Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Cement and Concrete Research 35 (2005) 703–710
CEMENT AND CONCRETE RESEARCH

Influence of inorganic pigments on the fluidity of cement mortars

Hyun-Soo Lee[a], Jae-Yong Lee[b,*], Myoung-Youl Yu[a]

[a]Department of Architecture, Seoul National University, 151-742 Seoul, South Korea
[b]Division of Architecture, College of Engineering, Pukyong National University, 608-739 San 100 Yongdang-Dong, Nam-gu Pusan, South Korea

Received 29 May 2003; accepted 7 June 2004

Abstract

Among the admixtures used for cement composites, an inorganic pigment, which contributes color to the final product, enhances the esthetic value of a building. It can be reasonably assumed that the use of inorganic pigments will increase, given the recent trend to make cities more beautiful with color. The aim of this study was to investigate the effects of inorganic pigments on the fluidity of cement mortar. For this purpose, a flow test was carried out on cement mortar mixed with inorganic pigments by changing the proportion of cement mortar, water–cement ratio, and ratio of pigment. When red and yellow pigment mortars were used, the fluidity rapidly decreased with increasing ratio of pigment. To secure an acceptable workability, the amount of mixing water had to be increased or a superplasticizer employed. When a green pigment mortar was used, however, the fluidity of the mortar recorded −2.4–6.9%, indicating almost no change in flow. When a black pigment mortar was used, the pigment had no effect on fluidity.

Keywords: Admixture; Mortar; Workability; Pigment; Fluidity

1. Introduction

Recently, because the use of cement composites has diversified, studies of the colored cement composites have intensified. Various types of methods can be reviewed for the coloring of cement composites in terms of construction, mixing, and materials to be used. It would be desirable, however, to consider the physical properties of the pigment itself among other materials to be used for achieving a proper workability.

Because the particles of inorganic pigments used in cement composites are very small and insoluble, they become distributed uniformly in the cement composites during mixing, and as a result, the cement composites have color [1,2]. In addition, pigments contain minute powders that pass through a No. 200 sieve with other ingredients, and the shapes of particles for each pigment are known to have a considerable influence on strength, drying shrinkage, and the durability of cement composites.

Furthermore, a suitable fluidity and consistency of a cement mortar must be obtained for use in construction work. According to the research by Bruce and Rowe [3], when a coloring admixture, i.e., an inorganic pigment, is mixed, the surface area of an inorganic pigment expands the surface area of cement by 10 times, thus decreasing the fluidity of the mortar. That is, the shapes of the particles and fine particles of inorganic pigments have been reported to reduce the fluidity of cement mortar, but our understanding of this is currently unclear.

This study presents some guidelines for the effective use of colored cement composites by examining the effects of the shapes of the particles and the inorganic pigments ingredients on the fluidity of a cement mortar.

2. Experimental procedure

2.1. Test factor and scope

To examine the effects of inorganic pigments on fluidity when inorganic pigments are mixed in a cement mortar, the test factor and scope were set as shown in the Table 1. That is, the weight proportion of cement and fine aggregate was fixed at 1:2.45 in KS L 5105("Testing method for compressive strength of hydraulic cement mortars"), defining the mixture of mortar for measuring the compressive

* Corresponding author. Tel.: +82-51-620-1390; fax: +82-51-622-8340.
E-mail address: jylee@pknu.ac.kr (J.-Y. Lee).

0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2004.06.010

Table 1
Test factor and scope

Item	Scope	
Mixture proportion (cement–sand)	1:1, 1:2 1:3	
Target flow	210, 230, 240 mm	
Water–cement ratio (W/C)	35%, 47.5%, 50%, 52.5%, 67.5%	
Type of Pigment	Korean product (A)	Red (RA), yellow (YA), green (GA), black (BA)
	German product (Z)	Red (RZ), yellow (YZ), green (GZ), black (BZ)
Pigment–cement ratio (P/C)	0%, 3%, 6%, 9%, 12%	

strength of cement. In Japan, America, and Germany, the weight mixture proportions of cement are defined as 1:2, 1:2.75, and 1:3, respectively.

The proportions of cement and sand in this experiment were fixed at 1:2 and 1:3, which are the proportions typically used at actual sites and are not the figures in regulation set by the Korean Industrial Committee for analyzing the compressive strength of cement. Furthermore, a proportion of 1:1 was additionally used to examine the possibility of manufacturing high-strength mortar.

In addition, the target flow was fixed at 210 mm for each mixture proportion, which is regarded as the most suitable fluidity to secure workability at a site. For the proportion of 1:2, 230 (W/C = 50.0%) and 240 mm (W/C = 52.5%) were also fixed as the target flows in the attempt to identify the physical properties of colored cement composites according to water–cement ratio and flow.

After examining four types of pigments, including red, yellow, green, and black, which are commonly used in related industries to select the pigments, the following pigments were selected: a pigment manufactured by A company, Korea (hereafter, "Korean product", A), and a pigment manufactured in and imported from Z company, Germany (hereafter, "German product", Z). For the ratio of pigment to the quantity of cement used, 9% and 12% were added to examine the suitability of less than 10% as indicated in ACI [4], as well as 3–6%, which is generally used in Korean industry.

2.2. Materials

Regarding the cement for this experiment, white portland cement from UNION, manufactured in Korea, was used, passing KS L 5204("White portland cement"). The physical properties and chemical composition of the cement are as shown in Tables 2 and 3.

Table 3
Chemical composition of white cement

Component	Fe_2O_3	MgO	SO_3	Ignition loss	Water-insoluble residue
Content (%)	0.27	1.16	2.90	2.87	0.42

With regard to the fine aggregate, standard sand was used, which had a specific gravity of 2.68, fineness modulus of 1.99, and unit weight of 1537 kg/m^3, as defined in KS L 5100 ("Standard sand for testing strength of hydraulic cement mortars"), to set the manufacturing and usage standard of the colored cement mortar because only few studies on the physical properties of colored cement mortar are available.

With regard to inorganic coloring pigments, such as red, yellow, green, and black—most commonly used in concrete products—two types of pigment were used: The first was a Korean product pigment (A), manufactured by A company, Korea, and the second was a German product pigment (Z) manufactured in and imported from Z company, Germany. The Types A and Z pigments do not refer to all inorganic pigments used in Korea and abroad because they were designated and separated as a Korean and a German product pigment in this experiment, as shown in Table 4, for the sake of convenience in carrying out this analysis and investigation.

The main ingredient of red, yellow, and black pigments is iron oxide (Fe_2O_3) and that of the green pigment is chrome oxide (Cr_2O_3). Fig. 1 shows the shapes of particles, observed by scanning electron microscopy (SEM). The red, green, and black pigments are spheroid in shape, the red pigment RZ was found to be finite, and the green pigment GA was found to be a green pigment painted on a finite stone dust. In addition, the black pigment BA was found to be a mixture of carbon black and fine powder, as shown in Fig. 1g, which enhanced the overall black chromaticity.

The yellow pigment particles were elongated, different from the spheroid shape of the red, green, and black pigments, as shown in Fig. 1c and d, and a considerable influence on lowering the fluidity [5,6].

Table 4 shows the physical properties as a result of an experiment carried out in accordance with KS M 5131 ("Testing method for pigment") and Quality standard of KS M 5102("Iron Oxide") for the German (Type Z) and Korean products (Type A) used in this experiment. The black pigment BA was found to contain iron oxide as the main ingredient in an amount that was 17% less than the amount of black pigment, BZ, achieved by mixing carbon black, as shown in Fig. 1g.

Table 2
Physical properties of white cement

Specific gravity	Blaine value (cm^2/g)	Soundness (%)	Compressive strength (kgf/cm^2)			White degree (Hunter type, Colorimeter)
			3 days	7 days	28 days	
3.15	3168	0.04	243	332	421	89.6

Table 4
Physical properties and chemical composition of pigments

Type		Specific gravity	Mean diameter of particle (μm)	Water-soluble residue (%)	Sieve residue on No.325 (%)	Fe_2O_3
Korean product (A)	Red (RA)	4.53	1.76	0.01	7.60	99.8
	Yellow (YA)	3.52	0.1 × 0.74[a]	0.02	1.70	88.6
	Green (GA)	2.77	7.94	0.02	13.2	0.003[b]
	Black (BA)	3.51	4.49	0.06	88.3	82.3
German product (Z)	Red (RZ)	4.99	0.17	0.40	0.06	96.0
	Yellow (YZ)	3.93	0.1 × 0.70[a]	0.50	0.05	86.5
	Green (GZ)	4.28	0.2	1.00	0.10	93.5[b]
	Black (BZ)	4.80	0.3	0.30	0.02	99.3

[a] Because the particles in the yellow pigment are elongated, the diameter of the particle is expressed as Width × Length.
[b] In addition, the main ingredient of the green pigment is Cr_2O_3.

On the other hand, a small amount of chrome oxide was present in green pigment GA. Generally, hydrochloric acid, sulfuric acid, and nitric acid solutions are used to analyze the pigment ingredients of the iron oxide system. The green pigment GA appears to have been manufactured by mixing very small amounts of chrome oxide with an inorganic matter, such as stone dust, rather than green pigment GA because it did not dissolve in this solution.

In addition, pigment production and processing technology in Korea is considered to be poor because Type Z pigment was found to be finer than the Type A pigment is, in terms of average diameter of pigment particles. In addition, when the considering main ingredient and water-soluble elements, the purity of Type A pigment is considered to be lower than that of the Type Z pigment. Accordingly, the production and processing technology of high-quality pigments must be studied more extensively, and standards for the quality of the pigment used should be established.

2.3. Mixing design, fabrication, and test

Eighteen mortar specimens 5 × 5 × 5 cm in size for each mixture were prepared, and experiments were carried out according to the preparation mixture table as shown in Table 5 and to the experiment factor and scope defined in Table 1 to clarify the physical properties of the colored cement composites.

The fresh-colored mortar was mixed and manufactured according to the method specified in KS L 5109 (“Testing method for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency”). The specimens were prepared in a mold of 5 × 5 × 5 cm, in accordance with KS L 5105, cured in a humidified atmosphere for 24 h, removed from the mold after 24 h, cured in water for 7 days, and then cured in air.

The flow value of the colored mortar was measured by means of a flow test, as shown below, in accordance with the regulation in KS L 5105, using the flow table specified in KS L 5111 (“Flow table for use in tests of hydraulic cement”). The upper part of the flow table was first carefully and cleanly wiped, and the plate was placed in the center of the flow table. About 2.5-cm-thick layers of colored mortar were then placed in the plate, followed by tamping 20 times with a tamper. After filling the flow mold with mortar and tamping it as in the first layer, the plate was lifted smoothly and immediately allowed to fall down the table 25 times for 15 s at a height of 1.27 cm. The diameter of the mortar was measured in the lower part four times at the same interval, and the flow value was expressed as an average of this measurement.

3. Results and analysis

3.1. Fluidity by pigment type

The following are changes in fluidity according to pigment mixing ratio (pigment/cement = P/C) and pigment type of the colored cement mortar. The flow of the red-colored mortar changed as a function of the mixing ratio of the red pigments RZ and RA, as shown in Fig. 2. The flow value decreased as the ratio of pigment used increased because the flow of the no-mixing mortar without pigment (hereafter, standard mortar) was fixed at 210 mm. On the whole, when pigment mixing ratio (P/C) was changed to 3%, 6%, 9%, and 12%, flow value decreased by about 9, 22, 30, and 39 mm for the standard flow of 210 mm, respectively; flow value decreased by 8, 20, 30, and 39 mm, respectively, in the case of the red pigment RA, and by 11, 23, 30, and 40 mm, respectively, in the case of red pigment RZ.

In addition, the flow value was found to be 168–201 mm at a proportion (cement–sand) of 1:1 when red pigment RA was mixed. When the red pigment RZ was used, the flow value was found to be 153–196 mm, a decrease of 5–17 mm. The red pigment was judged to have a lower fluidity because of water absorption, as the result of the increase in surface area contributed by the powder. This is due to the fact that the sizes and shapes of the particles of the red pigment RZ are minuter than those of the red pigment RA, an iron oxide, which is a byproduct of iron recycling. On the other hand, it was difficult to obtain an acceptable workability because the flow value decreased

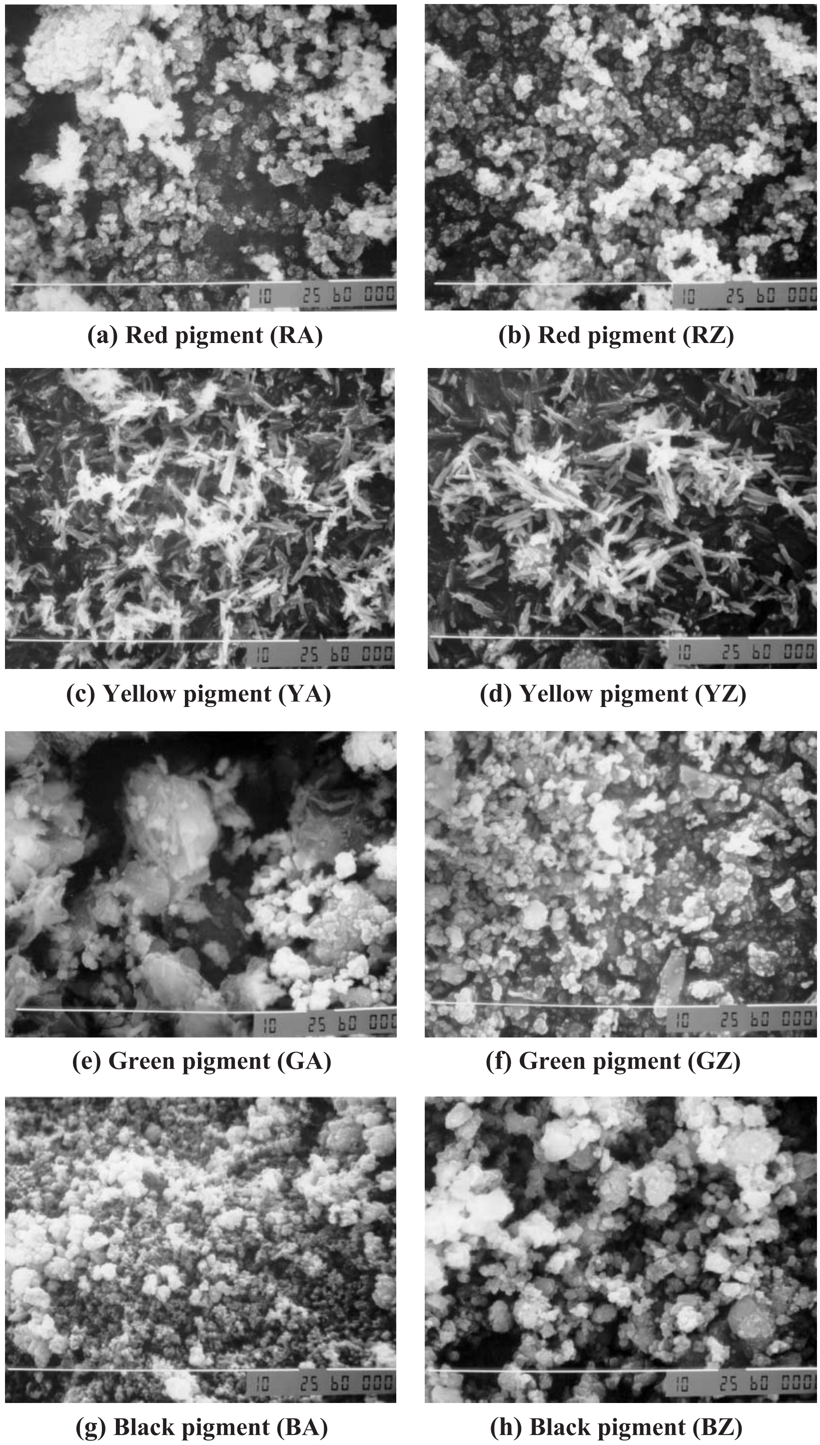

Fig. 1. SEM picture of Pigments A and Z (magnifying power × 7500).

26–58 mm for a standard flow when pigment mixing ratio was over 9%. Therefore, an acceptable mixing ratio for the red pigment must be fixed at under 9% to obtain proper fluidity.

With regard to flow change as a function of a change in the mixing ratio of the yellow pigment, as shown in Fig. 3, the fluidity was found to decrease rapidly as the mixing ratio increased compared with the other colored pigments. On the whole, when the mixing ratio for the yellow pigment was changed to 3%, 6%, 9%, and 12%, the flow decreased by 28, 49, 69, and 81 mm, respectively; by 32, 59, 79, and 94 mm decrease in case of the yellow pigment YA; and by 24, 40, 58, and 68 mm in the case of the yellow pigment YZ. The flow value for a standard mortar is 210 mm.

On the basis of this result, we concluded that the needle-shaped particles of the yellow pigment cause a greater

Table 5
Mixture proportion of cement mortar

Specimen code	Mix ratio (C–S)	W/C (%)	P/C (%)	Mixture content (kg/m^3)			
				Cement	Sand	Pigment	Water
N1a00	1:1	35.0	0	2396	2396	0	839
N2a00	1:2	47.5	0	1511	3022	0	718
N2b00	1:2	50.0	0	1493	2986	0	747
N2c00	1:2	52.5	0	1476	2952	0	775
N3a00	1:3	67.5	0	1075	3225	0	726
A1a03	1:1	35.0	3	2396	2396	72	839
A1a06			6	2396	2396	144	839
A1a09			9	2396	2396	216	839
A1a12			12	2396	2396	288	839
A2a03	1:2	47.5	3	1511	3022	45	718
A2a06			6	1511	3022	91	718
A2a09			9	1511	3022	136	718
A2a12			12	1511	3022	181	718
A2b03		50.5	3	1493	2986	45	747
A2b06			6	1493	2986	90	747
A2b09			9	1493	2986	134	747
A2b12			12	1493	2986	179	747
A2c03		52.5	3	1476	2952	44	775
A2c06			6	1476	2952	89	775
A2c09			9	1476	2952	133	775
A2c12			12	1476	2952	177	775
A3a03	1:3	67.5	3	1075	3225	32	726
A3a06			6	1075	3225	65	726
A3a09			9	1075	3225	97	726
A3a12			12	1075	3225	129	726

For this experiment, the case where no pigment is present was marked as N; the case that does not use domestic pigment, as A; and the case that uses foreign pigment, as Z. In addition, the cases of red, yellow, green, and black pigments were marked as R, Y, G, and B, respectively. (Example: RA1a03 represents the case with flow 210 mm at mixture proportion 1:1, mixed with red pigment RA, and flow 230, 240 mm were marked as b and c, respectively).

decline in fluidity compared with the spherical shape of the other pigments. Accordingly, appropriate action must be taken to increase the fluidity; a fluidity agent can be used or the mixing amount can be increased to obtain an acceptable workability because the flow may decrease rapidly to 180

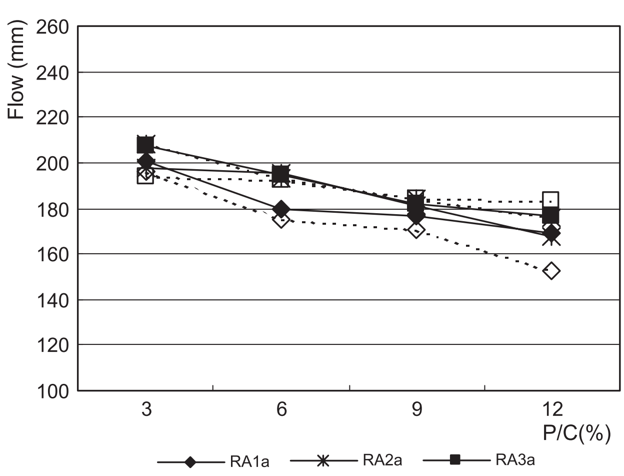

Fig. 2. Flow of red-colored mortar.

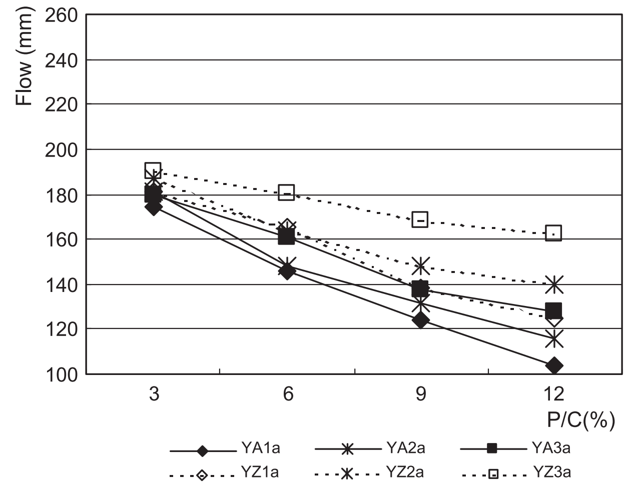

Fig. 3. Flow of yellow-colored mortar.

mm, which is the limit for workability if the yellow pigment is mixed at over 6%.

Flow change as a function of a change in the mixing ratio of the green pigment was found to be less than those of other colored mortars, as shown in Fig. 4. On the whole, when the mixing ratio of the green pigment was changed to 3%, 6%, 9%, and 12%, the flow changed by -5, -1, 5, and 14 mm, respectively, from the standard flow of 210 mm; by -7, -4, 1, and 10 mm, respectively, in case of green pigment GA; and by -4, 2, 9, and 19 mm in case of green pigment GZ. In general, we found that the flow might not change due to the addition of pigment to the green mortar because the scope of the target flow was set at ± 5 mm when the fluidity was measured.

Compared with the fluidity of other pigments, the fluidity of the green pigment at certain mixing ratios is due to the creation of repulsive forces between particles because the main ingredient is chrome oxide, as well as due to the considerable ball-bearing action caused by the large-diameter particles. Accordingly, the problem of flow decrease

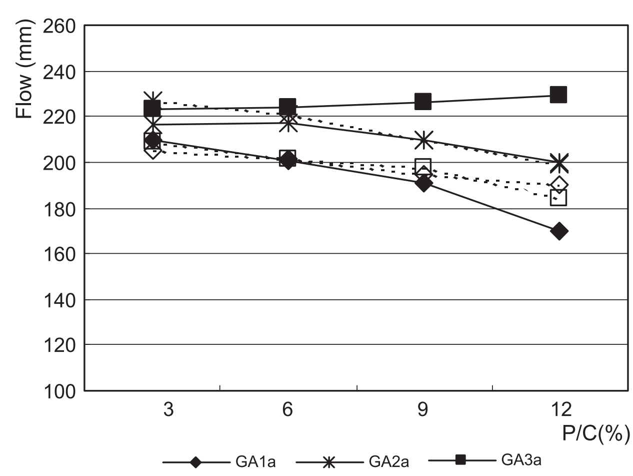

Fig. 4. Flow of green-colored mortar.

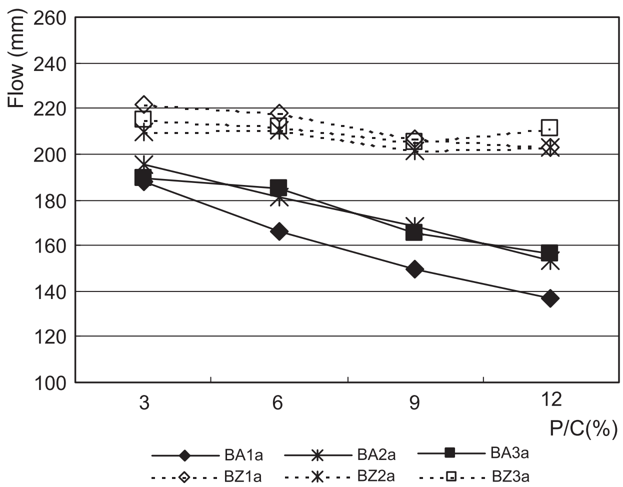

Fig. 5. Flow of black-colored mortar.

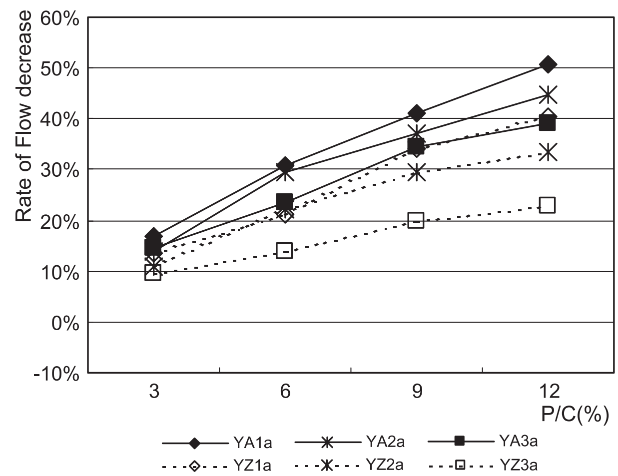

Fig. 7. Flow decrease rate of yellow-colored mortar.

due to mixing does not need to be considered if a green pigment is used.

Flow change due to the change of the mixing ratio of black pigment was found to rapidly decrease when the black pigment BA was used, as shown in Fig. 5, and no significant change was found in the case of black pigment BZ. That is, as a whole, when the mixing ratio of black pigment changed to 3%, 6%, 9%, and 12%, the flow decreased to 7, 15, 27, and 33 mm, respectively, from the standard flow of 210 mm. When the black pigment BA was mixed at the same mixing ratios, the flow declined suddenly to 19, 33, 49, and 61 mm, respectively, but in the case of black pigment BZ, the flow showed a change of −5, −4, 6, and 4 mm, respectively; that is, no significant effect on fluidity was observed. Accordingly, a decrease in fluidity due to mixing does not need to be considered if black pigment BZ is used, but a fluidity agent must be used or the amount mixed must be increased to obtain an acceptable workability if black pigment BA is mixed at levels over 9%.

3.2. Fluidity by pigment mixing ratio

As shown in Figs. 6–9, the change in flow rates compared with the flow decrease values for mortar with each color mixed with an inorganic pigment was different for each pigment used. In the case of red and yellow mortars, an increase in the ratio of pigment causes a rapid decline in fluidity. Green mortar was found to undergo almost no change in fluidity due to mixing. Black mortar showed rapid decrease in fluidity when black pigment BA was mixed, but no significant change was found when black pigment BZ was used.

When red mortar was examined, the flow value showed decreased rates of 4.4–18.7%, relative to the standard flow value of 210 mm, as the pigment mixing ratio increased to 3%, 6%, 9%, and 12%. Yellow mortar showed a rapid decrease in flow rate of 13.3–38.6%. However, green mortar showed a decrease in flow rate of −2.4–6.9%, showing no significant flow change, as shown in Fig. 8. As

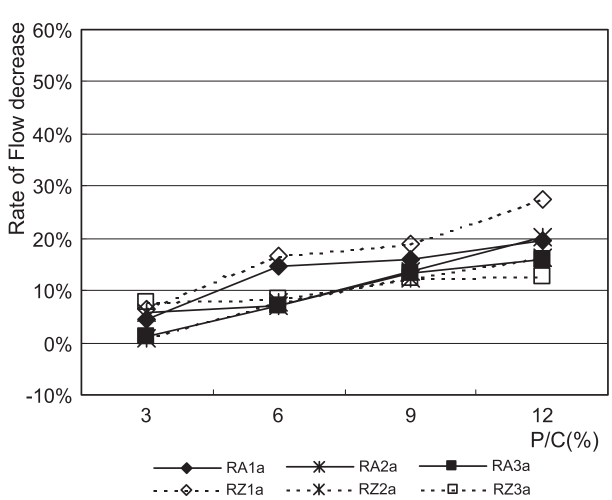

Fig. 6. Flow decrease rate of red-colored mortar.

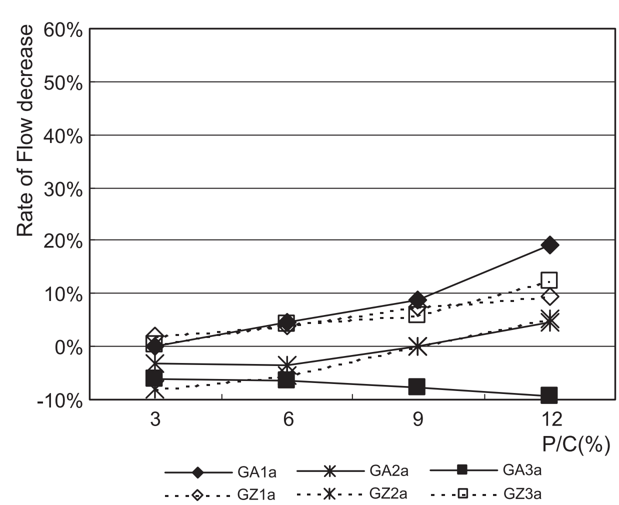

Fig. 8. Flow decrease rate of green-colored mortar.

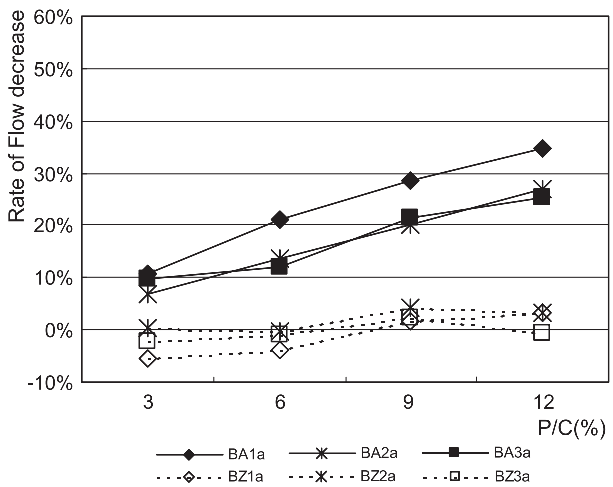

Fig. 9. Flow decrease rate of black-colored mortar.

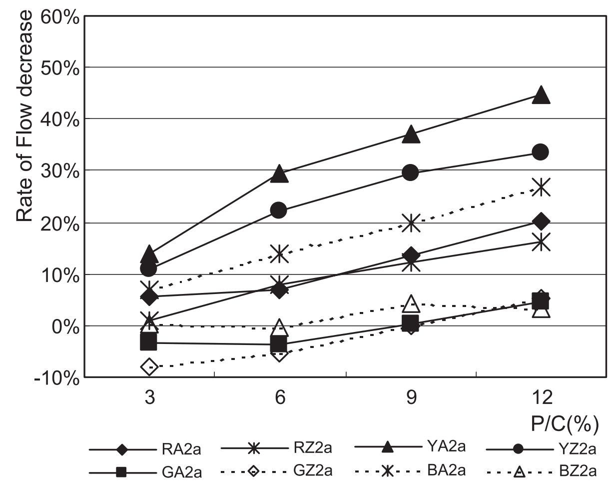

Fig. 11. Flow of a mix proportion 1:2.

shown in Fig. 9, black mortar showed a change in flow rate from −2.5% to 2.1% when black pigment BZ was used. Pigment particles are considered to participate in ball-bearing reactions and further increase the fluidity because the pigment acts as a filler inside the matrix.

3.3. Fluidity by mixture proportion

Flow changes according to the proportion of cement and sand used, 1:1, 1:2, and 1:3, are shown in Figs. 10–12. In the case of mortar prepared using a proportion of 1:1, the flow value decreased in all mortars, except black mortar BZ, as shown in Fig. 10. That is, red mortar showed a flow decrease of 4%, 15%, 16%, and 20% as the ratio of red pigment RA is increased to 3%, 6%, 9%, and 12%, respectively, and a flow decrease of 7%, 17%, 19%, and 27% for the red pigment RZ at the same mixing ratio. The mixing ratio at which pigment was at 6% and 9% produced a similar decrease in flow rate, indicating that there is no substantial flow decrease if the mixing ratio is over 6%. On the other hand, the yellow mortar showed a flow decrease of 17%, 31%, 41%, and 51% when yellow pigment YA was added and a decrease of 14%, 21%, 34%, and 40% when yellow pigment YZ was added at ratios of 3%, 6%, 9%, and 12%, respectively, showing a significant flow decrease according to the mixing rates.

In the case of mortar with a mixture proportion of 1:2, a flow decrease was substantial when the yellow pigment was used, as shown in Fig. 11, and the green mortar showed a slight flow increase at mixing ratios of 3% and 6%. In addition, the black pigment BZ also showed no flow change at mixing ratios of 3% and 6%. Mortar with mixture proportion of 1:3 (less cement), as shown in Fig. 12, showed a flow change rate of −9–39%, smaller than −5–51%, the flow change rate at thin mixing ratio of 1:1; thus, the flow change rate showed no rapid change in fluidity. However, the flow rates showed a slow decrease in fluidity, compared with the standard flow, as the mixing ratio was increased. That is, since the flow rate decreased less in the mixture proportion of 1:3 than in 1:1, the absolute quantity

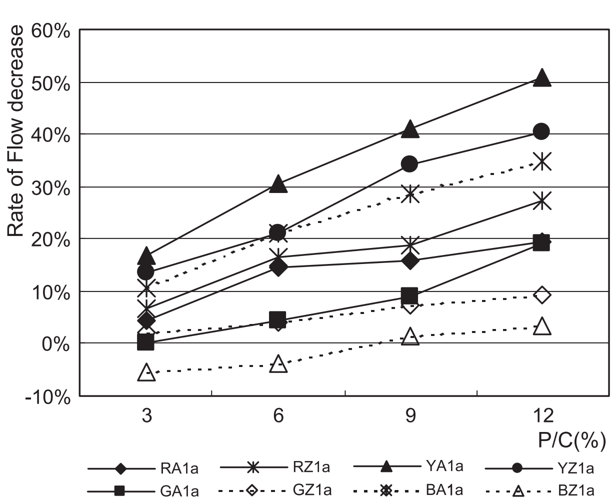

Fig. 10. Flow of a mix proportion 1:1.

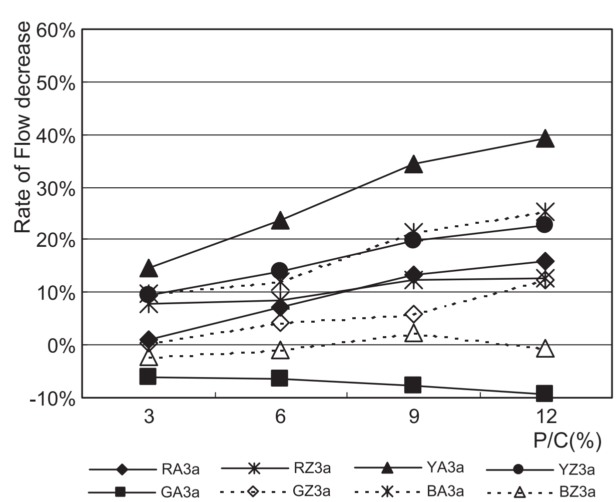

Fig. 12. Flow of a mix proportion of 1:3.

of pigment mixing is higher with a ratio of 1:1 than of 1:3, and that more mixing water is absorbed.

4. Conclusions

This study involved fluidity experiments on colored mortar samples. The proportion of cement and sand and water–cement and pigment mixing ratios, which are most widely used in cement composites, were varied to examine the properties of colored cement mortar containing mixtures of inorganic pigments. The following conclusions can be drawn:

(1) In terms of the average particle diameter of inorganic pigments, the German product pigment was found to be smaller than the Korean product. In terms of water-soluble and main ingredients, the Korean product pigment was less pure than that of the German pigment. The production and processing technology of high-quality pigments must be studied more extensively.

(2) When the mixing ratio of the red pigment (P/C) RA was changed to 3%, 6%, 9%, and 12%, the flow of the red mortar decreased by 8, 20, 30, and 39 mm, respectively, and when the red pigment RZ was used, the flow of the red mortar RZ decreased by 11, 23, 30, and 40 mm compared with the standard flow of 210 mm. If the pigment mixing ratio exceeded 9%, flow value decreased to 26–58 mm from the standard flow. Accordingly, the acceptable mixing ratio of the red pigment must be below 9% to obtain fluidity over a flow of 180 mm, considering its workability at the site.

(3) When the yellow pigment was mixed with the cement mortar, the pigment decreased the fluidity of the mortar because it contained needle-shaped particles. If the mixing ratio of the yellow pigment exceeded 6%, the flow of the yellow mortar may decrease to 180 mm, as well as the fluidity of the mortar, adversely affecting workability. In this regard, the proper mixing ratio should be below 6%.

(4) In the case where the green or black pigment BZ was mixed with the cement mortar, a flow decrease as the result of mixing of the pigments does not need to be considered because there was almost no change in fluidity. However, when the mixing ratio exceeded 9%, black pigment BA showed a considerable flow decrease. In this regard, the mixing ratio should be set to less than 6%.

Red mortar also showed a flow decrease of about 4.4–18.7% for a standard flow value of 210 mm as the pigment mixing ratio increased to 3%, 6%, 9%, and 12%, and the red mortar showed a rapid decrease in flow rate of 13.3–38.6%. However, green mortar showed a decrease in flow rate of −2.4–6.9%, showing almost no flow change, and black mortar also showed a flow change of −2.5–2.1% when black pigment BZ was mixed; therefore, fluidity does not need to be considered in those cases.

References

[1] G.E. Kurz, A.E. Jungk, The use of coloured concrete in creative design, Proceedings of the 3rd International Conference on Concrete Block Paving, Pavitalia, Rome, 1988, pp. 37–40.

[2] P. Bartos, Fresh Concrete Properties and Test, Elsevier, Amsterdam, 1992.

[3] S.M. Bruce, G.H. Rowe, The influence of pigments on mix designs for block paving units, Proceedings of the 4th International Conference on Concrete Block Paving 2, Pave New Zealand '92, New Zealand, 1992, pp. 117–124.

[4] ACI Committee 212, Chemical admixtures for concrete, ACI Mater. J. 86 (3) (1989) 297–327.

[5] B. Gunter, Industrial Inorganic Pigment, VCH Publishers, Inc., New York, 1993.

[6] L.A. Peter, Pigment Handbook, John Wiley & Son, New York, 1988.