

# Development of reference materials for cement paste

Dong Kyu Lee<sup>1a</sup> and Myoung Sung Choi<sup>\*2</sup>

<sup>1</sup>National Disaster Management Research Institute, Ulsan, 44538, Republic of Korea

<sup>2</sup>Department of Civil and Environmental Engineering, Dankook University, Gyeonggi-do Jukjeon-ro 152, Republic of Korea

(Received April 3, 2020, Revised May 20, 2020, Accepted March 23, 2020)

**Abstract.** This study aimed to develop reference materials (RMs) that are chemically stable and can simulate the flow characteristics of cement paste. To this end, the candidate components of RMs were selected considering the currently required properties of RMs. Limestone, slag, silica, and kaolin were selected as substitutes for cement, while glycerol and corn syrup were selected as matrix fluids. Moreover, distilled water was used for mixing. To select the combinations of materials that meet all the required properties of RMs, flow characteristics were first analyzed. The results revealed that silica and kaolin exhibited bilateral nonlinearity. When an analysis was conducted over time, slag exhibited chemical reactions, including strength development. Moreover, fungi were observed in all mixtures with corn syrup. On the other hand, the combination of limestone, glycerol, and water exhibited a performance that met all the required properties of RMs. Thus, limestone, glycerol, and water were selected as the components of the RMs. When the influence of each component of the RMs on flow characteristics was analyzed, it was found that limestone affects the yield value, while the ratio of water and glycerol affects the plastic viscosity. Based on this, it was possible to select the mixing ratios for the RMs that can simulate the flow characteristics of cement paste under each mixing ratio. This relationship was established as an equation, which was verified under various mixing ratios. Finally, when the flow characteristics were analyzed under various temperature conditions, cement paste and the RMs exhibited similar tendencies in terms of flow characteristics. This indicated that the combinations of the selected materials could be used as RMs that can simulate the flow characteristics of cement paste with constant quality under various mixing ratio conditions and construction environment conditions.

**Keywords:** reference material; rheology; cement paste; mixing ratio; flow characteristics

## 1. Introduction

Construction technologies are developing at a rapid pace to construct skyscrapers and various types of buildings (Han *et al.* 2006, Hwang *et al.* 2007). In 2020, in particular, it is expected that robots and humans will coexist, and the robot industry will form a large market owing to the advent of the fourth industrial revolution. Furthermore, 3D printing technology will also be commercialized in the construction industry. Owing to these trends, it is necessary to secure construction technologies that are superior to the existing construction technologies, which are typically evaluated on a qualitative basis, in terms of systemized construction, information and knowledge, and efficiency. To this end, technologies capable of evaluating construction performance on a quantitative and a numerical basis must be developed (Hwang *et al.* 1998). As such, various studies have been conducted in the construction structure and design industries to develop technologies capable of evaluating construction performance on a quantitative basis (Sunil *et al.* 2017). Many studies have also been conducted in the construction material industry by introducing the

concept of rheology to quantitatively evaluate the flow characteristics of concrete (Eugene *et al.* 1922, Ferraris *et al.* 1922, Ferraris 1999, Tattersall *et al.* 1983, Swindells *et al.* 1954). In general, rheology is a science to represent flow properties for substance through the relationship with transformation and movement of substance. However, to quantitatively evaluate the flow characteristics of concrete through rheology, it is necessary to consider various factors, such as the particle characteristics of cement, fine aggregate, and coarse aggregate, which are the components of concrete, various mix designs according to the construction conditions, and environmental elements (Bauchkar *et al.* 2018, Choi *et al.* 2014, Tattersall *et al.* 1983, Roussel *et al.* 2010, Nehdi *et al.* 1998, Wallevik *et al.* 2009). For this reason, various rheometers capable of measuring the flow characteristics of concrete have been developed, and studies have been conducted to quantitatively evaluate the flow characteristics of concrete. However, only relative comparisons of rheological results have been presented because measured value is different for each instrument even though it is the same material (Ferraris *et al.* 2000). This is because it is not possible to correct for the differences between the developed rheometers. The currently available reference materials (RMs) are Newtonian fluids without particles. In this case, it is not possible to correct the measuring instruments for non-Newtonian fluids that contain particles. Although studies have been conducted overseas to develop RMs containing particles, there are still no definite forms of

\*Corresponding author, Professor

E-mail: choims@dankook.ac.kr

<sup>a</sup>Researcher

E-mail: leedk0418@korea.kr

Table 1 Steps taken to develop the RMs

Steps	Experimental plan
1 Step	Derivation of components for the RM - Selection of tentative materials for the RM - Analysis of flow characteristics - Analysis the effect of time
2 Step	Selection of mixing ratios for the RM - Analysis of cement paste flow characteristics - Influence of RM components - Suggestion of mixing ratios - Establish relationship - Verification
3 Step	Analysis of the change in flow characteristics with temperature - Analysis of flow characteristics of cement paste with temperature variation - Analysis of flow characteristics of RM with temperature variation - Comparison of flow characteristics with temperature variation

such RMs (Ferraris *et al.* 2012).

Through the development of RMs, it is possible to calibrate various rheometers for concrete as mentioned above. Moreover, as RMs may exhibit a constant quality over an extended period of time, it is possible to evaluate the overall construction process on a quantitative and a numerical basis using RMs, and to predict and evaluate the construction performance in advance (Ferraris *et al.* 2017, Roussel *et al.* 2007). Furthermore, the wear property and replacement period of piping can be evaluated through the recycling of the pump piping for concrete pumping and pouring (Jang *et al.* 2018), and RMs can be utilized in various areas, including cutting-edge areas, such as being utilized as a standard sample for the stable control of digital printers for concrete.

Meanwhile, it is necessary to develop RMs that meet certain properties. In NIST(National Institute of Standards and Technology), the suggested required properties of particulate RMs are as follows: 1) There should be no particle separation during testing, 2) the linear Bingham reaction must occur in a wide range of shear strains, 3) there should be sufficient yield stress to prevent the material separation of aggregate, 4) there should be little bilateral linear response behavior, i.e., hysteresis, and 5) there should be no change in flow and chemical characteristics between the fluid and particles over an extended period of time (Ferraris *et al.* 2012).

Therefore, the purpose of this study was to develop RMs for concrete, which exhibit performances that meet the requirements for factors that act as the variables in evaluating flow characteristics and the required properties of particulate RMs. To this end, RMs for cement paste, which is the most basic component of concrete, were developed first. Table 1 lists the steps taken to develop RMs for cement paste. As shown in the table, the combinations of components for the RMs that represented performances meeting all the required properties of particulate RMs were derived first. Secondly, the mixing ratios for RMs capable of simulating the flow characteristics of cement paste under each mixing ratio were selected. Lastly, the flow

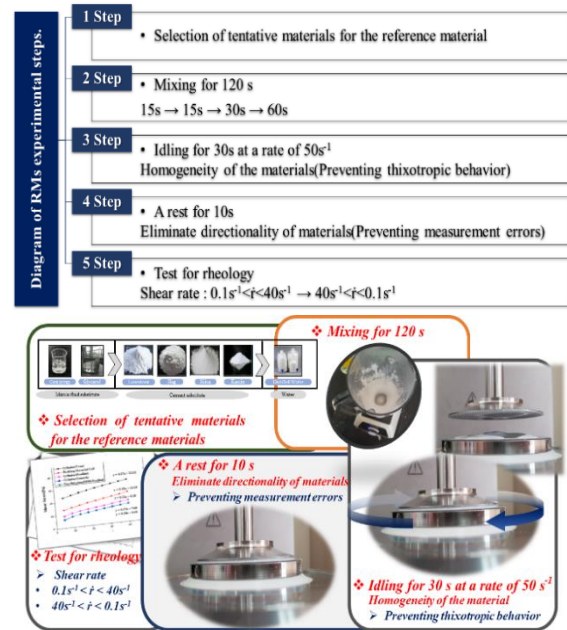


Fig. 1 Diagram for experimental procedures

characteristics of cement paste and RMs were analyzed according to the temperature, which had the largest influence on the rheological properties among environment conditions.

## 2. Experimental methods and materials used

### 2.1 Experimental methods

As for the rheometers used in all experiments, MCR-302 (Anton paar), a typical rheometer capable of measuring the flow characteristics of cement paste, was used. The mixing of all materials was performed in four steps for a total of 120 s (15 s, 15 s, 30 s, and 60 s in each step) using a high-speed mixer, and mixtures were kneaded using a scraper upon the completion of each step. In the steps for the derivation of components for the RMs and the selection of mixing ratios, experiments were performed at room temperature. The experiment on the analysis of flow characteristics according to the temperature was performed at five temperatures (5°C, 10°C, 20°C, 30°C, and 40°C) considering construction conditions. Before the experiments, idling was performed for 30 s at a rate of 50 s<sup>-1</sup> for the homogeneity of the material and for preventing thixotropic behavior (Struble *et al.* 1995). A rest of 10 s was provided to reduce the experimental error due to the directionality of the material produced by idling. For the experimental measurements, ten measurements were made as the shear rate was increased from 0.1 s<sup>-1</sup> to 40 s<sup>-1</sup>, and another ten measurements were made as the rate was decreased to 0.1 s<sup>-1</sup> (Fig. 1). A serrated spindle was used to prevent the slip phenomenon (Fig. 2(b)).

In this study, the Bingham model, which is the most commonly used model in the concrete area, was used to determine the plastic viscosity and yield value, as shown in Eq. (1) (Eugene *et al.* 1922, Kulasegarm *et al.* 2011,



(a) Rheometer for parallel plate measurement system



(b) Serrated spindle for parallel plate (Ø50 mm)

Fig. 2 Anton-paar rheometer and spindle

Ferraris *et al.* 1922, Feys *et al.* 2017, Ferraris 1999). In this equation, the plastic viscosity is defined as the slope of the shear rate and shear stress, and the yield value represents the value of the y-intercept.

$$\tau = \eta \dot{\gamma} + \tau_0 \quad (1)$$

where,

$\tau$  = Shear Stress

$\eta$  = Plastic Viscosity

$\dot{\gamma}$  = Shear Rate

$\tau_0$  = Yield Stress

## 2.2 Materials

In general, cement paste is a mixture of cement and water, and its viscosity is the result of a chemical reaction, between cement and water. This property is an important factor that determines the flow characteristics of cement paste. In this study, therefore, the factors affecting the flow characteristics of cement paste were as follows: the cement particles, the viscous fluids generated through the chemical reaction, and water for mixing. Thus, substitutes for cement, viscous fluids, and water were determined as candidate components to develop RMs for cement paste that exhibit long-term chemical stability. Among the candidate components for the substitutes for cement, limestone, slag,

Table 2 Combinations of materials

Cement replacements	Matrix fluid replacements	Water
Limestone		
Slag	Glycerol	Distilled water
Silica	Corn syrup	
Kaolin		

silica, and kaolin were selected as materials with particle sizes similar to the average particle size of cement as shown in Table 2. As for viscous fluids, i.e., substitutes for the matrix fluid, glycerol and corn syrup, which are chemically stable and have viscosities similar to that generated by chemical reaction in cement paste, were selected. Moreover, as for the water used for mixing, distilled water was used to reduce experimental errors. Table 3 shows the physical and chemical properties of each material. As for the corn syrup, 100% pure corn syrup was used.

## 3. Development of RMs

### 3.1 Derivation of components for RMs

To realize materials that exhibit satisfactory performances for all the required properties of particulate RMs, the substitutes for cement were first examined among the selected candidate materials, and then the matrix fluids were examined. For the substitutes for cement, their performances with regard to the following four required properties were evaluated through an analysis: 1) There should be no particle separation during testing, 2) the linear Bingham reaction must occur in a wide range of shear strain, 3) there should be sufficient yield stress to prevent the material separation of aggregate, and 4) there should be little bilateral linear response behavior, i.e., hysteresis. In addition, the performances of the materials with regard to property, i.e., 5) there should be no change in flow and chemical characteristics between the fluid and particles over an extended period of time were evaluated by an analysis over time (Ferraris *et al.* 2012). To evaluate the matrix fluids, changes in the chemical properties of the fabricated specimens over time were observed in the analysis that was conducted over time.

#### 3.1.1 Analysis of flow characteristics.

To select combinations that exhibit the most suitable

Table 3 Chemical and physical properties of the materials

Cement replacements	Constituent (%)								
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>
Limestone	0.30	0.10	0.02	0.20	99.30	-	-	-	-
Slag	34.69	14.31	0.50	3.93	41.95	-	-	2.61	-
Silica	99.50	0.40	0.05	0.02	0.02	0.02	0.02	-	0.05
Kaolin	53	44	0.25	0.22	0.40	0.23	-	-	-
Matrix fluid	Constituent (%)								
	Content	NH <sub>4</sub>	SO <sub>4</sub>	As	Fe	Pb	Acid-base	Fatty acid ester	
Glycerol	99.0	Within limits	0.002	0.0002	0.0003	0.0004	Within limits	0.2	

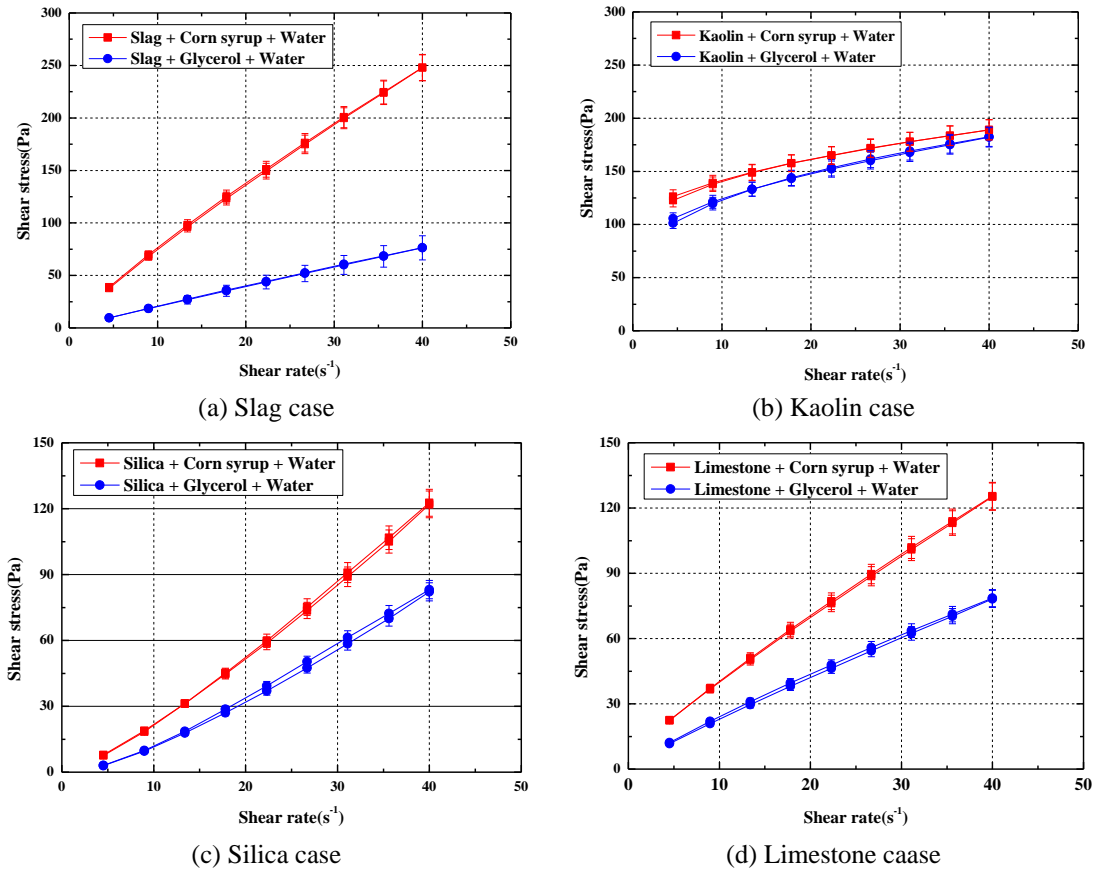


Fig. 3 Results of flow analysis

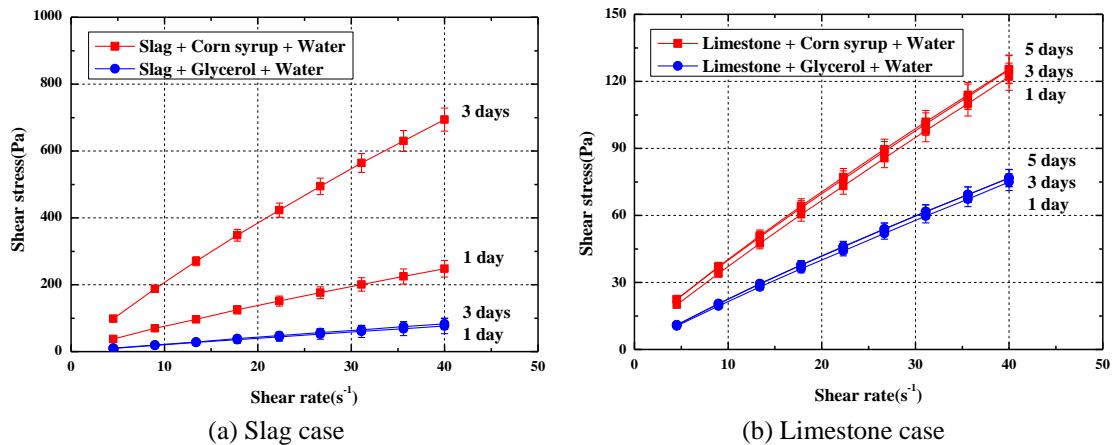


Fig. 4 Rheology for elapsed time

performances for the required properties of particulate RMs, the flow characteristics of all combinations were analyzed. Figure 3 shows the results of rheology measurements for various combinations with tentative components.

The results revealed that kaolin exhibited the shear thinning phenomenon, in which the plastic viscosity decreases as the shear rate increases. On the other hand, silica experienced the shear thickening phenomenon, in which the plastic viscosity increases as the shear rate increases (Cross 1979, Poslinski *et al.* 2018, Fall *et al.* 2012, Khandavalli *et al.* 2014). In other words, kaolin and silica exhibited bilateral nonlinearity in all mixtures and,

thus, could not meet the required properties of RMs. On the contrary, slag and limestone exhibited performances in all mixtures that met the required properties of particulate RMs.

### 3.1.2 Analysis with over time

In the next step, the flow characteristics were analyzed over time to evaluate whether limestone and slag, which had been selected through the initial flow analysis, showed chemical stability over an extended period of time. All the experiments were performed by fabricating specimens and performing remixing. Fig. 4 shows the results of the

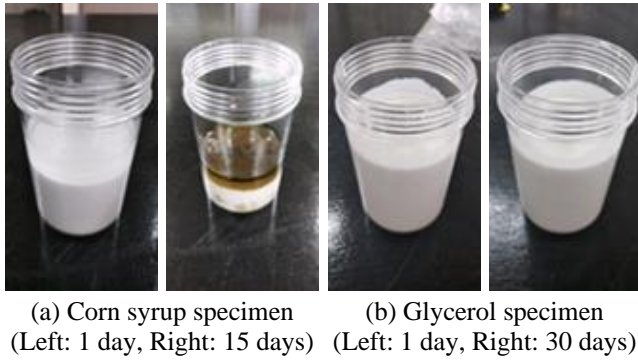


Fig. 5 Chemical change of specimen with long-term (Lee *et al.* 2018c)

Table 4 Evaluation of the required rheology properties of RMs for all combinations (Lee *et al.* 2018c)

Item	Separating resistance	Linearity	Yield value	Hysteresis	Chemical stability	Evaluation
Limestone	Corn syrup	O <sup>1</sup>	O	O	X	NG
	Glycerol	O	O	O	O	OK
Slag	Corn syrup	O	O	O	X	NG
	Glycerol	O	O	O	X	NG
Silica	Corn syrup	O	X <sup>2</sup>	X	X	NG
	Glycerol	O	X	O	O	NG
Kaolin	Corn syrup	O	X	O	X	NG
	Glycerol	O	X	O	O	NG

<sup>1</sup> indicates conformity, <sup>2</sup> indicates unconformity.

analysis of flow characteristics over time. For slag, higher rheological properties were observed on 3 days than on 1 day in all mixtures owing to its latent hydraulic property. Experimental measurement was not possible after day 5 because of strength development (Kolani *et al.* 2012, Kourounis *et al.* 2007). For limestone, however, constant rheological properties were observed in all mixtures over time. Therefore, limestone was selected as the final substitute for cement. When in the chemical changes of the specimens were observed over time, corn syrup could not meet the required properties of RMs because its chemical properties change after approximately 15 days, but glycerol exhibited chemical stability for over 30 days with no change in its chemical properties (Fig. 5). In other words, the combination of limestone, glycerol, and water was finally selected because it met all the required properties of particulate RMs, as shown in Table 4.

### 3.2 Determination of mixing ratios for the RMs

In construction, various combinations of concrete were made depending on the construction conditions and workability. Moreover, the cement paste mix was adjusted at various ratios according to the developed combinations. These characteristics indicate that the various mixing ratios of cement paste are also an important factor that must be considered in the development of RMs that can simulate the flow characteristics of cement paste. Therefore, the flow characteristics of cement paste under each mixing ratio

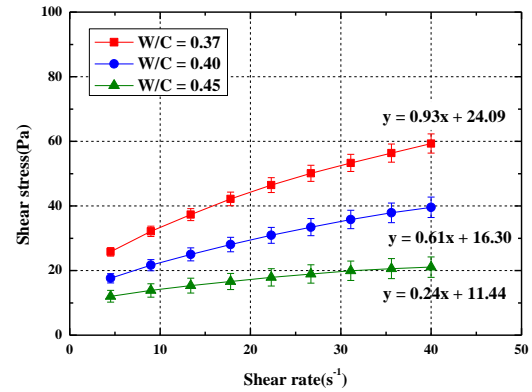


Fig. 6 Rheology measurement of the selected three mixing ratios for cement paste

Table 5 Measured rheological ranges for tested mixing ratios

Mixing ratios (W/C)	Plastic viscosity (Pa·s)	Yield stress (Pa)
0.37	$1.0 \pm 0.1$	$22.0 \pm 0.3$
0.40	$0.5 \pm 0.1$	$15.0 \pm 0.3$
0.45	$0.3 \pm 0.1$	$10.0 \pm 0.3$

were analyzed first using the ordinary Portland cement to select the reference rheological properties to be derived through RMs. Moreover, mixing ratios that exhibited satisfactory performances for the derived rheological properties were selected by analyzing the influence of each component of the RMs on flow characteristics. This relationship was established as an equation that represented the mixing conditions of RMs according to the various mixing ratios of cement paste.

#### 3.2.1 Flow characteristics of cement paste

First, to select the reference rheological properties to be derived through the RMs, flow characteristics were analyzed using three mixing ratios for cement paste ( $W/C=0.37$ ,  $0.40$ , and  $0.45$ ) that are most commonly used in construction sites. For cement paste, some errors may occur in measuring flow characteristics because of several reasons such as a chemical reaction with time and insufficient measuring device itself (Ferraris *et al.* 2001, Rößler *et al.* 2008, Lee *et al.* 2019). Considering this, the experiment was conducted five minutes after the cement pastes were mixed. The experiment was performed five times, and the average values were obtained as shown in Fig. 6. The results reveal that the rheological properties of the materials containing particles showed a tendency to decrease as the  $W/C$  ratio increased. This finding is similar to those in studies that demonstrated that the rheological properties exhibited a tendency to increase as the concentration increase (Farris *et al.* 1968, Uchikawa *et al.* 1985). Based on these analysis results, it was possible to select the reference rheological properties to be derived through the RMs, as shown in Table 5.

#### 3.2.2 Influence of each component of the RMs on flow characteristics



Table 6 Mixing ratios to determine yield stress

No.	$S/L^1$	Water: Glycerol
1	0.40	4 : 6
2	0.45	
3	0.47	
4	0.57	

<sup>1</sup>  $S$ =Water+Glycerol,  $L$ =Limestone

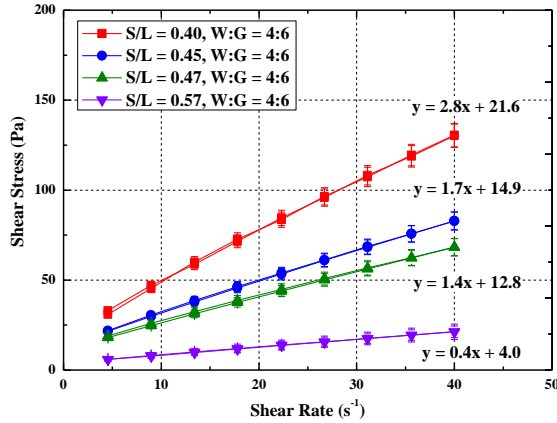


Fig. 7 Variation in rheology with limestone ratios

To derive mixing ratios that meet the reference rheological properties (Table 5) through the developed RMs, the influence of each component of the RMs on flow characteristics was analyzed. For this, the experiment was performed by increasing the amount of limestone at a certain rate, while the ratio of water to glycerol was fixed, as shown in Table 6. The results are shown in Fig. 7. The rheological properties showed a tendency to increase as the amount of limestone increased. In particular, the yield value significantly increased compared to the plastic viscosity, indicating that the amount of limestone has the largest influence on the yield value. Meanwhile, under the mixing ratios of  $S/L=0.40$  and water:glycerol=4:6, a somewhat high plastic viscosity and a similar yield value were observed when compared with the rheological properties under  $W/C=0.37$ . To derive comparative rheological properties, a method to reduce the plastic viscosity while the yield value is maintained was required. As shown in Table 7, an experiment was performed by adjusting the ratio of water to glycerol, while the amount of limestone was fixed at  $S/L=0.40$ . As a result, the ratios of water to glycerol increase, the plastic viscosity showed a tendency to decrease, while the yield value remained constant, as shown in Fig. 8. In other words, it was found that the ratio of water to glycerol affects the plastic viscosity. By adjusting the ratios of water to glycerol, the ratios of  $S/L=0.40$  and water:glycerol=7:3 relatively just met the yield value and plastic viscosity ranges of  $W/C=0.37$  cement paste.

### 3.2.3 Determination of the RM mixing ratios and establishment of a relationship

Through analyzing the influence of each component of the RMs on flow characteristics, it was found that the ratio of water to glycerol affects the plastic viscosity, while

Table 7 Mixing ratios used to determine the plastic viscosity

No.	$S/L$	Water:Glycerol
1	0.40	4:6
2		5:5
3		6:4
4		7:3

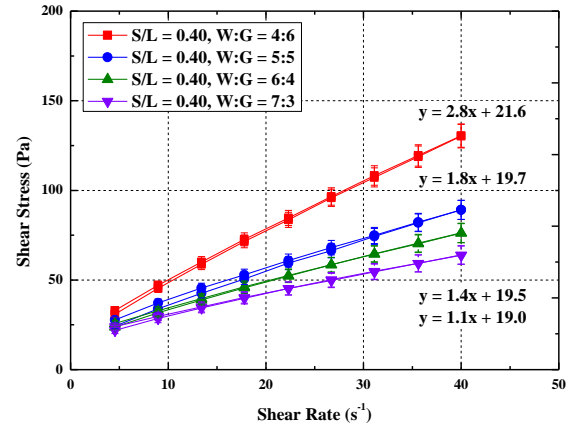


Fig. 8 Variation in rheology with water and glycerol ratios

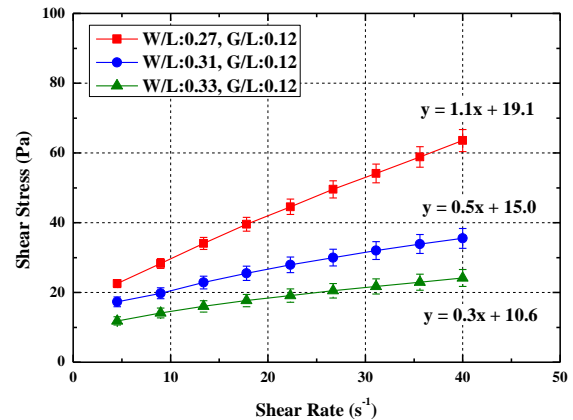


Fig. 9 Results of rheology for the derived RM mixing ratios

limestone affects the yield value. Where the relation of  $\frac{S}{L} = \frac{W+G}{L} = \frac{W}{L} + \frac{G}{L}$ ,  $G/L$  was found to play a role in preventing the occurrence of hysteresis, which as found in a previous study to select the combinations of the components of RMs (Lee *et al.* 2018d). Meanwhile, for an RM mixing ratio ( $S/L=0.40$ , water: glycerol=7:3) that meets the rheological properties of  $W/C=0.37$ , the amount of glycerol was calculated to be approximately 12% that of limestone. Therefore, an experiment was performed while the ratio of water to limestone was adjusted with an amount of glycerol that was 12% of that of limestone. As a result, it was possible to derive RM mixing ratios that met all the ranges of the derived rheological properties as shown in Fig. 9. Based on these results, it was possible to select RM mixing ratios that can simulate the flow characteristics of cement paste under each mixing ratio. This relationship was established as an equation as shown in Eq. (2).

Table 8 Comparison between RM mixing ratios and cement paste mixing ratios

Items	Cement paste	Reference materials	
	W/C	W/L	G/L
Mixing ratios	0.50	0.38	0.12
	0.55	0.45	

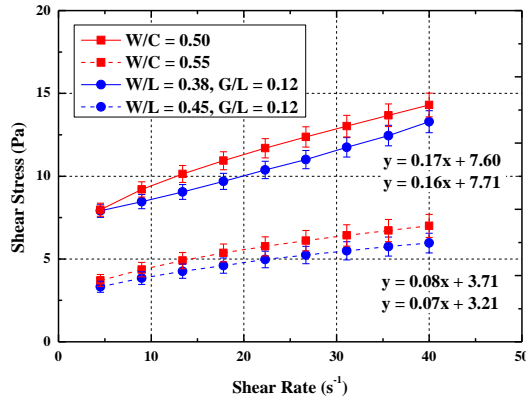


Fig. 10 Experiments for validation for derived equation.

$$W/L = a(W/C)^2 + b(W/C) + c \quad (1)$$

$$G/L = 0.12 \quad (2)$$

where,  $a=2.629$ ,  $b=-1.491$ ,  $c=0.471$

The values of the constants were derived from the material and experimental conditions used in this study

### 3.2.4 Verification with other mixing ratios.

Cement paste and the RMs showed a relationship as shown in Eq. (2). For verification of the relationship, an experiment was performed to compare the rheological properties of various cement paste mixing ratios with those of the RM mixing ratios calculated through the relationship as shown in Table 8. The results are shown in Fig. 10. It was possible to verify the relationship because the RM mixing ratios calculated through the relationship exhibited the rheological properties that met all the flow characteristics of cement paste.

### 3.3 Effect on flow characteristics with temperature

The flow characteristics of all materials are generally known to be affected by the ambient temperature and their own temperatures. In the case of cement paste, in particular, it is known that various errors may occur in measuring flow characteristics because the hydration rate, as well as pores, gaps, and filling between particles, is affected by the temperature change (Uchikawa *et al.* 1985, Fernández-Altable *et al.* 2006, Wu *et al.* 2013, Petit *et al.* 2010, Kasai *et al.* 1996). In other words, the temperature change is also an important element that should be considered in the development of RMs capable of simulating the flow characteristics of cement paste. As such, the flow characteristics of cement paste according to the temperature were compared with those of RMs under various mixing ratios. The experiment was performed at five temperatures

Table 9 Variation in the flow characteristics of cement paste and the RM at various temperatures

Temperature (°C)	Mixing ratios	
	Cement paste	Reference materials
5	W/C=0.40	W/L=0.30
10	W/C=0.45	W/L=0.33
20	W/C=0.50	W/L=0.38
30	W/C=0.55	W/L=0.45
40		

$G/L=0.12$

(5°C, 10°C, 20°C, 30°C, and 40°C) depending on the construction conditions using rheometers capable of setting the temperature in a -35°C~+200°C range. Moreover, the materials were prepared in advance through a constant-temperature bath to minimize the time taken to reach the measurement temperature.

### 3.3.1 Comparison of flow characteristics according to the temperature

To analyze the variation in the flow characteristics of cement paste and RMs with temperature, the flow characteristics of cement paste were compared with those of RMs under various mixing ratios as shown in Table 9. The results are shown in Fig. 11. In all mixtures, the plastic viscosity and yield stress values showed a tendency to decrease as the temperature increased. In particular, the overall plastic viscosity exhibited a change rate of approximately 50% at 5°C and 10°C, i.e., low temperatures, and the change rate showed a tendency to decrease as the temperature increased. In addition, the overall yield value also exhibited high change rates at low temperatures, and the change rate showed a tendency to decrease as the temperature increased. In other words, most changes in flow characteristics due to temperature changes occurred at low temperatures, and relatively constant rheological properties were maintained as the temperature increased (Lee *et al.* 2018e).

Meanwhile, for the shear thinning phenomenon, in which the plastic viscosity decreases as the shear rate increases, the travel directions of the particles are arranged in the shear direction at a high shear rate; thus, the collision frequency between the particles decreases compared to the equilibrium state, thereby causing the plastic viscosity to slowly reduce before reaching a constant value (Cross *et al.* 1979, Poslinski *et al.* 2018). Similarly, for the phenomenon in which the rheological properties are reduced or maintained as the temperature increases, the rheological properties are high at low temperatures because a strong binding force between the particles leads to a high collision frequency, but the binding force decreases and, thus, the inter-particle distance increases as the temperature increases, thereby causing the rheological properties to reduce to a constant value. In other words, from a rheology perspective, cement paste and RMs have states similar to those of materials with the shear thinning phenomenon at high temperatures. Therefore, it appears that the rheological properties are reduced and maintained as the temperature increases.

Moreover, as can be seen from the experiment results, it was found that cement paste and the RMs exhibited similar

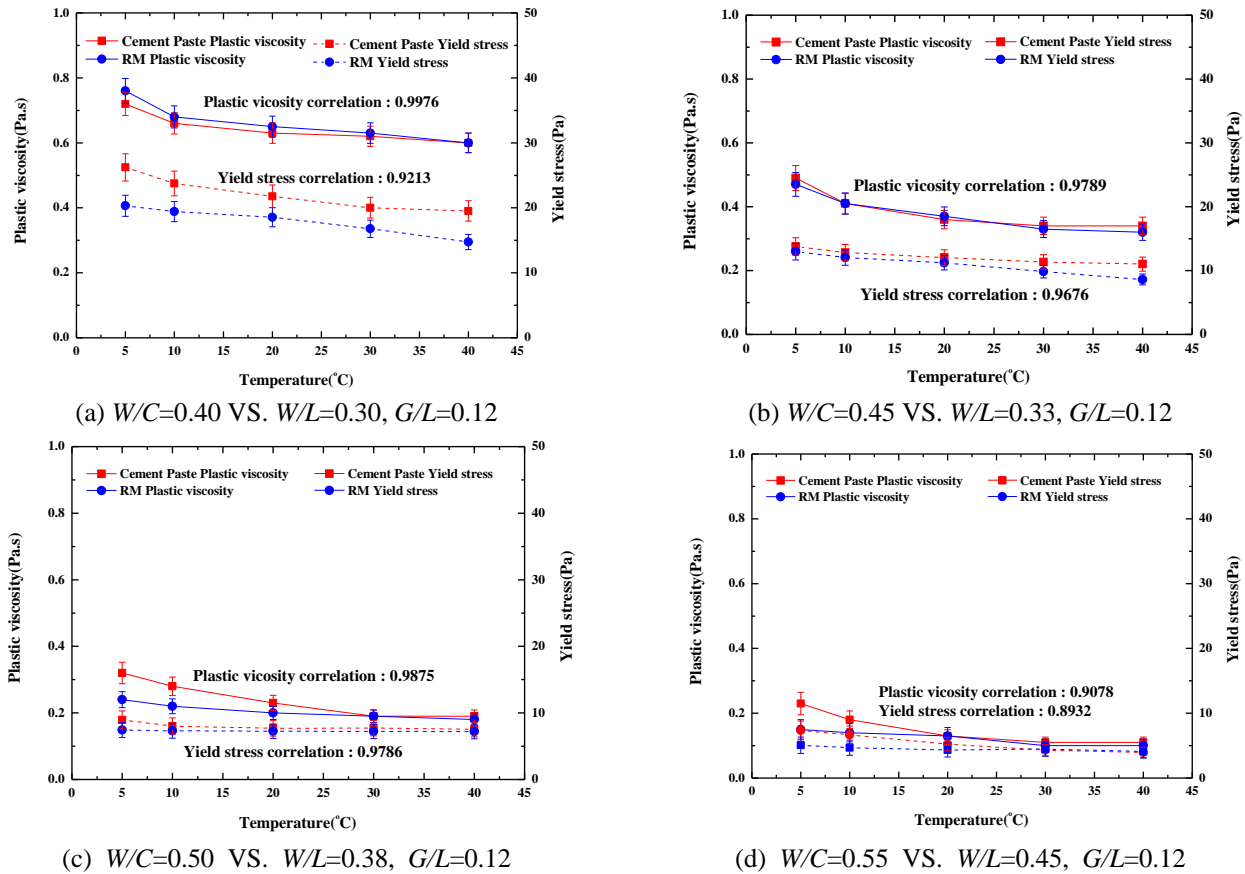


Fig. 11 Comparison of the rheological properties of cement paste and the RMs with temperature

changes in flow characteristics according to the temperature for all mixtures. In other words, the combinations of limestone, glycerol, and water, which are the components of the RMs for cement paste, can be used as RMs that can simulate the flow characteristics of cement paste under various construction conditions because their sensitivity to temperature is low.

#### 4. Conclusions

This study aimed to develop reference materials (RMs) that can simulate the flow characteristics of cement paste. To this end, the candidate components of the RMs were selected considering the currently required properties of RMs. Limestone, slag, silica, and kaolin were selected as substitutes for cement, while glycerol and corn syrup were selected as matrix fluids. As for the water used in mixing, distilled water was selected. Various combinations of the selected candidates that can meet all the required properties of particulate RMs were prepared, and an attempt was made to develop RMs capable of simulating the flow characteristics of cement paste under various cement paste mixing ratio conditions and temperature conditions. The major results of this study are as follows.

1. To derive the combinations of materials that meet the required properties of particulate RMs, flow characteristics were analyzed as well as over time. The analysis of flow characteristics showed that all mixtures

that used silica and kaolin exhibited nonlinearity. Moreover, the analysis over time revealed that chemical reactions occurred in all mixtures that used slag and corn syrup. Therefore, limestone, glycerol, and water were finally selected as the components of the RMs.

2. To select mixing ratios for RMs that can simulate the flow characteristics of cement paste under various mixing ratios, the influence of each component of the RM on flow characteristics was analyzed. It was found that limestone affects the yield value, while the ratio of water to glycerol affects the plastic viscosity. Based on these results, mixing ratios for RMs capable of simulating the flow characteristics of cement paste under each mixing ratio were derived, and this relationship was established as an equation. Moreover, the relationship derived from various cement paste mixing ratio conditions was verified.

3. The rheological properties of all materials are most closely related to the temperature. Therefore, flow characteristics were analyzed in the range of 5°C-40°C depending on the construction conditions to analyze the flow characteristics of cement paste and RMs according to the temperature. In this instance, the rheological properties of cement paste and RMs showed a tendency to decrease as the temperature increased. Moreover, both cement paste and RMs exhibited similar tendencies in terms of flow characteristics.

4. In conclusion, we found that combinations of limestone, glycerol, and water, which are the



components of the RMs for cement paste, can be used as chemically stable RMs that can simulate the flow characteristics of cement paste under various construction environment conditions and various cement paste mixing ratio conditions.

## Acknowledgments

This research was supported by a grant(20AUDP-B106327-06) from Architecture & Urban Development Research Program funded by Ministry of Land, Infrastructure and Transport of Korean Government.

## References

- Bauchkar, S.D. and Chore, H.S. (2017), "Experimental studies on rheological properties of smart dynamic concrete", *Adv. Concrete Constr.*, **5**(3), 183-199. <https://doi.org/10.12989/acc.2017.5.3.183>.
- Bauchkar, S.D. and Chore, H.S. (2018), "Effect of PCE superplasticizers on rheological and strength properties of high strength self-consolidating concrete", *Adv. Concrete Constr.*, **6**(6), 561-583. <https://doi.org/10.12989/acc.2018.6.6.561>.
- Choi, M.S., Kim, Y.J., Jang, K.P. and Kwon, S.H. (2014), "Effect of the coarse aggregate size on pipe flow of pumped concrete", *Constr. Build. Mater.*, **66**, 723-730. <https://doi.org/10.1016/j.conbuildmat.2014.06.027>.
- Cross, M.M. (1979), "Relation between viscoelasticity and shear-thinning behavior in liquids", *J. Rheol. Acta*, **18**, 609-614. <https://doi.org/10.1007/BF01520357>.
- Eugene Cook Bingham (1922), *Fluidity and Plasticity*, McGraw-Hill Book Co, Inc.
- Fall, A., Bertrand, F., Ovarlez, G. and Bonn, D. (2012), "Shear thickening of cornstarch suspensions", *J. Rheol.*, **56**, 575-591. <https://doi.org/10.1122/1.3696875>.
- Farris, R.J. (1968), "Prediction of the viscosity of multi-modal suspensions from unimodal viscosity data", *Tran. Soc. Rheol.*, **12**, 281-301. <https://doi.org/10.1122/1.549109>.
- Fernández-Altable, V. and Casanova, I. (2006), "Influence of mixing sequence and superplasticiser dosage on the rheological response of cement pastes at different temperatures", *Cement Concrete Res.*, **36**(7), 1222-1230. <https://doi.org/10.1016/j.cemconres.2006.02.016>.
- Ferraris, C.F. (1999), "Measurement of the rheological properties of cement paste, A new approach", *Proceedings of the RILEM International Symposium on the Role of Admixtures in High Performance Concrete Monterrey*, Mexico, 21-26.
- Ferraris, C.F. and Gaidis, J.M. (1992), "Connection between the rheology of concrete and rheology of cement paste", *ACI Mater. J.*, **89**, 388-393.
- Ferraris, C.F., Billberg, P., Ferron, R., Feys, D., Hu, J., Kawashima, S., Koehler, E., Sonebi, M., Tanesi, J. and Tregger, N. (2017), "Role of rheology in achieving successful concrete performance", *Concrete Int.*, **39**, 43-51.
- Ferraris, C.F., Brower, L.E., Banfill, P., Beaupré, D., Chapdelaine, F., de Larrard, F., ... & Wallevik, O. (2001), *Comparison of Concrete Rheometers: International Test at LCPC (Nantes, France) in October*, US Department of Commerce, National Institute of Standards and Technology.
- Ferraris, C.F., Obla, K.H. and Hill, R. (2001), "The influence of mineral admixtures on the rheology of cement paste and concrete", *Cement Concrete Res.*, **31**(2), 245-255. [https://doi.org/10.1016/S0008-8846\(00\)00454-3](https://doi.org/10.1016/S0008-8846(00)00454-3).
- Ferraris, C.F., Stutzman, P.E., Guthrie, W.F. and Winpiger, J. (2012), Certification of SRM 2492: Bingham Paste Mixture for Rheological Measurements, SP-260-174\_Rev. National Institute of Standards and Technology, Gaithersburg, MD, USA.
- Feys, D., Cepuritis, R., Jacobsen, S., Lesage, K., Secrieru, E. and Yahia, A. (2017), "Measuring rheological properties of cement paste. Most common techniques, procedures and challenges", *RILEM Tech. Lett.*, **2**, 129-135.
- Han, C.G., Lee, G.C. and Heo, Y.S. (2006), "A comparison study between evaluation method on the rheological properties of cement paste", *J. Korea Inst. Build. Constr.*, **21**, 75-82. <https://doi.org/10.5345/JKIC.2006.6.3.075>.
- Hwang, H.J., Lee, S.H. and Lee, W.J. (2007), "Effect of particle size distribution of binder on the rheological properties of slag cement pastes", *J. Korea Ceram. Soc.*, **44**, 6-11. <https://doi.org/10.4191/KCERS.2007.44.1.006>.
- Hwang, S.Y., Lee, H.K. and Kang, B.H. (1998), "A study on the applicability of high-workable concrete in field", *J. Korea Soc. Civil Eng.*, **14**, 71-78.
- Jang, K.P., Kime, W.H., Choi, M.S. and Kwon, S.H. (2018), "A new method to estimate rheological properties of lubricating layer for prediction of concrete pumping", *Adv. Concrete Constr.*, **6**(3), 465-483. <https://doi.org/10.12989/acc.2018.6.5.465>.
- Kasai, T. (1996), "Effect of temperature on rheological property of fresh cement paste in high flowing concrete", *Soc. Mater. Sci.*, **45**(2), 230-234.
- Khandavalli, S. and Rothstein, J.P. (2014), "Extensional rheology of shear-thickening fumed silica nano-particles dispersed in an aqueous polyethylene oxide solution", *J. Rheol.*, **58**, 411-431. <https://doi.org/10.1122/1.4864620>.
- Kolani, B., Lacarriere, L.B., Sellier, A., Escadeillas, G., Boutillon, L. and Linger, L. (2012), "Hydration of slag-blended cements", *Cement Concrete Compos.*, **34**, 1009-1018. <https://doi.org/10.1016/j.cemconcomp.2012.05.007>.
- Kourounis, S., Tsivilis, S., Tsakiridis, P.E., Papadimitriou, G.D. and Tsiabouki, Z. (2007), "Properties and hydration of blended cements with steel making slag", *Cement Concrete Res.*, **37**, 815-822. <https://doi.org/10.1016/j.cemconres.2007.03.008>.
- Kulasegarm, S., Karihaloo, B.L. and Ghanbari, A. (2011), "Modeling the flow of self-compacting concrete", *Int. J. Numer. Anal. Meth. Geomech.*, **35**, 713-723. <https://doi.org/10.1002/nag.924>.
- Lee, D.K. and Choi, M.S. (2018), "Standard reference materials for cement paste, Part I: suggestion of constituent materials based on rheological analysis", *J. Mater.*, **11**(4), 1-12. <https://doi.org/10.3390/ma11040624>.
- Lee, D.K. and Choi, M.S. (2018), "Standard reference materials for cement paste, Part II: determination of mixing ratios", *J. Mater.*, **11**(5), 1-12. <https://doi.org/10.3390/ma11050861>.
- Lee, D.K. and Choi, M.S. (2018), "Standard reference materials for cement paste, Part III: analysis of the flow characteristics for the developed standard reference material according to temperature change", *J. Mater.*, **11**(10), 2001. <https://doi.org/10.3390/ma11102001>.
- Lee, D.K., Lee, K.W. and Choi, M.S. (2018), "Study on filling capacity of self-consolidating concrete for modular lng storage tank", *J. Korean Soc. Saf.*, **33**(6), 50-57. <https://doi.org/10.14346/JKOSOS.2018.33.6.50>.
- Lee, D.K., Lee, K.W., Park, G.J., Kim, S.W., Park, J.J., Kim, Y.J. and Choi, M.S. (2018), "Guideline for filling performance of concrete for modular LNG storage tanks", *J. Korean Soc. Saf.*, **33**(2), 86-93. <https://doi.org/10.14346/JKOSOS.2018.33.2.86>.
- Lee, K.W., Lee, H.J. and Choi, M.S. (2019), "Evaluation of 3D concrete printing performance from a rheological perspective", *Adv. Concrete Constr.*, **8**(2), 155-163. <https://doi.org/10.12989/acc.2019.8.2.155>.
- Nehdi, M., Mindess, S. and Aitcin, P.C. (1998), "Rheology of high

- performance concrete: Effect of ultrafine particles”, *Cement Concrete Res.*, **28**, 687-697. [https://doi.org/10.1016/S0008-8846\(98\)00022-2](https://doi.org/10.1016/S0008-8846(98)00022-2).
- Petit, J.Y., Wirquin, E. and Khayat, K.H. (2010), “Effect of temperature on the rheology of flowable mortars”, *Cement Concrete Compos.*, **32**(1), 43-53. <https://doi.org/10.1016/j.cemconcomp.2009.10.003>.
- Poslinski, A.J., Ryan, M.E., Gupta, R.K., Seshadri, S.G. and Frechette, F.J. (1988), “Rheological behavior of filled polymeric systems I. Yield stress and shear-thinning effects”, *J. Rheol.*, **32**(7), 703-735. <https://doi.org/10.1122/1.549987>.
- Rößler, C., Eberhardt, A., Kučerová, H. and Möser, B. (2008), “Influence of hydration on the fluidity of normal Portland cements pastes”, *Cement Concrete Res.*, **38**(7), 897-906. <https://doi.org/10.1016/j.cemconres.2008.03.003>.
- Roussel, N. (2007), “Rheology of fresh concrete: from measurements to predictions of casting processes”, *Mater. Struct.*, **40**(10), 1001-1012. <https://doi.org/10.1617/s11527-007-9313-2>.
- Roussel, N., Lemaître, A., Flatt, R.J. and Coussot, P. (2010), “Steady state flow of cement suspensions. A micro mechanical state of the art”, *Cement Concrete Res.*, **40**, 77-84. <https://doi.org/10.1016/j.cemconres.2009.08.026>.
- Struble, L.J. and Lei, W.G. (1995), “Rheological changes associated with setting of cement paste”, *Adv. Cement Bas. Mater.*, **2**(6), 224-230. [https://doi.org/10.1016/1065-7355\(95\)90041-1](https://doi.org/10.1016/1065-7355(95)90041-1).
- Swindells, J.F., Hardy, R.C. and Cottingham, R.L. (1954), “Precise measurement with Bingham viscometers and cannon master viscometers”, *J. Res. Nat. Bureau Stand.*, **52**, 105-115.
- Tattersall, G.H. and Banfill, P.F. (1983), *The Rheology of Fresh Concrete*, Pitman, London, UK.
- Uchikawa, H., Ogawa, K. and Uchida, S. (1985), “Influence of character of clinker on the early hydration process and rheological property of cement paste”, *Cement Concrete Res.*, **15**, 561-572. [https://doi.org/10.1016/0008-8846\(85\)90053-5](https://doi.org/10.1016/0008-8846(85)90053-5).
- Wallevik, J.E. (2009), “Rheological properties of cement paste: Thixotropic behavior and structural breakdown”, *Cement Concrete Res.*, **39**, 14-29. <https://doi.org/10.1016/j.cemconres.2008.10.001>.
- Wu, D., Fall, M. and Cai, S. (2013), “Coupling temperature, cement hydration and rheological behavior of fresh cemented paste backfill”, *Miner. Eng.*, **42**, 76-87. <https://doi.org/10.1016/j.mineng.2012.11.011>.