate professor of civil engineering at Meijo University, Nagoya, Japan. A major research theme of his is the rheology of fresh concrete. He has published two papers on rheology at international conferences, one the RILEM Seminar on Fresh Concrete at Leeds University, U.K.,in 1973, and the other the International Symposium on Cement and Concrete at Beijing, China, in 1985. He is a member of JSCE, JSR, JCI, and JSMS. He was a recipient of a Yoshida Citation from JSCE in 1969 for "Studies on the Rheology of Fresh Concrete."

1. INTRODUCTION

Ever since Einstein published his relative viscosity equation on dilute suspensions in 1906 [1], there have been valuable proposals made by many researchers regarding their respective studies concerning viscosity equations for dispersed systems [2]- [7]. Cement paste is a type of highly-concentrated suspension, but few investigations have been made with respect to its viscosity equation, and only the works of Kakuta and Akashi [8] and Vom Berg [9] were to be found in the past so that many points remain unknown even now.

One of the most important things needed to be done in aiming for rationalization of concrete construction is gaining a grasp of the physical properties to be used in analyzing fluidity of concrete. The method presently used is that of making measurements by viscometer, but testing procedures are generally complicated and require skill, and it is not a simple matter to carry out tests in the field. It is said that yield value among physical values of a Bingham body can be estimated based on slump [10], but a convenient method of measuring viscosity is yet to be found, and it is thought a promising means would be to rely on a viscosity equation as is done with dispersed systems in general. That is, it will be possible to estimate the viscosity of concrete from the material characteristics and mix proportioning conditions with the viscosity equation as a medium.

Concrete is a type of highly concentrated suspension with coarse aggregate said to be the solute and mortar the solvent. It is also deemed to be suitable to consider fine aggregate as the solute of mortar and cement paste as the solvent [11]. Therefore, the viscosity of the solvent in mortar can be estimated from the viscosity equation of cement paste, the viscosity of the solvent in concrete can be estimated from the viscosity equation of mortar, and in the end, the viscosity of concrete can be estimated from the viscosity equation of concrete.

In this sense, the viscosity equation of cement paste has an extremely important significance for the purpose of rationalization of concrete construction, while it is thought that even the viscosity equation of cement paste by itself can be used effectively for prediction of pumping and filling of grout for prestressed concrete (cement paste).

This paper is a summarization of studies begun in 1977 on the viscosity equation of portland cement paste extending Roscoe's viscosity equation concerning high-concentration suspensions [5] to suit cement paste, further making corrections for temperature conditions and time elapsed after mixing, and discussing the influences of various chemical admixtures.

2. MATERIALS USED

The cements used in experiments were three brands of ordinary portland cement and one brand each of high-early-strength, ultra-high-early-strength, and moderate heat portland cements. The chemical compositions and physical test results of these cements are given in Table 1.

Water from a well in the premises of the Faculty of Science and Engineering, Meijo University, was used for mixing.

The chemical admixtures used were the 16 varieties listed in Table 2, consisting of air-entraining agents, air-entraining water-reducing agents, water-reducing agents, and as many others as possible to ascertain effects on the viscosity of cement paste.

Table 1 Test results of portland cements.

Item		Ordinary			High-early-strength	Ultra-high-early-strength	Moderate heat
		A	B	C			
Chemical analysis	Ignition loss (%)	0.7	0.7	0.6	0.7	1.0	0.6
	Insoluble residue (%)	0.1	0.1	0.1	0.6	0.2	0.5
	SiO_2 (%)	22.2	22.1	22.8	21.3	19.5	23.3
	Al_2O_3 (%)	5.2	5.6	5.3	4.7	5.2	4.2
	Fe_2O_3 (%)	3.1	2.9	2.7	2.7	2.7	4.0
	CaO (%)	65.0	64.2	63.8	65.9	65.6	63.2
	MgO (%)	1.4	1.8	1.8	1.2	1.1	1.5
	SO_3 (%)	1.9	2.0	2.1	2.3	3.6	1.9
	Total	99.6	99.4	99.2	99.4	98.9	99.2
Specific gravity		3.16	3.16	3.16	3.14	3.13	3.20
Fineness (cm²/g) *		3290	3150	3180	4390	5870	3240
Time of setting	Temperature (℃)	20.0	20.3	20.0	20.3	20.6	20.0
	Humidity (%)	85	86	92	94	96	91
	Water (%)	26.9	27.8	28.0	29.9	33.0	27.4
	Initial (h-min.)	2-23	2-34	2-32	2-10	2-07	3-30
	Final (h-min.)	3-32	3-52	4-13	3-26	3-12	4-47
Soundness		good	good	good	good	good	good
Compressive strength (kgf/cm²)	Flow	252	264	265	245	224	252
	3 d	145	143	143	253	340	125
	7 d	238	239	222	360	403	170
	28 d	412	422	407	454	468	350
Curing temperature (℃)		20.0	20.0	20.0	20.1	20.0	20.2

1 kgf/cm² = 98 Pa

* Blaine specific surface

Furthermore, a cellulose-base water-retention agent (NL 1850 used 0.25 percent by weight of cement) was added, except in the series testing the effects of chemical admixtures, with the purpose of preventing segregation of samples while measuring viscosities of cement pastes by rotation viscometer.

3. METHOD OF TESTING

3.1 Method of Mixing

The volume of one batch of cement paste was 10 ℓ and mixing was done using a Hobart-type mortar mixer of capacity of 20 ℓ. All the materials were introduced simultaneously into the mixer and mixed for 1 min at 80 rpm after which the mixer was stopped for 20 sec. During this intermission, material that had adhered to the inner wall and mixing blades of the mixer was scraped off, and mixing was again done for 2 min at 80 rpm.

Samples finished mixing were immediately subjected to rheological constant measurements and flow tests.

3.2 Method of Rheological Constant Measurement

a) Viscometer

The viscometer used was an inner-cylinder-rotating type, double-cylinder

Table 2 Varieties of admixtures used.

Variety	Symbol	Component	Dosage (wt·%)*
AEA	a	Alkylaryl ether	0.04
	b	Abietic acid	0.03
AE water reducer	c	Calcium lignosulfonate	0.25
	d	Oxycarboxylic acid with alkyl radical	0.1
Water reducer	e	Sodium oxycarboxylate	0.2
	f	Polyol complex	0.25
Super-plasticizer	g	Naphthalene sulfonate formaldehyde high condensate	0.6
	h	Melamine resin (high condensate triazine compound)	3.0
	i	Naphthalene sulfonate - lignosulfonate co - condensate	1.0
Other	j	Protein	1.0
	k	Epoxy resin	2.0
	l	Calcium chloride	4.0
	m	Silicofluoride	0.25
	n	Composite fluidifier (grouting agent)	1.0
	o	Polyoxyethlene alkylphenol ether and special organic high polymer compound	0.25
	p	Methacrylic ester - acrylamide copolymer	0.01

* Standard dosage by weight of cement

rotation viscometer with radius of inner cylinder 7 cm, length 12 cm, and radius of outer cylinder 9 cm.

In the past, the viscometers used for measuring viscosity of cement paste had inner cylinders with radii of about 20 mm, and spacings between inner and outer cylinders of 1 to 5 mm. The reason a viscometer of a fairly large size was used in the experiments reported here was that the breadth of flow of sample in the container is proportional to the radius of the inner cylinder [12], and when this study is to be extended to mortar and concrete, the inner cylinder can be used without alteration under the consideration that questions will not arise regarding the interrelations with test values obtained in these experiments.

The reason the outer cylinder radius was made 9 cm and the space between the outer and inner cylinders 2 cm was that as a result of measuring the flow velocities at various parts of the sample by a multi-point method [13] using a vessel of outer cylinder radius 11.5 cm, it was ascertained that a breadth of flow of 2 cm is obtained even in case of a cement paste of relatively stiff consistency.

b) Procedure of Measurement

Since it was determined that all of the sample in the vessel would flow, slipping between the sample and the wall surfaces of the outer and inner cylinders was taken into consideration, and the method of measuring flow velocities at two points of the sample very close to the surfaces of the outer and inner cylinders was adopted.

The procedure followed in making the measurements was as described below.

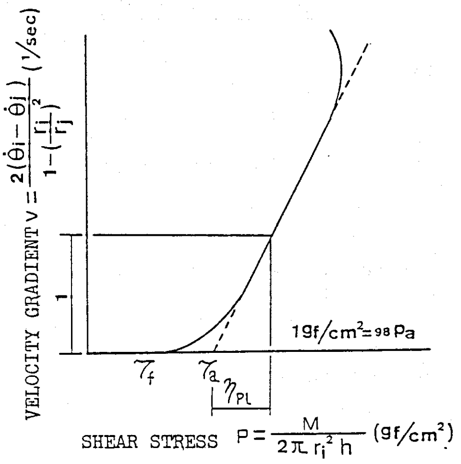


Fig. 1—Consistency curve of cement paste.

i) Correctly set the outer and inner cylinders at their proper locations. Pour sample into the space between the two cylinders and finish the top surface of sample to be flush with the top of the inner cylinder.

ii) Scatter foamed styrene powder near the wall surfaces of the outer and inner cylinders to serve as reference points for measuring flow velocity.

iii) Increase the speed of the inner cylinder in steps of 10 rpm between 10 and 30 rpm, 5 rpm between 30 and 60 rpm, and 10 rpm between 60 and 80 rpm, and film the movements of the reference points at the respective speeds by 8-mm camera, while also reading off torque.

iv) Project the images of the developed film on a screen by memo-motion apparatus with the images magnified and motion slowed down, and measure the flow velocity at a location 0.2 cm from the wall surfaces of the outer and inner cylinders.

v) Use the flow velocities measured at 0.2 cm from the outer and inner cylinder wall surfaces and plot the consistency curve with the ordinate and abscissa as given by Eq. (1) (see Fig. 1).

$$\left.\begin{aligned} &\text{Ordinate} \\ &V = \frac{2(\dot{\theta}_i - \dot{\theta}_j)}{[1 - (\frac{r_i}{r_j})^2]} \\ &\text{Abscissa} \\ &P = \frac{M}{2\pi r_i^2 h} = \frac{1}{2\pi r_i^2 h}\,\frac{M'}{1 + \alpha} \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where, r_i, r_j: respective radii (cm) at locations 0.2 cm from inner and outer cylinder wall surfaces (r_i = 7.2 cm, r_j = 8.8 cm), $\dot{\theta}_i$, $\dot{\theta}_j$: respective angular velocities at r_i and r_j (rad/s), h: length of inner cylinder (cm), M: corrected value of torque (gf·cm), M': measured value of torque (gf·cm), α: correction factor given in c).

vi) Determine plastic viscosity as inverse gradient of straight-line portion of consistency curve and compute yield value by Eq. (2).

$$\tau_f = \beta \cdot \tau'_f = \beta \cdot \frac{(\frac{r_i}{r_j})^2 - 1}{2\ln(\frac{r_i}{r_j})} \cdot \tau_a \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where, τ_f: yield value (gf/cm²), τ'_f: apparent yield value (gf/cm²), τ_a: longitude of intersecting point of straight-line portion of consistency curve and abscissa (gf/cm²), β: correction factor given in c).

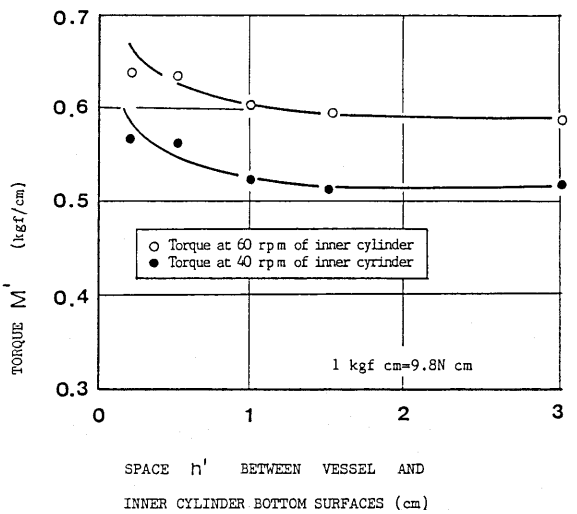


Fig. 2 - Relation of space h' between inner cylinder and vessel bottom with torque (cement paste, W/C = 0.50).

c) Correction of Test Values

The ratio of length to the radius of the inner cylinder of the viscometer used is large and it is necessary for test values to be corrected taking into consideration the end effect of the inner cylinder.

With total torque acting on the inner cylinder as M' (measured value), the torques acting on the side and bottom surfaces of the inner cylinder as M and M_e, respectively,

$$M' = M + M_e \qquad \ldots\ldots\ldots \; (3)$$

M_e is the torque due to sample at the bottom surfaces of the inner cylinder and the vessel, and if the yield value of the sample is ignored,

$$\frac{M_e}{M} = \frac{1}{8}\,\frac{R_i}{h'}\,\frac{R_i}{h}\,\{1 - (\frac{R_i}{R_o})\} = \alpha \qquad \ldots\ldots\ldots\ldots\ldots \; (4)[14]$$

where, h': space between bottom surfaces of inner cylinder and vessel (cm), R_i, R_o: radii of inner and outer cylinders (cm).

From Eqs. (3) and (4), $M'/M = 1 + \alpha$.

$$\therefore M = \frac{M'}{1+\alpha} \qquad \ldots\ldots\ldots\ldots\ldots \; (5)$$

Fig. 2 shows representative results of tests comparing values of M' when the space between the bottom surfaces of the inner cylinder and the vessel was varied between 0.2 and 3 cm, and when the space becomes 1 cm or more, differences in the values of M' are not seen. Consequently, correction factor was determined by Eq. (4) with h' = 1.0 cm.

Next, the following corrections were made regarding yield value.

With the torques due to resistances corresponding to the yield values of the sample acting on the side and bottom surfaces of the inner cylinder as M_f and M_{ef}, respectively,

$$\left.\begin{aligned} M_f &= 2\pi R_i^2 \tau_f \\ M_{ef} &= \int_0^{R_i} 2\pi r^2 \tau_f \cdot d_r = \frac{2}{3}\,\pi R_i^3 \tau_f \end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots\ldots \; (6)$$

$$\beta = \frac{M_f}{M_f + M_{ef}} = \frac{3h}{3h + R_i} \qquad \ldots\ldots\ldots\ldots\ldots \; (7)$$

Table 3 Influence of vessel dimensions on rheological constants (ordinary portland cement paste, W/C = 0.40).

Inner cylinder radius (r)		2.5cm	3.5cm	5.0cm	7.0cm
Inner cylinder length (h)		10 cm	10 cm	12 cm	12 cm
2r/h		0.50	0.70	0.83	1.17
η_{rl} (poise)	Before correction	27.3 (1.09)	26.3 (1.05)	27.6 (1.10)	30.2 (1.21)
	After correction	25.0 (1.00)	24.0 (0.96)	24.5 (0.98)	25.1 (1.00)
τ_f (gf/cm²)	Before correction	0.36 (1.09)	0.39 (1.18)	0.41 (1.24)	0.39 (1.18)
	After correction	0.33 (1.00)	0.34 (1.03)	0.36 (1.09)	0.33 (1.00)

1 poise = 0.1 Pa·s , 1 gf/cm² = 98 Pa

The values before and after correction of plastic viscosity and yield value in case of using inner cylinders of various radii and lengths are given in Table 3. This table shows no difference to exist between before and after correction for both plastic viscosity and yield value in case of ratio of diameter to height about 0.5, but as this ratio gradually becomes larger, the apparent rheological constant becomes considerably large when correction is not done. However, it is shown that if the abovementioned corrections are made, values similar to the case of using a small inner cylinder are obtained for both plastic viscosity and yield value even though an inner cylinder of radius about 7 cm and length smaller than diameter is used.

d) Flow Test

The table top of the flow testing apparatus specified in JIS R 5201 was replaced by one of the same weight but of diameter 450 mm, and this was used for measuring consistency of cement paste.

4. VISCOSITY EQUATION

To obtain basic data to provide a viscosity equation for cement paste, pastes of water-cement ratios ranging between 0.40 and 1.00 were mixed using the three brands of ordinary cement and one brand each of high-early-strength, ultra-high-early-strength, and moderate heat cements mentioned in 2., and the plastic viscosities and yield values immediately after mixing were measured by double-cylinder type rotation viscometer. The temperatures of samples were in the range of 20±2°C.

The results of the tests are given in Table 4. The test values in this table are all averages of four to five tests.

Viscosity equations for suspensions in general were investigated to seek out a viscosity equation for cement paste. The principal ones are listed in Table 5.

Kakuta and Akashi proposed a viscosity equation based on the Mori-Ototake equation in Table 5, Vom Berg proposed one considering the volume concentration and specific surface of cement, while the authors decided to adopt the following as the basic equation in view of the fact that Roscoe's equation yields data with trends similar to the test results shown in Table 4.

$$\eta_{re} = (1 - \frac{1}{C} V)^{-K} \quad \cdots\cdots (8)$$

Table 4 Plastic viscosity and yield value of cement paste.

Ordinary cement					High − ealy − strength cement			Ultra − high − early − strength cement			Moderate heat cement		
W/C	Volume concentration	Plastic viscosity, η_{rl} (poise) Yield value, τ_f (gf/㎠)			W/C	Volume concentration	η_{rl} τ_f	W/C	Volume concentration	η_{rl} τ_f	W/C	Volume concentration	η_{rl} τ_f
		A	B	C									
1.00	0.240	1.16 0.005	1.40 0.005	1.54 0.005	1.00	0.242	1.57 0.012	1.00	0.242	2.65 0.023	1.00	0.238	1.69 0.005
0.85	0.271	1.66 0.008	1.73 0.007	1.86 0.006	0.85	0.272	1.87 0.016	0.85	0.273	3.82 0.057	0.75	0.294	1.73 0.015
0.75	0.297	1.85 0.013	1.78 0.014	2.01 0.010	0.75	0.298	2.02 0.027	0.75	0.299	8.47 0.12	0.70	0.308	1.99 0.016
0.70	0.311	2.07 0.016	2.16 0.015	2.05 0.015	0.70	0.313	2.17 0.036	0.70	0.313	11.0 0.14	0.65	0.325	2.06 0.024
0.65	0.327	2.52 0.021	2.50 0.025	2.59 0.019	0.65	0.329	3.89 0.052	0.65	0.329	14.3 0.26	0.60	0.343	2.47 0.031
0.60	0.345	2.61 0.041	2.61 0.039	3.00 0.034	0.60	0.347	4.53 0.074	0.60	0.348	24.9 0.45	0.55	0.362	4.17 0.038
0.55	0.365	3.98 0.049	4.20 0.056	4.24 0.057	0.55	0.367	8.40 0.13	0.55	0.367	34.9 0.61	0.50	0.385	6.11 0.076
0.50	0.388	6.07 0.080	6.14 0.091	5.97 0.10	0.50	0.389	20.1 0.26	0.53	0.376	46.7 0.76	0.45	0.410	10.8 0.14
0.45	0.413	9.75 0.17	8.71 0.17	10.6 0.16	0.45	0.415	38.2 0.48	0.50	0.390	68.4 0.87	0.42	0.427	19.9 0.24
0.40	0.442	25.4 0.38	25.2 0.37	24.7 0.37	0.40	0.443	78.4 0.98	0.48	0.400	107 1.11	0.40	0.439	32.8 0.32
Percentage of solid volume		53.1	54.2	55.3			53.2			51.0			53.8

(Note) 1. Test value averages of 4 to 5 test results.
2. 1 poise = 0.1 Pa·s , 1 gf/㎠ = 98 Pa

Table 5 Viscosity equation of suspension system.

Author	Relative viscosity	Remark
A, Einstein [1]	$\eta_{re} = 1+2.5V$	Dilute suspension of spheres, V ; volume concentration
H, Brinkman [2]	$\eta_{re} = (1-V)^{-2.5}$	Broad particle-size distribution and high concentration V ; volume concentration
V, Vand [3]	$\eta_{re} = 1+2.5V+7.349V^2$	Suspension of equal-diameter spheres, V ; volume concentration
M, Mooney [4]	$\eta_{re} = \exp[2.5V/(1-KV)]$	K ; characteristic value of material, V ; volume concentration
R, Roscoe [5]	$\eta_{re} = (1-1.35V)^{-2.5}$	Equal-diameter spheres and high concentration, V ; volume concentration
J, Robinson [6]	$\eta_{re} = 1+[K(V/C)/(1-V/C)]$	K ; experimental constant, C ; percentage of absolute volume of solute, V ; volume concentration
Y,Mori T,Ototake [7]	$\eta_{re} = 1+3/(1/V-1/C)$	C ; limit high concentration, V ; volume concentration

where, η_{re}: relative viscosity of cement paste (ratio between viscosity of suspension and viscosity of solvent), c: absolute volume percentage of cement, V: volume concentration of cement, K: shape factor of cement particle assemblage.

Roscoe's equation is Brinkman's equation to which the concept of giant particles (agglomerated condition of solute particles) has been introduced, while in Eq. (8), an optional nature is further given to the shape factor of the particle agglomeration.

It is said that cement particles in a cement suspension do not act individually in flow but make up an agglomerated particle condition [13]. The K in Eq. (8) is the shape factor of the particle agglomeration, and its substance is studied below.

Fig. 3 shows the relation between volume concentration of cement and K, and Fig. 4 that between Blaine specific surface of cement and K. It may be seen from

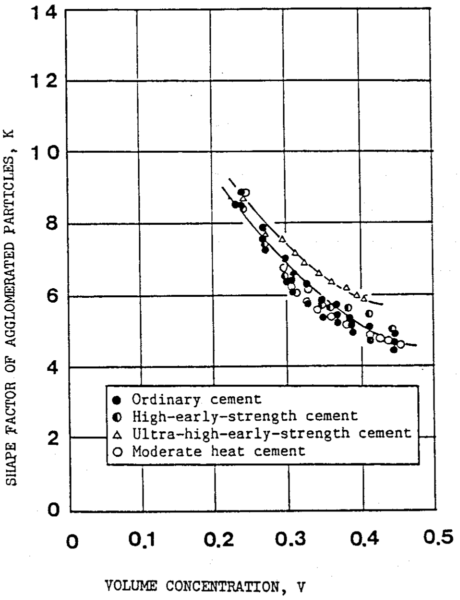


Fig. 3 - Relation of shape factor of agglomerated particles in cement paste and volume concentration of cement (W/C = 0.40- 1.00).

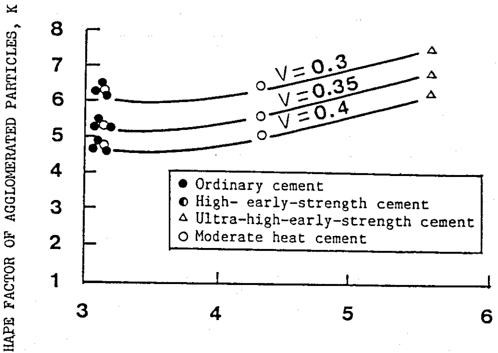


Fig. 4 - Relation of shape factor of agglomerated particles in cement paste and specific surface of cement (W/C = 0.40- 1.00).

Figs. 3 and 4 that K can be expressed by the exponential function of volume concentration and specific surface of cement. Accordingly, the exponent term in Eq. (8) is

$$K = \alpha \cdot V^{\beta} \cdot \phi^{\gamma} \qquad \text{(9)}$$

where, V: volume concentration of cement, ϕ: Blaine specific surface of cement (cm^2/g), α, β, γ: experimental constants

Therefore, the viscosity equation considering specific surface of cement and volume concentration of particle agglomeration will be as follows:

$$\eta_{re} = \left(1 - \frac{1}{c} V\right)^{-\alpha \cdot V^{\beta} \cdot \phi^{\gamma}} \qquad \text{(10)}$$

Computing K by Eq. (8) using the measured values given in Table 3 and applying the method of least squares to obtain α, β, and γ, the results obtained were $\alpha = -1.0$, $\beta = -1.03$, and $\gamma = 0.08$.

The plastic viscosity of portland cement paste can be estimated by Eq. (10) with the solvent viscosity (viscosity of water) as $\eta_o = 1.002$ cP (20°C). However, calculations by Eq. (10) are complicated. In Eq. (10), β is close to 1 while γ at 0.08 is small, and as shown in Fig, 4, there is hardly any influence of fineness except in case of extreme fineness as with ultra-high-early-strength cement. This is probably because the influence of fineness is already included in the percentage of absolute volume. For practical purposes, therefore, the following equation can be proposed ignoring the influence of fineness for the sake of

Table 6 Unit weight of portland cement.

Variety	Ordinary			High-early strength	Ultra-high-early strength	Moderate heat
	A	B	C			
Unit weight (kg/m³)	1677	1713	1746	1672	1595	1720

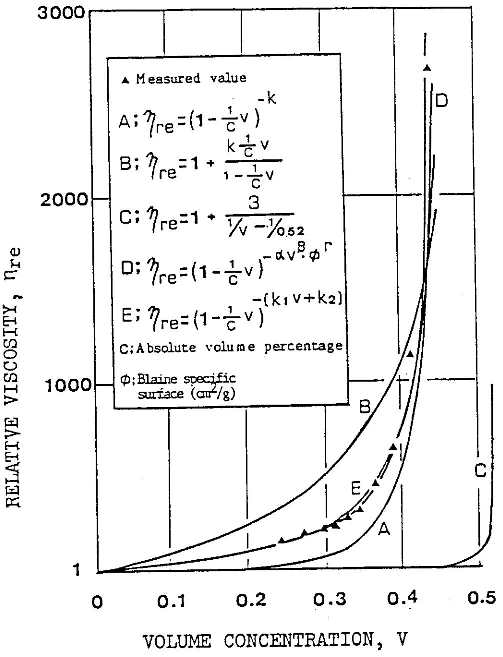


Fig. 5 - Relative viscosity of cement paste (ordinary portland cement B, W/C = 0.40- 1.00).

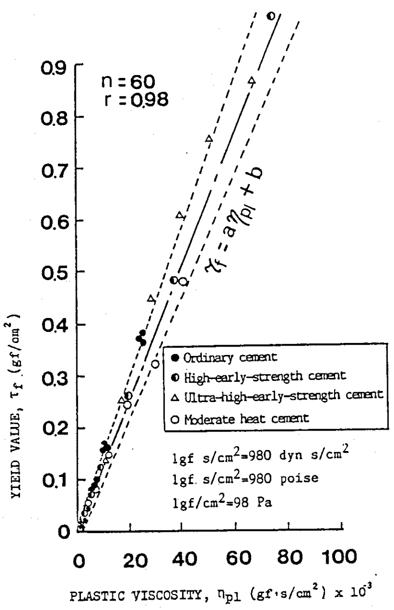


Fig. 6 - Relation of yield value and plastic viscosity of cement paste (W/C = 0.40- 1.00).

simplicity, and moreover, assuming K and volume concentration to have approximately a linear relationship.

$$\eta_{re} = (1 - \frac{1}{c} V)^{-(K_1V + K_2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

where, K_1 = -17.5 and K_2 = 12.0.

The percentage of absolute volume of cement was obtained by the method described below.

The percentages of absolute volume of cement in Eqs. (10) and (11) were measured by the method below using the test method for pigments [16] as reference and employing the cell and plunger of the Blaine air permeability apparatus specified in JIS R 5201. Filter paper was laid on the bottom surface of the cell, cement was filled to the top, and the plunger was pushed in. The plunger was pulled out, cement was filled to the top in the space left, the plunger was pushed in, and the volume of the cement was determined by the depth of insertion of the plunger. The weight of the cement was measured and absolute volume percentage c' calculated. The pressure when pushing in the plunger was made 15 kgf/cm^2. This was because at higher than approximately 10 kgf/cm^2 differences in unit weights were not recognizable.

The absolute volume percentage of cement in an agglomerated condition is expressed by $c = \xi c'$. The value of ξ is unknown, but since cement particles in an agglomerated condition are thought to have point contact with each other, it will be permissible to consider approximately that ξ is 1.0.

The unit weights of the portland cements measured are given in Table 6.

Fig. 5 shows the relationships between volume concentrations and relative viscosities of cement pastes using various viscosity equations. The curve D and E given by Eqs. (10) and (11) show good conformities with experimental values. The estimated errors when using Eq. (10) are in a range of approximately ±7 percent.

Next, the test results of Table 4 are used to graphically express the relationships between plastic viscosity and yield value as shown in Fig. 6.

In Fig. 6, it is seen that in the case of a two-phase material such as cement paste yield value indicates linear proportionality to plastic viscosity. This is thought to be because in case of a highly concentrated suspension plastic viscosity η_{pl} is increased more the higher the concentration of solute, while yield value τ_f also increases with increased proximity of solute particles.

The relation between plastic viscosity and yield value is given by the following equation:

$$\tau_f = a\eta_{pl} + b \quad \text{..........} \quad (12)$$

where, τ_f: yield value (gf/cm^2), η_{pl}: plastic viscosity (gf·s/cm^2), a, b: experimental constants, $a = 1.2 \times 10$ (s^{-1}), $b = 1.2 \times 10^{-2}$ (gf/cm^2).

In case of cement paste, yield value τ_f cannot be estimated from values such as of slump as in the cases of mortar and concrete, so that it is thought for practical purposes to be extremely effective to estimate yield value τ_f from plastic viscosity η_{pl} of cement paste using Eq. (12).

5. INFLUENCES OF TEMPERATURE OF CEMENT PASTE, TIME ELAPSED AFTER MIXING, AND ADMIXTURES

The viscosity equation given in 4. is applicable to cement paste of standard temperature immediately after mixing, which does not contain an admixture. Therefore, it is necessary to study a method of correcting the viscosity equation in case of variation in temperautre and elasped time.

5.1 Influence of Temperature of Cement Paste

The results of tests comparing plastic viscosities and yield values in case of

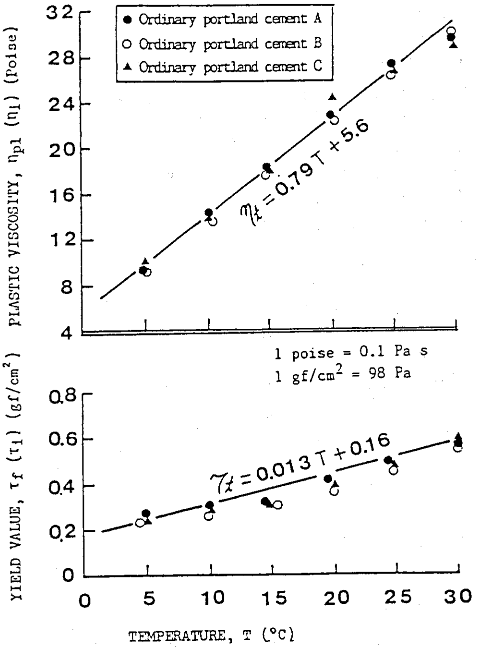


Fig. 7 - Temperature-dependent variations in rheological constants of cement paste (W/C = 0.40).

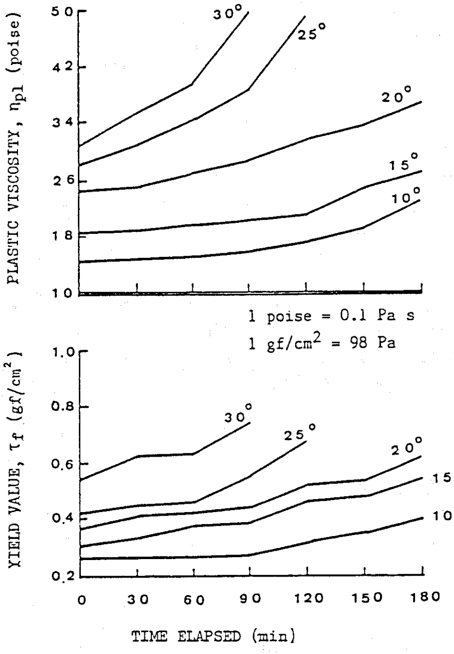


Fig. 8 - Time-dependent changes in rheological constants of cement paste (ordinary portland cement C, W/C = 0.40).

varying temperatures as mixed to be approximately 10°C, 20°C, and 30°C are shown in Fig. 7 for cement pastes of water-cement ratio 0.40 using the three brands of ordinary cement. Since there were hardly any differences between the three brands of cement, the points in Fig. 7 are indicated by averages of the three.

In Fig. 7 plastic viscosity and yield value are greater the higher the sample temperature indicating that in cement paste increase in viscosity due to solvation is more dominant than reduction in solvent viscosity due to temperature rise.

More or less linear relationships are recognized for sample temperature with plastic viscosity and yield value in the range of sample temperautre approximately 10 to 30°C, and in the case of plastic viscosity the relationship is expressed by the following equation:

$$\eta_t = 0.79\ T + 5.6 \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (13)$$

where, η_t =plastic viscosity of cement past at T°C, T : temperature of cement past.

In case of making a correction with the value at 20°C as the reference,

Correction Amount

$$\Delta\eta = \eta_t - \eta_{20} = 0.79\ T + (\eta_{20} - 15.8) \quad \cdots\cdots\cdots\cdots \quad (14)$$

Similarly, in case of yield value, the correction amount will be

$$\Delta\tau = 0.013 + (\tau_{20} - 0.26) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (15)$$

5.2 Influence of Time Elapsed After Mixing

Using one of the brands of ordinary cement (C in Table 1), plastic viscosities and yield values were measured for cement pastes of water-cement ratio 0.40 varying time elapsed after mixing and temperature at five levels each between 30 and 180 min. and approximately 10 and 30°C, respectively. The results of the tests are shown in Fig. 8.

The following trend can be recognized from Fig. 8. There is a time zone in which plastic viscosity increases more or less linearly with time from immediately after mixing. This time zone varies according to temperature and is 120 min at 10°C, 90 min at 20°C, and 60 min at 30°C. Plastic viscosities increased 1.4 poise/h, 1.5 poise/h, and 8.3 poise/h, respectively, during these times.

Consequently, it is thought that plastic viscosities after given lengths of time have elapsed can be determined for each temperature if these increase rates are taken into account in the plastic viscosities immediately after mixing at the respective temperatures corrected according to 5.1.

5.3 Influence of Admixture

It has been known that a chemical admixture can have a great influence on the viscosity of a cement paste [17]. In the study reported here, admixtures produced in Japan were used with the range of the varieties of admixtures expanded to include air-entraining agents, air-entraining water-reducing agents, water-reducing agents, high-range water-reducing agents, an accelerating agent, a retarding agent, a foaming agent, a grouting agent, an adhesive, and a flocculating agent as listed in Table 2, and the influences of these were examined.

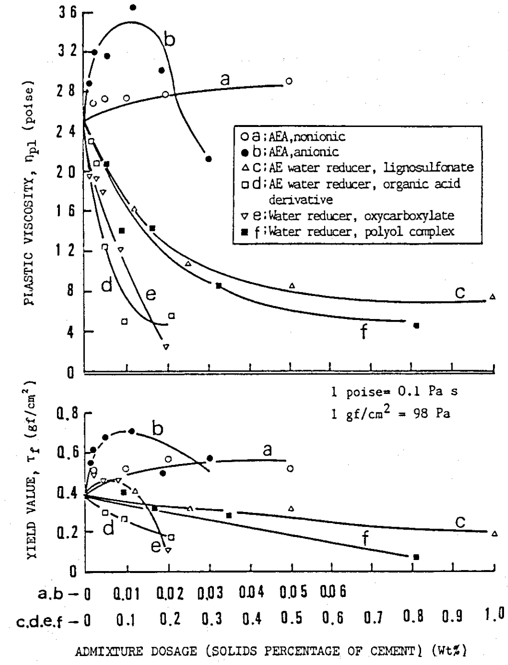
Cement pastes of water-cement ratio 0.40 were made using one of the ordinary portland cements, the various admixtures were added varying dosages at four or five levels with standard dosages as median, and the plastic viscosities and yield values were measured. The segregation inhibitor added in the other series of tests was not used in these cases.

The results of the tests are given in Figs. 9(a) to 9(c). The dosages of admixtures are indicated in these figures by ratios of solids by weight of cement.

In Fig. 9(a), "a" is a case of using a nonionic surface active agent and no influence of admixture dosage can be seen.

The case of "b" is for an ordinary air-entraining agent (anionic surface active agent) with both plastic viscosity and yield value increased up to dosage of 0.012 percent of the weight of cement, but turned around to show declining trends when this level was exceeded. The increase in viscosity is thought to have been caused by increase in attraction between particles due to impartation of hydrophobicity, and the decrease in viscosity by predominance of the influence of entrained air. That is, whereas air content was 7 percent in case of dosage of admixture 0.012 percent by weight of cement, air contents were approximately 9 and 10 percent, respectively, when dosages were 0.018 and 0.030 percent.

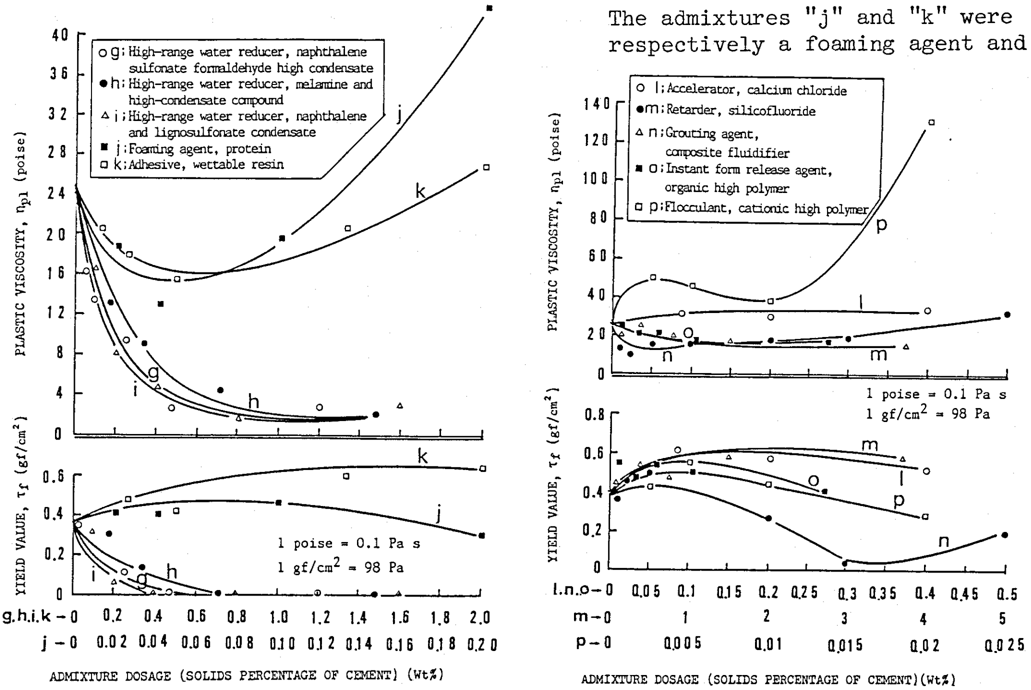
The admixtures "c," "d," "e," and "f" were air-entraining water-reducing agents and water-reducing agents with different main components. Although the effects differed slightly depending on the main component, it is thought both plastic viscosities and yield values were decreased chiefly due to the dispersion effects of the admixtures as dosages were increased.



(a)

In Fig. 9(b), the curves "g," "h," and "i" are for cases of using high-range water-reducing agents (superplasticizers) with different main components. In all cases, plastic viscosities and yield values were abruptly lowered by strong dispersing actions owing to large dosages of the admixtures, and minimum values were indicated at dosage of admixture approximately 0.5 percent by weight of cement. Particularly, yield values declined to 1/30 to 1/90 (0.004 to 0.012 gf/cm^2) of the case of no admixture to indicate that cement paste approximates a Newtonian body. This is the prominent feature of a high-range water-reducing agent, and is the factor for superplasticization of concrete. However, at the same time, this also hastens segregation of cement paste from voids between aggregate particles.

The admixtures "j" and "k" were respectively a foaming agent and



(b) (c)

Fig. 9 - Influences of admixtures on rheological constants of cement paste (ordinary portland cement C, W/C = 0.40).

an adhesive with the former a protein and the latter an epoxy resin admixture, and the two showed similar trends. That is, plastic viscosity temporarily declined with increase in admixture dosage and again showed a trend of increase. On the other hand, dosage of admixture had practically no effect on yield value.

Fig. 9(c) shows the results of experiments with an accelerator (l), a retarder (m), a grouting agent (n), an instant form release agent (o), and a flocculant (p). The addition of an accelerator stimulated solvation, and both plastic viscosity and yield value were increased, but when an inorganic retarder was used hardly any effect on the viscosity of paste was seen.

In the case of the grouting agent both plastic viscosity and yield value decreased with increase in dosage. This was probably because a water-reducing agent was contained in the grouting agent used in the experiments.

The instant form release admixture was a product made by combining a composite fluidifying agent and a water-reducing agent. Trends were seen for plastic viscosity to be lowered and yield value raised with increase in dosage of this admixture.

The use of the flocculant promoted flocculation, increased the apparent volume concentration of the solute, and caused plastic viscosity to show a trend of increase. Yield value, in contrast, showed a trend of decrease while behaving in a complex manner.

As described in the foregoing, the influence of an admixture varies characteristically depending on the type of the admixture. Accordingly, it is necessary within limits of practicality for viscosity equations to be studied for the principal admixtures. It is thought that in such cases also it will be advisable to provide measures to deal with the shape factor of Eq. (10) or (11) previously given.

6. CONCLUSIONS

The viscosity equation of cement paste was investigated as a basic study to establish viscosity equations for mortar and concrete, and also to effectively utilize it for predictions in pumping and filling grout for prestressed concrete.

The results obtained within the scope of these experiments may be summarized as follows:

(1) Viscosities were measured by double-cylinder rotation viscometer on cement pastes using three brands of ordinary portland cement, and one brand each of high-early-strength, ultra-high-early-strength, and moderate heat portland cements with water-cement ratios ranging from 0.40 to 1.00. According to the results, and with Roscoe's viscosity equation for high-concentration suspensions as the basis, the following was proposed as the viscosity equation for cement paste taking into consideration fineness and particle shape of cement, and volume concentration of cement:

$$\eta_{re} = (1 - \frac{V}{C})^{-\alpha V^{\beta} \cdot \phi^{\gamma}}$$

where, η_{re}: relative viscosity of cement paste, c: percentage of absolute volume of cement, V: volume concentration of cement, ϕ: Blaine specific surface of cement (cm^2/g), α, β, γ: experimental constants ($\alpha = -1.00$, $\beta = -1.03$, $\gamma = 0.08$).

The influence of the term for fineness was ignored since it is generally small, and the following was obtained as a handy equation;

$$\eta_{re} = (1 - \frac{V}{C})^{-(K_1 V + K_2)}$$

where, $K_1 = -17.5$ and $K_2 = 12.0$

The two equations above are applicable to cases of 20°C and immediately after mixing. Accordingly, when the conditions are different, the corrections indicated in (2) and (3) are to be made.

(2) The plastic viscosity of cement paste using ordinary portland cement and with water-cement ratio of 0.40 increased more or less linearly in a temperature range of approximately 10 to 30°C.

Consequently, the corrected values in case of analogizing plastic viscosities at other temperatures with 20°C as the basis are given by the following equation:

$$\Delta\eta = 0.79\ T + (\eta_{20} - 15.8)$$

where, T: temperature of sample (°C), η_{20}: plastic viscosity of cement paste at 20°C (poise).

(3) Plastic viscosity increases linearly with elapse of time after mixing. This trend of increase becomes abruptly stronger after a given length of time has elapsed and is no longer in a straight line. The zones in which linear relationships are valid are 120 min in case of 10°C, 90 min in case of 20°C, and 60 min in case of 30°C. Plastic viscosities increased 1.4 poise/h, 1.5 poise/h, and 8.3 poise/h, respectively, within these time zones.

Consequently, if the rates of increase in plastic viscosities at the individual temperatures are considered in the plastic viscosities immediately after mixing where temperature corrections were made in these time zones, it is thought possible for plastic viscosity when the given time has elapsed to be determined for each temperature level.

(4) The viscosity of cement paste differs greatly according to variety and dosage of admixture. That is,

a) An anionic air-entraining agent showed a trend of increasing plastic viscosity with increase in dosage, but when the dosage exceeded 0.012 percent by weight of cement, the influence of entrained air became predominant and a trend of decrease was indicated. In contrast, the influence of dosage was not recognizable with a nonionic air-entraining agent.

b) Ordinary water-reducing agents of lignosulfonate type and oxycarboxylate type caused rheological constants of cement pastes to be reduced with increased dosages. When using high-range water-reducing agents the reductions in rheological constants accompanying increased dosage were even more pronounced and rheological constants reached minimum values at ratios of solids by weight of cement of approximately 0.5 percent regardless of admixture brand. In such cases, yield values were 0.04 to 0.12 gf/cm^2, indicating that cement paste can be made to approximate a Bingham body through the use of a high-range water-reducing agent, that is, a superplasticizer.

c) Plastic viscosities were reduced with increased dosages of foaming agent, adhesive, grouting agent, and form release agent. However, these admixtures, with the exception of the form release agent, shift to a trend of increase in plastic viscosity when dosage is increased further. Regarding yield value, with most of these admixtures there was completely no influence of dosage or there was increase with increased dosage.

d) With an accelerator, both plastic viscosity and yield value are increased by addition. On the other hand, with an inorganic retarder, there is little influence of inorganic retarding agent dosage. With a flocculating agent cement particles are flocculated so that the apparent volume concentration is increased and plastic viscosity is increased. However, yield value is conversely reduced.

As described in the foregoing the influence of an admixture differs individually according to the type. Therefore, within practical limits, it is necessary for studies to be made of the principal admixtures beforehand.

(5) In case of a highly concentrated suspension such as cement paste, which is a two-phase material, the plastic viscosity η_{pl} increases more the higher the solute concentration, while yield value τ_f also increases as solute particles approach each other. The two have linear proportionality and correlate to each other. It is possible to estimate yield value from plastic viscosity by the following equation utilizing this relationship:

$$\tau_f = a\eta_{pl} + b$$

where, τ_f: yield value (gf/cm^2), η_{pl}: plastic viscosity ($gf \cdot s/cm^2$), a, b: experimental constants, $a = 1.2 \times 10$ (s^{-1}), $b = 1.2 \times 10^{-2}$ ($gf \cdot cm^2$).

This equation can be applied to cement paste immediately after mixing, at temperature approximately 20°C, and when an admixture is not used.

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