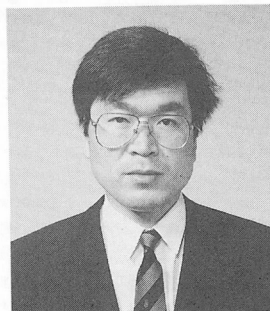


DOUBLE MIXING EFFECTS OF FRESH CEMENT PASTE

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SYNOPSIS

It was found that bleeding of fresh cement paste mixed with the same final water cement ratio is strikingly changed with divided addition of water each addition being followed by mixing (referred as double mixing: DM). Depending upon the amount of water which is added at the first stage mixing (referred as the primal water:  $W_1$ ), bleeding of the cement paste can be minimized or maximized. In this paper, mechanism of these DM effects and influences of various factors, such as fineness of cement, mixing time, type of mixing water, temperature, chemical components of cement etc. on the DM effects were experimentally investigated. From these experiments it was suggested that the double mixing effect is not only associated with physicochemical interaction between liquid and cement powder but also with chemical reaction of cement particles with water and electrostatic charge of cement particles that might be related to the early stage chemical reaction of cement with water.

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## 1. INTRODUCTION

Recently construction technology has been becoming more and more versatile, and in order to cope with the demands for rationalization, introduction of machinery and automation are progressing. On this connection, it is very important that the properties of fresh concrete is so adjusted as to match the new technology, and various investigations have been conducted on this field. Though mix proportion is one of the most dominant factors on the properties of fresh concrete, it is sometimes difficult to change mutually contradicting properties such as consistency, segregation, plasticity etc. at one time simply by changing cement content or sand aggregate ratio. For this purpose, admixtures such as flyash, silica fume or various additives such as water reducing agent or superplasticizer which can drastically change the properties of fresh concrete, are used.

While, it is well recognized that factors related to mixing such as type of mixer, mixing time or batching sequence of materials etc. influence the properties of fresh concrete, and it is generally believed that almost all aspects related to there factors have already been taken into practices. Under these circumstances, a new method of mixing named as SEC (Sand Enveloped with Cement) was found and construction method of shotcreting has been greatly improved. In SEC method, sand and gravel are coated with cement paste of low water cement ratio by mixing cement and aggregate with a small quantity of water after adjusting surface moisture of sand to a fixed value (this process is called as envelopping), and then the rest of water is added to manufacture concrete. Even for the same final mix proportion of concrete, properties of mixture have greatly been changed by changing water cement ratio at the primal mixing. But, afterwards a new experimental fact that is described in this paper was found. Namely, it was found that dry mixing of cement with sand is not necessarily required and decrease in bleeding or increase in yield value, which was also observed for SEC mixing, is attained by simply changing method of mixing cement paste without adding sand. In this method, cement is mixed with a part of water first and then the rest of water is added to prepare neat cement paste, and finally other materials are added to manufacture concrete. This method is named as "double mixing". Depending upon the deviding ratio of water, properties of concrete is remarkably changed. This experimental fact suggests that the primal mixing in SEC method where cement is dry-mixed with sand containing pre-adjusted surface moisture, can be evaluated as an actual double mixing process where water is divided into two parts and each part is separately mixed with cement. Therefore, double mixing can be regarded as a more basic conception that is ranked higher than SEC. Double mixing effects observed for cement paste are discussed in this thesis with reference to its mechanism and various factors influencing the effects.

## 2. OUTLINE OF EXPERIMENTS

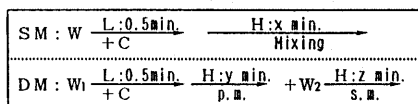
### 2.1 Materials and Mix Proportion

Normal portland cement having specific gravity of 3.16 was mainly used, though other types of cement are used in some chapters. Properties of those cement are referred in each chapter. In order to vary electrostatic repulsion force of cement particle in liquid, ethyl alcohol was used. Water cement ratios of cement paste were selected as W/C=40,50,60,80% for the experiments to investigate the influence of fineness of cement, and in other experiments W/C was 60% for all cases. For the cement paste in which a part of water is replaced with cement, cement to liquid ratio was so adjusted that the volumetric ratio became equal to that of cement paste W/C 60%. And replacement ratios of alcohol were

25,50,75,100% respectively.

## 2.2 Manufacturing Method of Cement Paste

Cement paste was manufactured by the process shown in Fig.1. In double mixing (DM), a part of mixing water (primal water:  $W_1$ ) is mixed with cement for some time, and then the rest of water (secondary water:  $W_2$ ) is added for the final mixing. While, conventional mixing is referred as single mixing (SM). Cement is continually added, for 30 seconds, to primal water previously placed in Hovert type mortar mixer rotating at low speed, and mixed at high speed for y minutes (primal mixing), and then the secondary water is added and mixed for z minutes (secondary mixing). In SM, mixing was done for x minutes after cement was added. The mixing times x,y,z were changed for different purposes of experiments, but in each cases x is selected as equal to y+z. Water cement ratio at the primal mixing is shown as  $W_1/C$ .



x: mixing time for SM, y, x: primal and secondary mixing time for DM, x=y+z, C: cement, W: water,  $W_1$ : primal water,  $W_2$ : secondary water, L: low speed, H: high speed, p.m.: primal mixing, s.m.: secondary mixing

Fig.1 Mixing method

## 2.3 Test Procedures

### (1) Bleeding Test

Bleeding ratio of cement paste was measured according to the JSCE standard "Testing methods of bleeding ratio and expansion ratio of grouting mortar for prepacked concrete".

### (2) Mixing Torque and Unit Weight after The Primal Mixing

Since electric current measured in the motor of mixer working at a constant voltage can be regarded as an indication of mixing torque, electric current was measured by a current meter attached to mixer. Unit weight was measured in a steel container with 0.4 l of capacity, compaction being made for three layers each layer is compacted with 20 times of dropping of 10kg weight.

### (3) Chemical Analysis of Liquid Phase of Cement Paste

Liquid phase of cement paste is vacuum-extracted at 10,20,60 minutes from initiation of mixing,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentration were quantitatively measured by EDTA method and gravitational method using  $\text{BaSO}_4$  respectively.

### (4) Continuous Feeding Test of The Primal Water

The primal water was continuously added by intermittent step of  $W_1/C$  7% and 30 seconds of mixing was done for each addition of water, and then  $W_2$  was added to prepare cement paste for testing. Therefore, DM paste prepared by  $W_1/C$  7% is exactly equal to the paste prepared in this test for  $W_1/C$  7%, but for  $W_1/C$  more than 14%, mixing condition for the two test series is not same. This experiment was done for  $W_1/C$  7 to 35% using final water cement ratio 50%, and comparison with DM was made.

## 3. DOUBLE MIXING EFFECT

The maximum bleeding of cement paste prepared by DM is shown in Fig.2 with contrast to that obtained for SM for every 7% of variation of  $W_1/C$ . Mixing time for paste was x=2.5 min., y=1 min. and z=1.5 min.. As is shown in the figure, the maximum bleeding of cement paste prepared in the same mix proportion is remarkably changed with  $W_1/C$ , the minimum value was obtained for  $W_1/C$  21-28%

regardless of the final water cement ratio  $W/C$ . While the maximum bleeding was observed for  $W_1/C$  7%, bleeding more than twice the value for SM yielded. The smaller  $W/C$ , the smaller was the change in bleeding with  $W_1/C$  and the range of  $W_1/C$  where the minimum bleeding is obtained became more restricted with increasing final water cement ratio  $W/C$ . As shown in Fig.2, DM effects with regard to bleeding are characterized with two peak values observed for  $W_1/C$  7% and 21% and the magnitude of bleeding shows two extreme values that is apposite each other. This phenomena is also well recognized from the test results shown in Fig.3 obtained from continuous feeding test of the primal water. Namely, bleeding larger than the corresponding DM was obtained for 14% of  $W_1/C$ , when the primal water is fed to cement intermittently by 7%, and for the  $W_1/C$  larger than 21% bleeding becomes less than the corresponding DM showing the constant value. Once cement paste is mixed at  $W_1/C$  21%, bleeding of the paste is not influenced with the mixing conditions thereafter. Based on the foregoing observations,  $W_1/C$  at which the minimum and the maximum bleeding are obtained are designated as the optimal  $W_1/C$  and the pessimal  $W_1/C$  respectively. And when bleeding is increased by DM compared to that obtained by SM, this effect is called positive DM effect and the reverse is called negative effect.

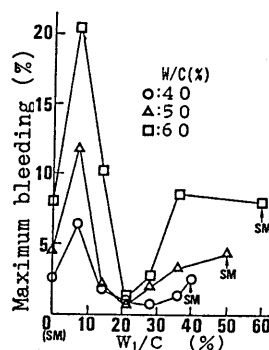


Fig.2 Relationship between  $W_1/C$  and bleeding

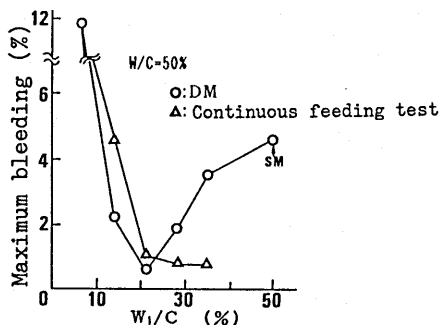


Fig.3 Results of continuous feeding test of the primal water

Mixing torque at the primal mixing and the unit weight after the primal mixing are shown in Fig.4 against  $W_1/C$ . Definite peak points are observed for the values of mixing torque and unit weight, and the corresponding  $W_1/C$  coincides with the optimal  $W_1/C$  previously shown. This facts suggest that interparticle attraction forces between cement grains became the maximum value and water retentive coagulated state is formed. At the optimal  $W_1/C$  mixing torque becomes maximum because the maximum mechanical energy is required to break the coagulation. And the unit weight becomes maximum, because cement and water is proportioned in a well blanced state. From the foregoing results, the optimal  $W_1/C$  can be predicted from the measurement of mixing torque at the primal mixing or unit weight after the primal mixing without conducting the bleeding test.

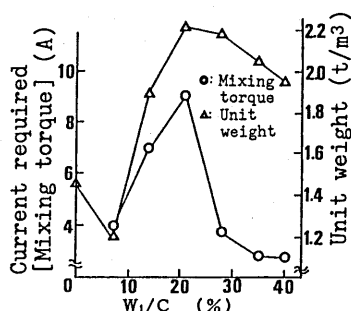


Fig.4 Relationship between  $W_1/C$  and mixing torque or unit weight

In Table 1, dried weight of floccules in cement paste prepared by the optimal and the pessimal  $W_1/C$ , are shown. Floccule was taken as the residue after screening the paste under running water above a sieve having 0.6mm opening. For

DM done by the optimal  $W_1/C$ , weight of floccules is very small compared to that observed for SM. While at the pessimal  $W_1/C$ , many floccules exist and drastic increase in bleeding can be attributed to this. Because small amount of water is fragmentally distributed at contacting points of particles at the primal mixing, firmly bonded floccules are formed by the capillary condensation force. At this point state of particles corresponds to a point which shows the minimum unit weight, that is, the maximum bulking in Fig.4. These floccules are not broken by the secondary mixing and bleeding is increased since larger particles subside more rapidly.

Table 1 Floccules weight in cement paste

Mixing method	Floccules weight(g)*
DM	7%
$W_1/C$	21%
SM	3.9

\*:  $W/C=60\%$ , in 5Kg cement

#### 4. INFLUENCES OF VARIOUS FACTORS ON DOUBLE MIXING EFFECTS

##### 4.1 Influence of Fineness of Cement

Relation between  $W_1/C$  and the maximum bleeding is shown in Fig.5 in case of high early strength portland cement (Blaine:4370 $\text{cm}^2/\text{g}$ ) and colloidal cement (Blaine:6280 and 8820  $\text{cm}^2/\text{g}$ ). Mixing times for this data are x:2.5 min., y:1 min. and z:1.5 min.. As was observed for portland cement in Fig.2, the optimal and pessimal  $W_1/C$  were also observed for high early strength cement and colloidal cements. But these values of  $W_1/C$  were different for different fineness of cement. The optimal  $W_1/C$  observed in Fig.2 and 5 were plotted against fineness of cement to produce Fig.6. The optimal  $W_1/C$  in DM is proportional with the fineness of cement and the larger is the fineness of cement the larger is the optimal  $W_1/C$ . This relationship was investigated by the following model of the particles. First it was assumed that the primal water consists of water film that is adsorped to cement particle up to a constant thickness and interstitial water that fills up void space. Next, cement particles are assumed to be spheres of uniform diameter and packing of space is assumed as face centered cubic or body centered cubic. Based on these assumptions, thickness of adsorped film was calculated from porosity

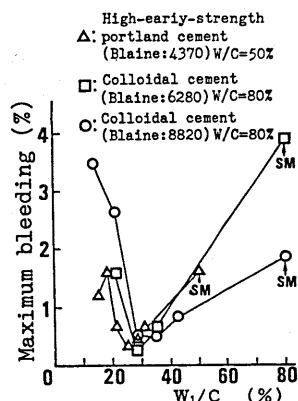


Fig.5 Relationship between  $W_1/C$  and bleeding

Table 2 Calculated value of thickness of adsorbed water film at optimal  $W_1/C$

Fineness ( $\text{cm}^2/\text{g}$ )	Average diameter ( $\mu\text{m}$ )	Optimum $W_1/C$ (%)	Porosity	Thickness of adsorbed water film	
				FCC ( $\mu\text{m}$ )	BCC ( $\mu\text{m}$ )
3240	6.17	21	0.398	0.22	0.14
4370	4.57	24	0.431	0.21	0.14
6280	3.20	28	0.469	0.19	0.14
8820	2.27	35	0.525	0.18	0.14

\*: Value calculated from proportion  
FCC: Face-centered cubic structure  
BCC: Body-centered cubic structure

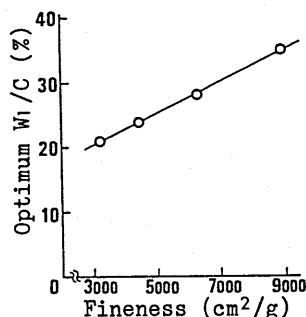


Fig.6 Relationship between fineness and optimal  $W_1/C$

after the primal mixing and specific surface of cement as shown in Table 2. In case that body centered cubic packing is assumed, film thickness of adsorped water at the optimal  $W_1/C$  was calculated as constant  $0.14 \mu m$  regardless of fineness of cement.

#### 4.2 Influence of Mixing Time

Influence of the primal mixing time is shown in Fig.7 for normal portland cement and constant secondary mixing time (1.5min.). Bleeding is shown against the primal mixing time or single mixing time for  $W_1/C$  ratios 7%, 21% which corresponds to the optimal and the pessimal ratios for DM respectively. Zero minute of the primal mixing corresponds to SM for mixing time 1.5 min.. At the optimal  $W_1/C$  21%, bleeding is monotonously decreased with increasing mixing time for the primal mixing. For 15 minutes of the primal mixing, little bleeding was observed. While bleeding is slightly increased until 1 minute at  $W_1/C$  7%, but for longer primal mixing bleeding is not changed. Also, bleeding is not much changed for longer mixing time of SM. In comparison with Fig.7, influence of the secondary mixing time for constant primal mixing 2 minutes is shown in Fig.8. In case of  $W_1/C$  7%, bleeding is decreased until 4 minutes of the secondary mixing time and is not changed for longer secondary mixing time. In case of 21% of  $W_1/C$ , bleeding is not changed for the secondary mixing time more than 1 minute. These experimental facts suggests that the primal mixing time is more important for DM effect than the secondary mixing time, and distribution of cement particles in water might be changed for longer duration of the primal mixing. Relation between the primal mixing time and mixing torque at the primal mixing is shown in Fig.9. In case of  $W_1/C$  7%, mixing torque is not changed, but for 21% of  $W_1/C$  mixing torque is increased with the increase in the primal mixing time. During this process, cement particles are considered to be wetted and dispersed uniformly in water. While, floccules of cement particles are formed in shorter time of the primal mixing in case of  $W_1/C$  7%, and bleeding is increased with mixing time while this increase proceeds. After this process is finished, distribution of water is not changed for longer duration of the primal mixing and bleeding is not changed.

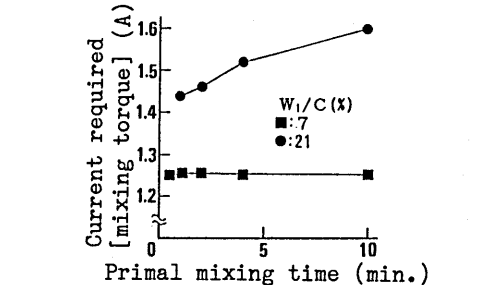


Fig.9 Relationship between primal mixing time and mixing torque

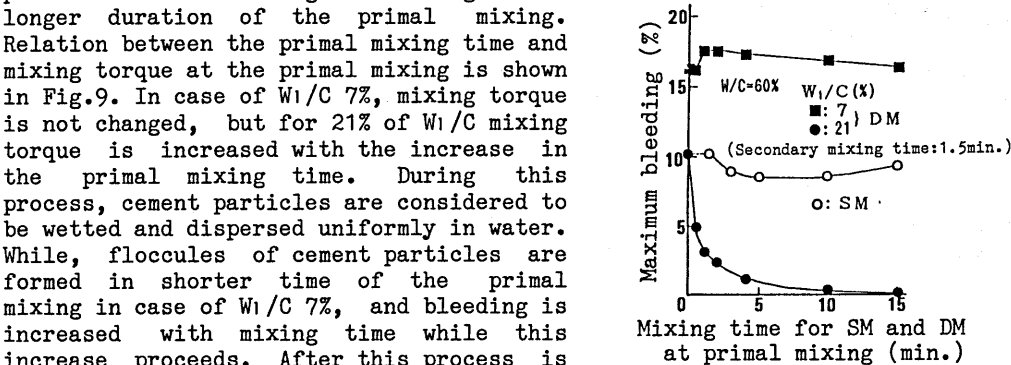


Fig.7 Relationship between primal mixing time and bleeding

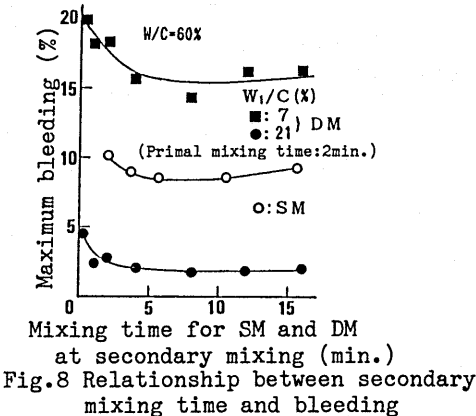


Fig.8 Relationship between secondary mixing time and bleeding

#### 4.3 Influence of Temperature

Influence of temperature of cement paste on the optimal and the pessimal  $W_1/C$  ratios is shown in Fig.10. Mixing times of cement paste were x:2.5 min., y:1 min. and z:1.5 min.. When temperature of cement paste is lowered by  $14^{\circ}\text{C}$ , the optimal and the pessimal  $W_1/C$  ratios are shifted from 24% to 20% and from 9% to 5% respectively being lowered by 4%. This fact suggests that surface chemical action between cement particle and

water at the primal mixing is basically same for every  $W_1/C$ , and extreme values corresponding to the maximum and minimum bleeding are shifted to the same direction by the same amount since surface chemical characteristics is changed with temperature by the same amount. Bleeding at the optimal  $W_1/C$  is hardly influenced by temperature at construction as well as the final  $W/C$ .

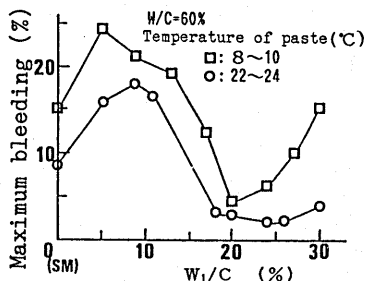


Fig.10 Relationship between temperature of paste and optimal or pessimal  $W_1/C$

### 5. DM EFFECTS INFLUENCED WITH ELECTROSTATIC REPULSION BETWEEN CEMENT PARTICLES

#### 5.1 Outline

Generally sedimentation volume of a suspension is increased, that is, bleeding is decreased with increasing interparticle forces. Sedimentation volume of cement particles was measured by T.C. Powers in water and also in a liquid where a part of water is replaced with ethyl alcohol in order to investigate the influence of electrostatic charge of particles. Namely, since solubility of calcium hydroxide is varied with replacement of water with alcohol, electrostatic charge of cement particles becomes positively maximum at 0% of replacement and negatively maximum at 100% of replacement generating the maximum repulsion force and in both cases sedimentation volume is minimized because attraction force due to van der Waal's force is canceled. While, in case of 50% replacement, Powers describes, zeta potential of particles become nearly naught so that electrostatic repulsion force is minimized and coagulation force between cement particles maximized and hence sedimentation volume is maximized. In this chapter, influence of electrostatic repulsion of cement particles on DM effects is investigated by conducting experiments similar to those done by T.C. Powers for cement paste prepared by DM. Bleeding in those experiments was obtained by measuring the volume of liquid generated on the top surface of sample every 30 minutes. Five hundred cc of paste sample was placed in a measuring cylinder having 5cm of diameter and 500 cc of capacity. Mixing times of paste were x:3 min., y:1 min. and z:2 min..

#### 5.2 Influence of Electrostatic Repulsion Force of Cement Particles on Bleeding Characteristics

Variation of bleeding with the time elapsed is shown in Fig.11 for plain cement paste and cement paste mixed with 100% ethyl alcohol. In T.C. Powers's experiment these figures correspond to the cases of the maximum and the minimum electrostatic repulsion force acting between cement particles. For plain paste prepared by DM of  $W_1/C$  9% and SM, linear portion and curved portion are clearly recognized in bleeding versus time relationship. It is understood that Stoke's

sedimentation of cement particles shifted to coagulation sedimentation in this case. For DM of  $W_1/C$  24%, coagulation sedimentation may be occurring from relatively early stage since linear portion is hardly recognized. While, for cement paste mixed with ethyl alcohol bleeding occurs at constant speed and stops after a certain limit value is reached in either cases of SM and DM. This fact suggests that only Stoke's sedimentation of cement particles occurs in ethyl alcohol and coagulation sedimentation does not occur. The final bleeding is dependent upon the primal liquid cement ratio. The maximum bleeding was observed for DM of 20%  $L_1/C$  and the minimum bleeding was observed for SM. For plain paste the final bleeding ratio was proportional with the initial bleeding speed, but for cement paste mixed with ethyl alcohol the final bleeding ratio is not dependent upon the initial speed. These differences in bleeding characteristics between plain cement paste and ethyl alcohol paste cannot be explained only by the differences in electrostatic charges of cement particles. These experimental facts, however, suggest electrostatic charge of cement paste exhibits significant influence on DM effects.

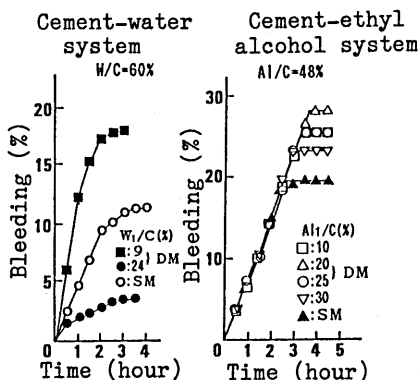


Fig.11 Relationship between bleeding and the time elapsed of cement suspension

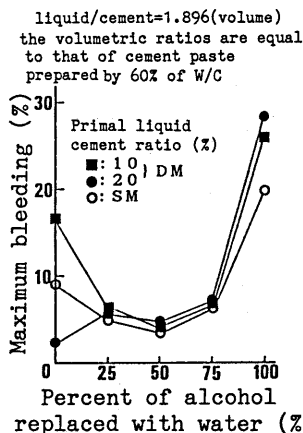


Fig.12 Relationship between replacement ratio of alcohol and bleeding

### 5.3 Influence of Electrostatic Repulsion Force of Cement Particles on DM Effect

Relationship between the maximum bleeding and replacement ratio of ethyl alcohol is shown in Fig.12. DM effect becomes dominant only when electrostatic charge of the particles is large, and positive DM effect is obtained for positive charge of particles and negative DM effect for negative charge. According to Nawa et al[6], electrostatic charge of cement particles is dependent upon variations in composition of liquid phase of cement paste due to hydration and particularly upon concentrations of  $Ca^{2+}$  and  $SO_4^{2-}$ . In liquid phase of cement paste, monovalent ions such as  $Na^+$ ,  $K^+$ ,  $OH^-$  can exist in higher concentration than  $Ca^{2+}$  or  $SO_4^{2-}$ , but higher the valence of ion the greater is the influence on electrostatic charge. For example  $Ca^{2+}$  about 1/25 of  $Na^+$  in concentration exhibits the same effect on coagulation of quartz particles[5]. Therefore, it is presumed that DM effect is dependent upon concentrations of  $Ca^{2+}$  and  $SO_4^{2-}$  in liquid phase of cement paste.

## 6. INITIAL HYDRATION REACTION OF CEMENT AND DM EFFECTS

### 6.1 Outline



It was found that DM effects are hardly recognized or only negative effects are recognized for a certain type of low heat portland cement. In this chapter DM characteristics of these low heat portland cements are presented and influence of chemical composition of liquid phase during initial hydration stage of cement paste prepared by SM and DM, particularly influence of concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  on DM effects was investigated. Chemical compositions of cements used in this chapter are shown in Table 3. Hereafter cement is referred by the symbol in the table. Mixing times of cement paste were x:5 min., y:3 min. and z:2 min..

Table 3 Used portland cement

Type	Symbol	Chemical composition (%)								
		ig. loss	insol.	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	HgO	$\text{SO}_3$	Total
Normal p. cement	NP	1.1	0.1	20.5	6.4	3.0	62.5	1.7	1.9	97.2
Moderate heat p. cement	MP-A	0.9	0.6	21.2	4.9	4.4	62.1	2.2	2.1	98.4
	MP-B	1.4	0.4	21.8	4.7	4.3	61.8	2.0	2.3	98.7
	MP-C	0.4	0.4	21.6	4.8	3.8	62.6	3.1	1.8	98.5

## 6.2 Bleeding Characteristics

Bleeding and mixing torque obtained for 4 types of cement are shown against  $W_1/C$  in Fig.13 and Fig.14. For every types of cement,  $W_1/C$  at which mixing torque reached to the maximum value does exist. In chapter 3. it was shown that bleeding is minimized at  $W_1/C$  at which mixing torque is maximized. But as shown in Fig.14, for MP-A and MP-B cement,  $W_1/C$  at which bleeding is minimized does not exist, and particularly for MP-B cement bleeding is significantly increased for all  $W_1/C$  compared to SM. This means that DM effect is not universally manifested for every types of cement powder. Relationship between bleeding and  $W_1/C$  obtained for MP-A cement which showed no DM effect is shown in Fig.15, when saturated solution of  $\text{Ca}(\text{OH})_2$  is used for mixing water or when primal mixing time is increased by twice (6 min.). In each cases, bleeding for SM is same with the value obtained for service water, but bleeding for DM is decreased at  $W_1/C$  22% and positive DM effect is clearly recognized. These facts suggest variation in ion concentration of liquid phase by addition of  $\text{Ca}(\text{OH})_2$  and also in distribution in cement particles by prolonged duration of primal mixing time gave positive influences on DM effect.

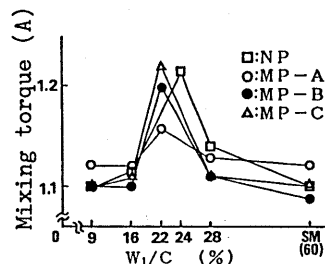


Fig.13 Relationship between  $W_1/C$  and mixing torque

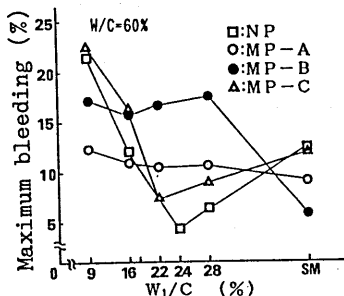


Fig.14 Relationship between  $W_1/C$  and bleeding

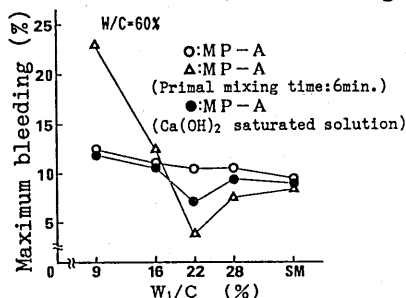


Fig.15 Relationship between  $W_1/C$  and bleeding

### 6.3 Influence of Chemical Composition of Liquid Phase in Cement Paste on DM Effects

Concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in liquid phase of cement paste prepared by SM and DM of  $W_1/C$  at which mixing torque during primal mixing gets to maximum are shown against the time elapsed in Fig.16. For MP-A cement, data also include the cases in which saturated solution of  $\text{Ca}(\text{OH})_2$  is used or prolonged primal mixing is done. Even for the same type of cement, concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  are different for SM and DM and the difference between the two cases is larger for initial age (for 10 min. of the time elapsed). As was described in 5., ratio of concentrations,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ( $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ) that controls electrostatic charge of cement particles is considered to have some influence on DM effects. Ratios of  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  for each paste calculated from Fig.16 are shown in Fig.17. No direct correlation between bleeding of paste and  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  ratio was observed. But, if  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  ratios up to 20 minutes from mixing for SM and DM are compared, positive DM effects are observed for cement paste in which the values of  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  for SM is smaller than those for DM (NP, MP-C, MP-A(6min. of primal mixing), MP-A( $\text{Ca}(\text{OH})_2$  saturated solution), and negative DM effect or no DM effect was observed for the paste in which the values of  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  for SM is larger than those for DM (cf Fig.14,15). In Fig.18, relation between ratios of bleeding obtained for DM and SM ( $\text{BL}_{\text{DM}}/\text{BL}_{\text{SM}}$ ) and ratios of ( $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ) after 10 minutes from mixing for DM and SM ( $(\text{Ca}^{2+}/\text{SO}_4^{2-})_{\text{DM}}/(\text{Ca}^{2+}/\text{SO}_4^{2-})_{\text{SM}}$ ) is shown. If the ratio  $(\text{Ca}^{2+}/\text{SO}_4^{2-})_{\text{DM}}/(\text{Ca}^{2+}/\text{SO}_4^{2-})_{\text{SM}}$  is larger than unity, positive DM effect is obtained, and negative DM effect is the case for the ratio lower than unity. It is recognized that DM effects in cement paste are dependent upon  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  ratio in liquid phase of the paste.

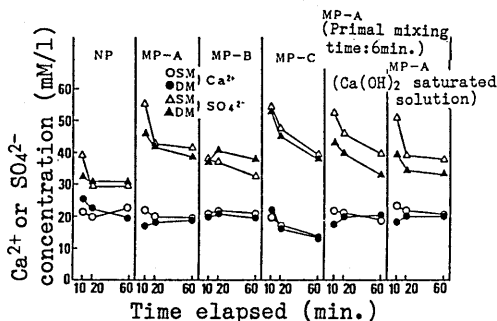


Fig.16 Relationship between  $\text{Ca}^{2+}$  or  $\text{SO}_4^{2-}$  concentration and the time elapsed

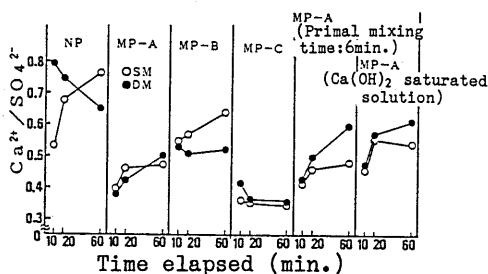


Fig.17 Relationship between  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  and the time elapsed

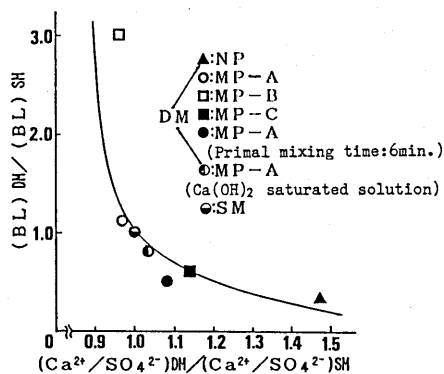


Fig.18 Relationship between DM/SM ratio of bleeding and DM/SM ratio of  $\text{Ca}^{2+}/\text{SO}_4^{2-}$

## 7. CONCLUSION

The following facts are clarified from experimental investigations on DM effects of cement paste.

- (1) Bleeding of cement paste manufactured by DM is varied with  $W_1/C$ , and there

exist the pessimal  $W_1/C$  at which the maximum bleeding yields and the optimal  $W_1/C$  at which the minimum bleeding yields. The optimal  $W_1/C$  coincides with  $W_1/C$  at which mixing torque during primal mixing becomes maximum and the maximum unit weight after primal mixing is obtained.

(2) The optimal  $W_1/C$  for DM is dependent upon fineness of cement, the finer the cement the larger the optimal  $W_1/C$ .

(3) Positive DM effect is strongly influenced by primal mixing time at the optimal  $W_1/C$ . When primal mixing time is increased, bleeding can be minimized for the same mix proportion.

(4) The optimal and the pessimal  $W_1/C$  are influenced by temperature of cement paste, both the optimal and the pessimal  $W_1/C$  are lowered by 4% respectively if temperature of paste just after mixing is lowered by 14°C.

(5) In cement paste prepared by the pessimal  $W_1/C$  bleeding is increased since cement concentrations of resultant slurry is decreased with formation of floccules and increase in heterogeneity caused by this during primal mixing.

(6) According to chemical compositions of cement, there exist cements for which DM effect for bleeding cannot be expected or only negative DM effect is observed.

(7) It is predicted from the fact how the ratio  $Ca^{2+}/SO_4^{2-}$  of liquid phase extracted after 10 minutes from adding water is changed by DM whether positive or negative DM effect appears. Positive DM effects appear when the ratio  $(Ca^{2+}/SO_4^{2-})_{DM}/(Ca^{2+}/SO_4^{2-})_{SM}$  is larger than unity.

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