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Short Communication

Effect of Superplasticizer Concentration on Cement Hydration at Low Water to Cement Ratios: Electrochemical Impedance Spectroscopy Study

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The hydration behavior and the fluidity of cementitious mortar samples with water to cement ration of less than 0.2 were studied. Polycarboxylate ether (PCE) superplasticizers in different dosages were used to investigate the hydration process of fresh cementitious mortar. In this procedure, the measurement of fluidity was carried out based on Mini cone method. The results indicate that superplasticizers have significant impact on the hydration behavior. Charge transferring resistance (R_{ctr}) factor was measured by the Nyquist curve that varies with increasing concentration of PCE superplasticizer from 0.6% to 1.5%, indicating PCE superplasticizer actually has a significant impact on adhesion transferability and more influences the body of new cementitious matrix. The R_{ctr} factor indicated a close relationship with the fluidity of cementitious matrix which is demonstrated by a small cone test, as well. With increasing value of superplasticizer in the matrix, the dryness in the cementitious matrix decreases more steeply.

Keywords: Polycarboxylate ether superplasticizers; Hydration behavior; Fluidity of cementitious mortar; Electrochemical impedance spectroscopy

1. INTRODUCTION

The most prevalent material in construction is cement. The cementitious matrix is the basics of the composition of mortar and concrete. Thus, the fluidity characteristics of cement matrix is in high level of importance since the quality of the concrete products are based upon that [1].

The emergence of chemical reactions happens when cement is mixed with water. Different phases of reactions happen when the cement is mixed with water. Hydrolysis and hydration processes are two of the most important among these reactions [2]. Different characteristics of hydration reaction such as thermodynamic, kinetic and structural factors lead to the formation of hydrates which are the basics of hydration process as a chemical procedure [3, 7]. Set the time to transfer the dough from soft to hard. Changing the physical phase of water and concentration of ion in water measurements resulting in the alteration of electrical conductivity in cementitious matrix. Which is determined by many measurement techniques [8-11].

Today, a wide range of non-destructive techniques (NDT) is available for monitoring health and assessing the conditions for the construction of concrete structures, due to reinforced corrosion as the main issue [12]. NDT methods are categorized into 2 different categories which are electrochemical and non-electrochemical procedures. Electrochemical impedance spectroscopy (EIS) is known as NDT method [13, 14].

The hydration process and its responsive behavior of the new cementitious matrix is very significant due to its impact on compatibility, performance and cement setting characteristics. Knowing the way to assess the hydration behavior of new cementitious mortar is of great importance in order to measure the financial efficiency of concrete and the various methods of mixing and forming. The hydration process and behavior of cementitious matrix in water to cement ratio of 0.2 is studied in this paper using electrical impedance spectroscopy (EIS) technique. The fluidity of cementitious matrix is investigated using mini cone method, as well. The aim of the study is to investigate the effect of water reducing component (superplasticizer) in different dosage on the hydration behavior of cementitious matrix.

2. MATERIALS AND METHODS

The materials used in this study included Portland cement and the polycarboxylate ether (PCE) polymer as the super plasticizer which works for reducing water content (produced by Handy Chemical Dysal). The composition and chemical characteristics of Portland cement and Properties of PCE superplasticizer are shown in Table 1 and 2, respectively.

Table 1. Chemical composition of Portland cement

Compositions	Contents (wt%)
CaO	64.7
SiO_2	22.6
Al_2O_3	3.9
Fe_2O_3	2.3
MgO	1.8
SO_3	3.8
Blaine (m^2/kg)	371
LoI	2.1

Table 2. Properties of PCE superplasticizer

Phase	Liquid
pH	6.2
Color	Yellowish
Density	1.116
Mass average molecular weight	50000

In the present study, the water to cement ratio was set at 0.2. The concentration of PCE superplasticizer were set at 0.6%, 0.9%, 1.2% and 1.5% of cement mass. The hydration behavior and fluidity characteristics of the cement matrix were examined according to these dosages. In this paper, the dosages from 0.6% to 1.5% are called S1, S2, S3 and S4, respectively. The fluidity was examined using the mini cone technique to investigate the fluidity of the cementitious matric which was based on the standard ASTM C-143. The dimension of the mini cone is illustrated in Fig. 1.

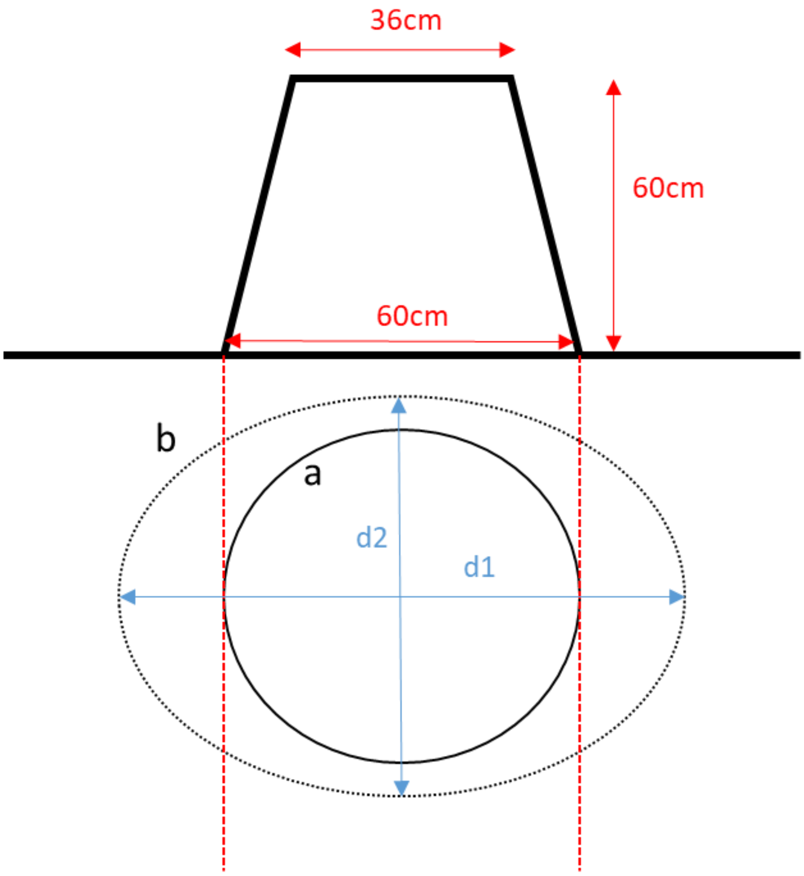

Figure 1. Used mini cone test for the spread measurement of fresh mixture

The dimension of the mini cone in top and bottom are 36mm and 60mm with the height of 60mm. The short conical mold is put on a plate made of glass and the mold is filled with fresh cementitious matrix. The diameter of fresh cementitious sample is the calculation of the mean of d1 and d2 in fig. 1.

Additionally, for every cementitious matrix, measurements were carried out on 0.5 hour, 1 hour, 1.5 hours and 2 hours after the start of the process. The timing in the mixing of cement and water was calculated.

The viscosity of all cementitious matrixes in different dosage of the super plasticizer was used to define and justify the friction of cementitious matrix and resistance of flow in fresh matrix.

These experiments were executed under rotor speed control with cylinder spindle of 60 rpm.

The prepared matrix is immediately place in the grout mold after mix. The whole procedure was 1 minute which was less than the first setting time. The approximate cutting rate was the same while the apparent viscosity was collected in a constant rotor speed. Thus, the results for the viscosity were contemplated for comparison.

The progress of structure in cementitious matrix considering the hydration behavior is investigated using electrochemical impedance spectroscopy (EIS). A two-point electrode method was used to measure the electrochemical impedance. Electrodes are made in a way to be resistant to high alkaline environment. In this paper, in order to put the resistance of weak contact between electrodes and sample surfaces at the lowest level, the electrodes were placed directly facing the fresh cementitious matrix.

3. RESULTS AND DISCUSSION

The raise in fluidity by changing the dosage of super plasticizer from 0.6% to 1.5% is similar to the studies in previous works [15, 16].

For example, the S1 fluidity in the first 60 minutes was 75 mm, which was larger than the lower diameter of the mini cone used in the test, showing the weakness of the S1 fluidity. Although, the dose of super plasticizer increased to 0.9%, 1.2% and 1.5%, the fluidity was 180 mm, 220 mm, 280 mm, respectively which were 140%, 193%, 273% risen from the S1 fluidity level, reaching its highest value in S1, S2, S3 and S4 in the first 60 minutes. When the time of adjustment takes place, the fluidity of the new mixes is reduced to varying degrees. When the measurement time was 120 minutes, the fluidity S1, S2, S3, S4 were 65 mm, 125 mm, 160 mm, and 245 mm, respectively.

It has been pointed out in this article that when the dosage of PCE superplasticizer is more than 1.5%, the water-drop phenomenon will be clear. Therefore, super plasticizer dose optimization is fixed at 1.5% of the cement mass weight.

The values of slump loss for different samples are shown in Figure 2. Figure 2 indicates slump against time elapse for different concentrations of superplasticizer. The fluidity decreases with time because the continuous hydration process generate calcium silicate hydrate (CaH_2O_4Si) to fill the pores between the cement particles and aggregate [17]. Consequently, the concrete setting will decrease the fluidity of concrete, therefore, decrease the slump too. Once observation is completed on the superplasticizer content, increase in the chemical admixture concentration will slow down the rate of concrete setting. Given that the superplasticizer will aid to retain concrete in the state of liquid for a longer time, therefore, reduce the slump loss throughout the concrete transportation to the site. However, overdose of the additives leads to high slump loss, which will not give real slump.

Furthermore, comparisons between the superplasticizer and normal concrete indicate that the setting time for the conventional concrete is shorter than the superplasticizer concrete. As a result, superplasticizer is more efficient and effective in maintaining the slump of the concrete.

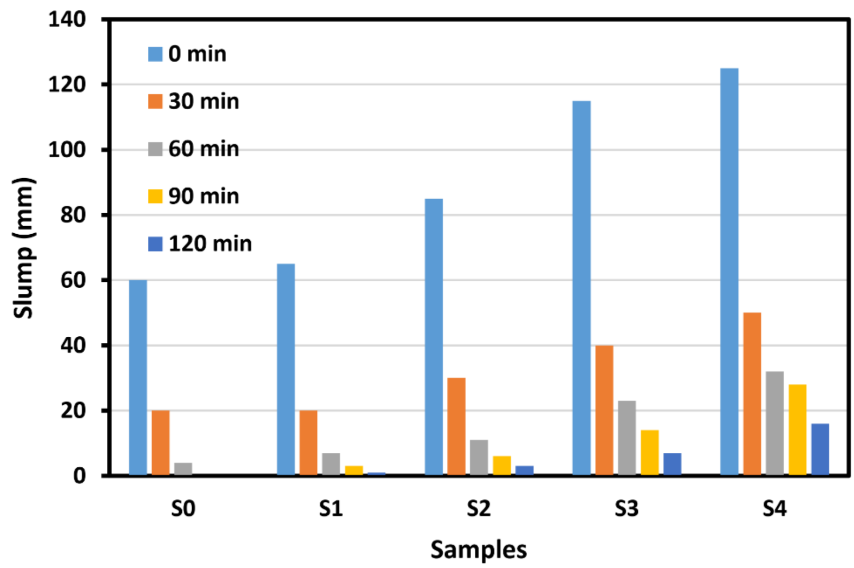

Figure 2. The values of slump loss for different dosages of superplasticizer at various setting time

To determine the greater resistance in cementitious matrix to super plasticizer, the viscosity factor was measured. Viscosity outputs are shown as a function of time set in Figure 3.

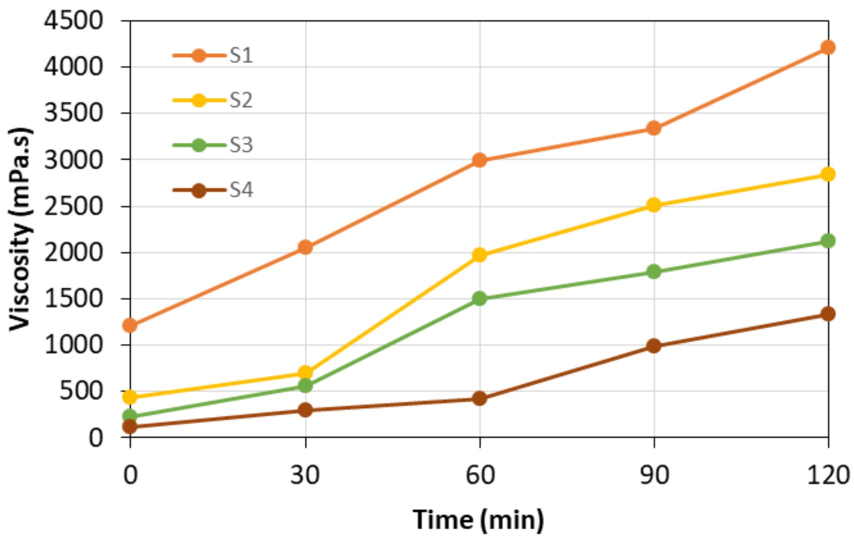

Figure 3. The viscosy as a function of setting time at different dosages of PCE superplasticizer

In different dosages of PCE superplasticizer in the cementitious matrix, the viscosity raise in the time setting function.

While the dosages of PCE superplasticizer increase from 0.6% to 1.5%, the viscosity decrease. Considering Figure 2, viscosity index is relatively reversed to the fluidity index which presents great accordance to results in previous studies [18, 19].

From the electrochemical point of view, an electrochemical medium experimentally consists of electrodes and electrolytes. Electrolytes plays the role of the solvent. The current discussed model is considered to evaluate the electrochemical impedance in cementitious mortar [20, 21]. In figure 4 an equivalent circuit system is presented for the cementitious mortar.

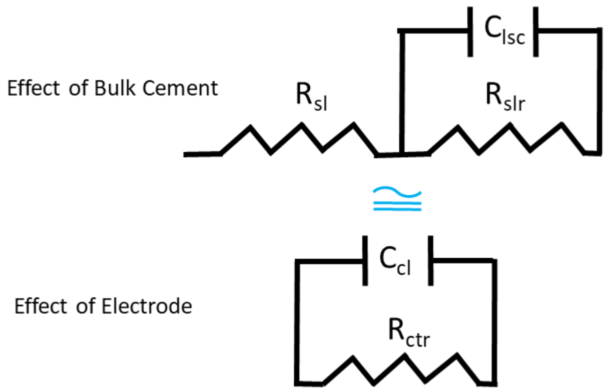

Figure 4. Circuit equalization of system in cementitious mortar

As shown in Fig. 4, R_{sl} represents the total volume of solid and liquid in the medium, R_{slr} represents resistance of solid and liquid components, C_{lsc} represents the relationship between liquid-solid capacity, C_{cl} matches to the capacitance of double layer or the electrode-cement system and R_{ctr} represents the charge transferring resistance [22,23].

Figure 5 shows the electrochemical impedance evaluation in different dosages of PCE superplasticizer. The curves in figure 4 imply that the cementitious matrix with different dosages of PCE superplasticizer have the dynamic behavior and emission control in a wide range of frequency from 0.015 to 12000 Hz. The conversion from the conventional to new cementitious system is difficult to take place in the first two hours. The emission control is the prevalent phenomenon happening to S1 in low frequency. Thus, the Nyquist curve of S1 proves that fluidity structure in S1 is different from other mortars. The parameter R_{sl} is an indicator of electrolyte resistance in the cementitious matrix and does not show significant change. Thus, it is concluded that no resistance is happening in the electrolyte solution. While the dosages of PCE superplasticizer rises from 0.6% to 1.5% the location of impedance which is a result of charge transfer varies widely.

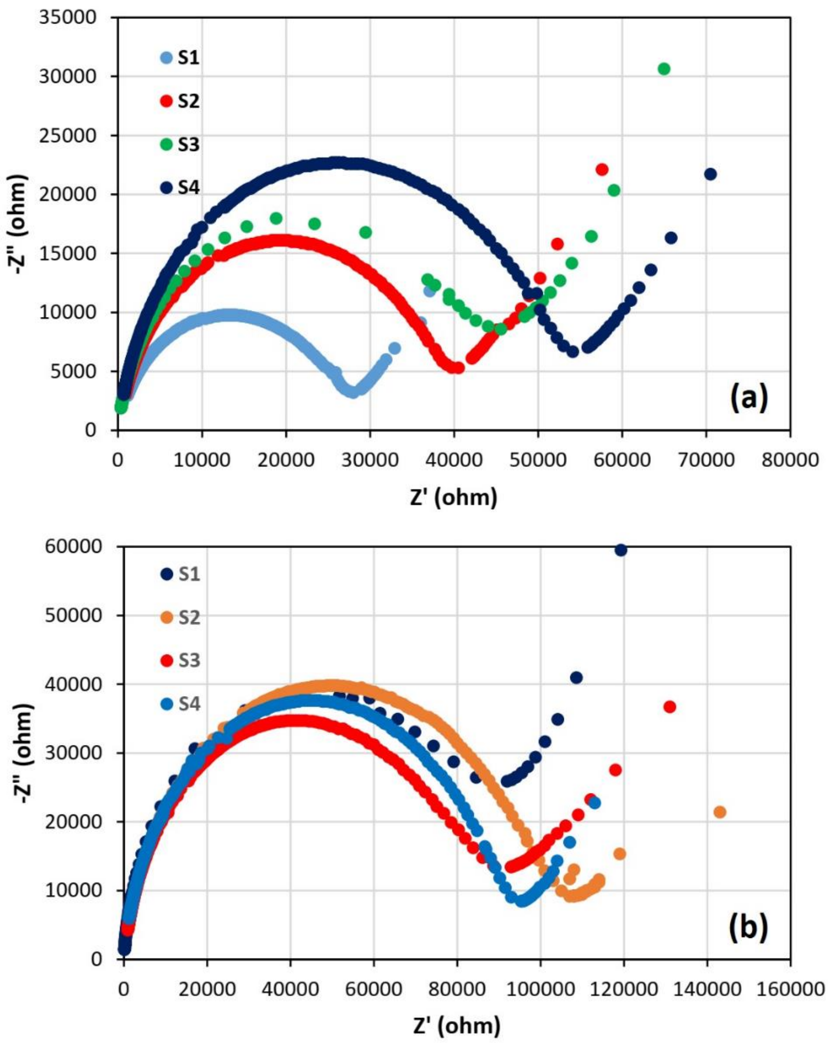

Figure 5. Nyquist curve for the different cement sample in time interval of (a) 60 minutes and (b) 120 minutes

The increase in R_{ctr} is higher than the dosages of superplasticizer. The Nyquist curve tends to be similar to the dosages of superplasticizer in cement mortar. Based on figure 5, the S1 results differs more significantly. R_{ct} changes while the dosage of PCE superplasticizer changes and increase from 0.6% to 1.5% in the time interval of 60 minutes and 120 minutes. For the different values of S2, S3, the R_{ct} value is almost the same or slightly increases. Comparing R_{ct} with its respective dosage of S4, it is concluded that the R_{ct} value is smaller which indicates that the S4 has an improved behavior in transfer ability. The results show the fact that the dosages of PCE superplasticizer impacts the ability to transfer the load significantly and also represents more structured influence on new cementitious matrix.

The fitted data of the parameters in the equivalent circuit model are listed in Table 3 and Table 4, respectively. As shown in table 3, the value of R_{sl} increases with the dosages of PCE superplasticizer, which indicates that the thickness of the formed protective film on the concrete increases with the concentration of PCE superplasticizer [24].

Table 3. Electrochemical parameters from the fitting using the equivalent circuit in Figure 3 in time interval of 60 minutes

Samples	R_s (Ω cm^2)	C_{ls} (μF cm^{-2})	R_{sl} (Ω cm^2)	C_{cl} (μF cm^{-2})	R_{ct} (Ω cm^2)
S1	50.9	58.2	27980	189.4	10750
S2	40.2	39.4	42755	68.2	25280
S3	65.4	47.6	47635	164.7	34905
S4	58.7	54.8	56450	98.6	38640

Table 4. Electrochemical parameters from the fitting using the equivalent circuit in Figure 3 in time interval of 120 minutes

Samples	R_s (Ω cm^2)	C_{ls} (μF cm^{-2})	R_{sl} (kΩ cm^2)	C_{cl} (μF cm^{-2})	R_{ct} (kΩ cm^2)
S1	90.8	47.6	102.2	223.6	69.8
S2	88.4	43.3	109.9	86.9	64.5
S3	72.9	55.4	94.6	94.3	58.7
S4	78.6	46.7	91.5	180.7	56.3

Furthermore, the value of Rct dramatically increases with the dosages of the PCE superplasticizer, which reveals that the corrosion process is clearly retarded [25]. Table 4 shows a slightly decreasing trend for Rct from 69.8 to 56.3 with the PCE superplasticizer content changing from 0.6% to 1.5% which indicates the breakdown of passive film.

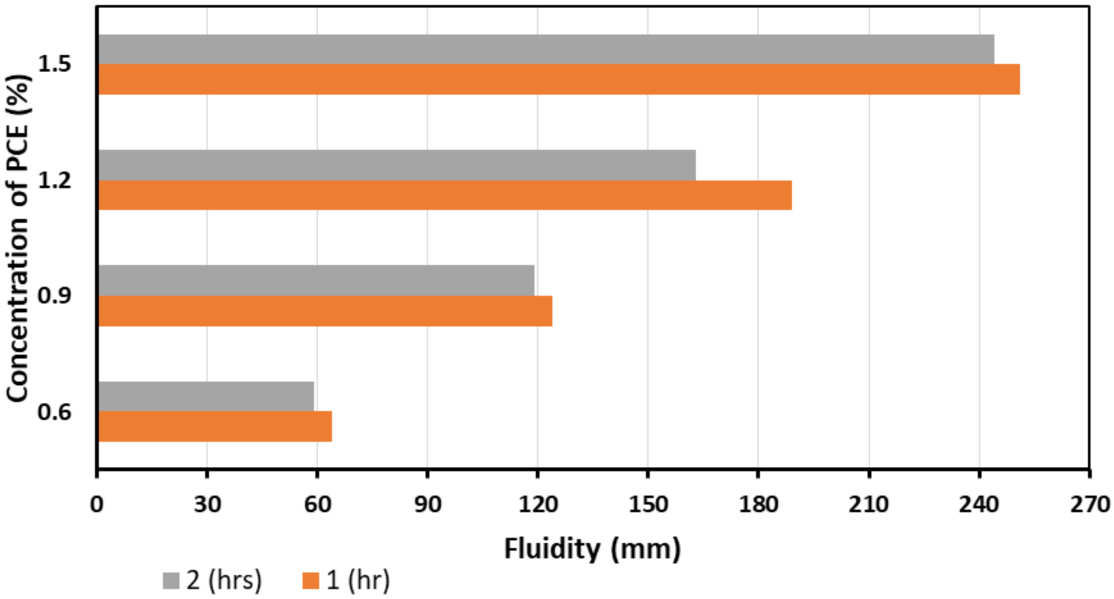

Figure 6. Analysis of fluidity for cement samples in different time intervals

In addition, fresh cementitious mortar was measured for the fluidity response by using mini cone which is presented in Fig. 6. R_{ct} index is used and derived from Nyquist curve in the electrochemical impedance method [26]. If the fluid is reduced by changing the measuring time from 60 minutes to 120 minutes, the R_{ct} impedance of the charge transfer process should be oscillating. In other case, if the fluid has a constant or uniform variation the R_{ct} in the first two 2 hours is lower than the its changing value in the 1^{st} hour. Thus, it is concluded that R_{ct} variation has a meaningful relationship with the changing dosages of PCE superplasticizer and is more likely to affect the evolving structure of new cement paste that is being investigated in future studies.

4. CONCLUSION

The electrochemical impedance method was used to investigate the effect of different mass weight of PCE superplasticizer on the cementitious mortar samples. The fluidity of the samples had been investigated as well. When the dosage of PCE superplasticizer varies from 0.6% to 1.5%, the fluidity increases. Thus, there is a vivid relationship between fluidity and mass weight of superplasticizer. The fluidity of the samples with different dosage of superplasticizer varies over the time. Another phenomenon which affects the cementitious mortar is the dynamics of super plasticizer and the distribution within the matrix because of the altering fluidity of the resultant mixture. R_{ctr} index increases greatly while the dosage of super plasticizer raises from 0.6% to 1.5% in the first 60 minutes which is a representative of increasing in loading strength. The test time interval increases from 60 minutes to 120 minutes and the R_{ctr} value decreases in S4 grade. Thus, the transport ability is enhanced in S4. R_{ctr} index which is derived from the Niquist curve is collected using mini cone test in electrochemical impedance method. The prolongation is affected by the fluidity. R_{ctr} value is lesser in 120 minutes than 60 minutes if fluidity does not change because of prolongation. The R_{ctr} is in highest value if the fluidity sets to be unchanged while we are in the time interval of 60-120 minutes.

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References

1. D. Feys, R. Cepuritis, S. Jacobsen, K. Lesage, E. Secrieru and A. Yahia, *RILEM technical letters*, 2 (2018) 129.
2. J.W. Bullard, H.M. Jennings, R.A. Livingston, A. Nonat, G.W. Scherer, J.S. Schweitzer, K.L. Scrivener and J.J. Thomas, *Cement and concrete research*, 41 (2011) 1208.
3. C. Fan and S.A. Miller, Construction and Building Materials, 167 (2018) 918.
4. H. Chen, S.Q.Zhang, Z.X.Zhao,M. Liu, Q. R. Zhang, Process in Chemsitry,31(2019)571.
5. S.F. Tang, N. Li, D.L. Yuan, J. C. Tang, Xue. Li, C, Zhang, Y.D. Rao, Chemosphere, 324（2019）658.
6. P.H. Shao, J.Y.Tian, F. Yang, X. G. Duan, S.S. Gao, W.X.Shi, X. B. Luo,F.Y.Cui, S.L.Luo,S.B.Wang, Advanced functional materials,28(2018)1705295.

7. J. Rouhi, C.R. Ooi, S. Mahmud and M.R. Mahmood, Materials Letters, 147 (2015) 34.
8. L. Czarnecki, P. Woyciechowski and G. Adamczewski, KSCE Journal of Civil Engineering, 22 (2018) 755.
9. Y. Lu, J. Zhang and Z. Li, *Construction and Building Materials*, 46 (2013) 183.
10. X.Y. He, F. Deng, T.T. Shen, L.M.Yang, D.Z.Chen, J.F.Luo, X.B.Luo, X.Y.Min,F.Wang, *Journal Of Colloid And Interface Science*, 539(2019)223.
11. M. Wyrzykowski, K. Scrivener and P. Lura, *Cement and Concrete Research*, 116 (2019) 191.
12. Wong, W.W. Lai, J.F. Sham and C.-s. Poon, *NDT & E International*, 107 (2019) 102123.
13. F. Husairi, J. Rouhi, K. Eswar, A. Zainurul, M. Rusop and S. Abdullah, *Applied Physics A*, 116 (2014) 2119.
14. G. Monrrabal, B. Ramírez-Barat, A. Bautista, F. Velasco and E. Cano, *Metals*, 8 (2018) 500.
15. J.-Y. Petit and E. Wirquin, *Cement and Concrete Research*, 40 (2010) 235.
16. L. Yang, E. Yilmaz, J. Li, H. Liu and H. Jiang, *Construction and Building Materials*, 187 (2018) 290.
17. E. L'Hôpital, B. Lothenbach, D. Kulik and K. Scrivener, *Cement and Concrete Research*, 85 (2016) 111.
18. J.J. Assaad, *Construction and Building Materials*, 77 (2015) 74.
19. M. Sonebi, M. Lachemi and K. Hossain, *Construction and Building Materials*, 38 (2013) 126.
20. C. Scuderi, T.O. Mason and H. Jennings, *Journal of materials science*, 26 (1991) 349.
21. G. Song, *Cement and concrete research*, 30 (2000) 1723.
22. M. Husairi, J. Rouhi, K. Alvin, Z. Atikah, M. Rusop and S. Abdullah, *Semiconductor Science and Technology*, 29 (2014) 075015.
23. N. Naderi, M. Hashim, K. Saron and J. Rouhi, *Semiconductor Science and Technology*, 28 (2013) 025011.
24. T. Ji, F. Ma, D. Liu, X. Zhang, X. Zhang and Q. Luo, *International Journal of Electrochemical Science*, 13 (2018) 5440.
25. F.E.-T. Heakal and A.E. Elkholy, *Journal of Molecular Liquids*, 230 (2017) 395.
26. P. Han, P. Han, Y. Yan and X. Bai, *International Journal of Electrochemical Science*, 13 (2018) 10548.