The influence of chosen factors on the rheological properties of cement paste

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Abstract

Rheological investigations were conducted into cement paste made of various cement types (CEM I 42.5 R, CEM II/B-S 42.5 R, CEM III/A 32.5 N LH/HSR/NA), with and without superplasticizer. The tests were performed at 15°C, 20°C and 25°C, for one hour. Rheological parameters (yield value and plastic viscosity) were designated according to the Bingham model. The influences of hydration time, the presence of superplasticizer and of temperature on the occurrence of the thixotropy phenomenon in cement paste were identified. The thixotropy was analysed by measuring hysteresis loops surfaces using a numerical integral method.

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Keywords: cement paste; rheological; superplasticizer; thixotropy

1. Introduction

Due to the size of cement grains, cement pastes should be included in dispersion systems. Research into the rheological properties of cement pastes shows that these properties depend on many factors, including water cement ratio (w/c), the specific surface area of the cement, grain composition of the cement, mineral composition, conditions and methods of measurement, and also the presence of chemical admixtures and mineral additives

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The rheological properties of cement pastes in the initial stage of hydration depend on the type and quantity of products produced from the hydration of C₃A and C₃S. The complexity of the cement-water system causes great difficulty in the interpretation of rheological research results. This is mainly due to the non-Newtonian characteristics of cement pastes and changes in the phase composition of cement pastes during the hydration process progress. These factors mean that the results of rheological measurement are dependent on the method of conducting the experiment, i.e. the methods used for sample preparation, the intensity and time of mixing, conditions of shear etc. [4,5,6].

Cement pastes can exhibit different rheological properties, such as the Newtonian fluids, pseudoplastic, plastic and dilatant fluids. The flow curves of cement pastes may be reversible or may exhibit hysteresis (being thixotropic or anti-thixotropic). The presence of thixotropy and antithixotropy, during the shear stress of cement suspension, indicates the strong influence of time in shaping the rheological properties of cement pastes [7].

Quantitative measurement of thixotropy is not an easy task, because material exhibiting thixotropic properties is sensitive to shear rate gradient changes and the rheological history of the sample.

Many methods for the research of fluids with thixotropic properties are described in the literature, among them the “area of hysteresis” [8,9]. None of the methods demonstrate a clear rheological characteristics of these fluids. One method for thixotropic fluid is that proposed by Kemblowski and Petera, based on the determination of equilibrium flow curves, which gives results independent of the method of conducting the experiment [10].

This paper presents the rheological research results of cement pastes with and without the addition of superplasticizer in different temperatures. The analysis paid particular attention to the thixotropy of cement suspensions. Quantitative measurements of thixotropy were made by measuring the surface area of the hysteresis loop of flow curves. Future research plans involve applying the method recommended by Kemblowski and Petera.

**Nomenclature**

| Symbol | Description |
|--------|-------------|
| τ₀     | yield stress (Pa) |
| η      | plastic viscosity (Pa·s) |
| S      | surface area of hysteresis loop (Pa/s) |

**2. Materials**

The experimental investigation was carried out on various cement pastes prepared from different types of cements: CEM I 42.5 R (CEM I), CEM II/B-S 42.5 R (CEM II) and CEM III/A 32.5 N LH/HSR/NA (CEM III). The chemical composition of cements is described in Table 1. The specific surface area (Blaine) of CEM I is 379 m²/kg, CEM II - 417 m²/kg and CEM III - 419 m²/kg.

| Cement | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Cl⁻ | Na₂O_eq | SO₃ |
|--------|------|-------|-------|-----|-----|-----|---------|-----|
| CEM I  | 17.9 | 5.8   | 2.9   | 63.1| 1.2 | 0.01| 0.7     | 2.1 |
| CEM II | 22.2 | 6.2   | 2.6   | 59.6| 2.4 | 0.02| 0.8     | 2.6 |
| CEM III| 30.2 | 7.7   | 1.6   | 50.1| 5.7 | 0.02| 0.7     | 2.0 |
| Clinker| 20.2 | 6.5   | 3.4   | 65.0| 1.5 | 0.01| 0.7     | 0.7 |

Table 1. Chemical composition of cement and the corresponding clinker.
Polycarboxylate superplasticizer (SP), was used as a 30% water solution. The chemical admixture was added 1% by cement mass. Measurements of cement pastes were performed for a water/cement ratio of 0.4 for cement paste without SP and of 0.27 with SP.

3. Methods

The measurement of the rheological parameters of the cement pastes were carried out using a rotational viscometer with co-axial cylinders, Haake Mars III type. The same procedure for the preparation samples for measurements and the same measurement conditions were maintained. During preparation and when conducting tests the temperature in the laboratory was kept at 20±2°C. After hand-stirring the mixing cement with water (3 min), the sample was immediately loaded into the cylinder for testing. The shear rate was increased and decreased in a range from 0 to 150 s⁻¹ in 6 minutes. The results of the tests were presented as a flow curves. The measurements were performed at temperatures of 15°C, 20°C and 25°C, after 10, 30 and 60 minutes. Yield stress and plastic viscosity was calculated using the Bingham model. The area of the hysteresis loop of flow curves was calculated using a numerical integral method (trapezoidal rule).

4. Results and discussion

The flow curves of cement pastes with and without SP are shown in Figure 1. The yield stress, plastic viscosity and area of the hysteresis loop of cement pastes CEM I, CEM II and CEM III with and without SP at various temperatures are presented in Tables 2 - 7.

Table 2. Yield stress (τ₀), plastic viscosity (η) and area of hysteresis loop (S) for cement paste CEM I at various temperatures.

| t (min) | 15°C | 20°C | 25°C |
|--------|------|------|------|
|        | τ₀ (Pa) | η (Pa·s) | S (Pa/s) | τ₀ (Pa) | η (Pa·s) | S (Pa/s) | τ₀ (Pa) | η (Pa·s) | S (Pa/s) |
| 10     | 18.6  | 0.14 | lack  | 19.9  | 0.14 | lack  | 22.8  | 0.14 | lack  |
| 30     | 21.8  | 0.16 | 1237  | 20.0  | 0.14 | 1118  | 29.0  | 0.17 | 769   |
| 60     | 22.3  | 0.17 | 1208  | 17.0  | 0.12 | 705   | 31.7  | 0.20 | 960   |

Table 3. Yield stress (τ₀), plastic viscosity (η) and area of hysteresis loop (S) for cement paste CEM II at various temperatures.

| t (min) | 15°C | 20°C | 25°C |
|--------|------|------|------|
|        | τ₀ (Pa) | η (Pa·s) | S (Pa/s) | τ₀ (Pa) | η (Pa·s) | S (Pa/s) | τ₀ (Pa) | η (Pa·s) | S (Pa/s) |
| 10     | 23.2  | 0.12 | lack  | 24.3  | 0.13 | lack  | 21.0  | 0.12 | lack  |
| 30     | 30.2  | 0.17 | 308   | 31.1  | 0.16 | 615   | 23.0  | 0.12 | 641   |
| 60     | 30.7  | 0.17 | 436   | 34.5  | 0.17 | 163   | 23.6  | 0.11 | 426   |

Table 4. Yield stress (τ₀), plastic viscosity (η) and area of hysteresis loop (S) for cement paste CEM III at various temperatures.

| t (min) | 15°C | 20°C | 25°C |
|--------|------|------|------|
|        | τ₀ (Pa) | η (Pa·s) | S (Pa/s) | τ₀ (Pa) | η (Pa·s) | S (Pa/s) | τ₀ (Pa) | η (Pa·s) | S (Pa/s) |
| 10     | 32.2  | 0.21 | 514   | 42.3  | 0.24 | 719   | 35.3  | 0.19 | 309   |
| 30     | 34.5  | 0.22 | 1294  | 44.6  | 0.24 | 1300  | 35.3  | 0.17 | 467   |
| 60     | 36.4  | 0.23 | 1052  | 45.3  | 0.23 | 1319  | 37.3  | 0.20 | 820   |
Fig. 1. The flow curves of the cement paste CEM I with and without SP at temperatures: (a) 15°C, (b) 20°C and (c) 25°C.
Table 5. Plastic viscosity (η) and area of hysteresis loop (S) for cement paste CEM I with SP at various temperatures.

| t (min) | 15ºC | 20ºC | 25ºC |
|---------|------|------|------|
|         | η (Pa·s) | S (Pa/s) | η (Pa·s) | S (Pa/s) | η (Pa·s) | S (Pa/s) |
| 10      | 0.62  | lack  | 0.65  | lack   | 0.54  | lack   |
| 30      | 0.82  | 4384  | 0.82  | 4789   | 0.71  | 3913   |
| 60      | 0.86  | 4886  | 0.88  | 4973   | 0.73  | 4491   |

Table 6. Plastic viscosity (η) and area of hysteresis loop (S) for cement paste CEM II with SP at various temperatures

| t (min) | 15ºC | 20ºC | 25ºC |
|---------|------|------|------|
|         | η (Pa·s) | S (Pa/s) | η (Pa·s) | S (Pa/s) | η (Pa·s) | S (Pa/s) |
| 10      | 0.58  | lack  | 0.45  | lack   | 0.40  | lack   |
| 30      | 0.60  | 2665  | 0.61  | 2719   | 0.57  | 3271   |
| 60      | 0.69  | 2651  | 0.70  | 2950   | 0.64  | 3509   |

Table 7. Plastic viscosity (η) and area of hysteresis loop (S) for cement paste CEM III with SP at various temperatures

| t (min) | 15ºC | 20ºC | 25ºC |
|---------|------|------|------|
|         | η (Pa·s) | S (Pa/s) | η (Pa·s) | S (Pa/s) | η (Pa·s) | S (Pa/s) |
| 10      | 0.75  | lack  | 0.77  | lack   | 0.70  | lack   |
| 30      | 0.77  | 2365  | 0.82  | 2874   | 0.68  | 2642   |
| 60      | 0.77  | 2179  | 0.80  | 3280   | 0.72  | 2411   |

Comparisons of the values for yield stress and plastic viscosity for cement pastes CEM I, CEM II and CEM III, with and without SP at various temperatures is presented in Figure 3 and Figure 4, respectively.

As we can see (Figure 2) yield stress increased over time (from 10 to 60 minutes) and with increasing temperature for CEM I, whereas in the case of cement pastes CEM II and CEM III yield stress decreased at 25ºC.

![Fig. 2. Yield stress after 10, 30 and 60 min at 15ºC, 20ºC and 25ºC for cement pastes: (a) CEM I, (b) CEM II and (c) CEM III.](image)

In general, the plastic viscosity of cement pastes CEM I and CEM II also increased over time (from 10 to 60 min), but cement paste CEM III remained at the same level at each testing temperature. For cement paste CEM II a decrease in plastic viscosity at 25ºC was demonstrated. It was also found that cement paste CEM I in temperature at 20ºC shows lower plastic viscosity than at 15ºC and 25ºC. The highest value of plastic viscosity, at different times and temperatures, was observed for cement paste CEM III.
Fig. 3. Plastic viscosity after 10, 30 and 60 min at 15ºC, 20ºC and 25ºC for cement pastes: (a) CEM I, (b) CEM II and (c) CEM III.

It was demonstrated, that the plastic viscosity of cement pastes CEM I, CEM II and CEM III with SP increases over time (from 10 to 60 min) and with an increase of temperature from 15ºC to 20ºC. An increase temperature to 25ºC results in a decrease of plastic viscosity in the investigated cement pastes with different cements (Figure 4). All cement pastes containing SP display Newtonian fluid properties.

Fig. 4. Plastic viscosity after 10, 30 and 60 min at 15ºC, 20ºC and 25ºC for cement pastes with SP: (a) CEM I, (b) CEM II and (c) CEM III.

A comparison of the hysteresis loop surfaces of flow curves obtained in the investigation of cement pastes with and without SP is presented in Figure 5. As we can see, an SP addition to the cement pastes (CEM I, CEM II and CEM III) results in an increase in the hysteresis loop surface in comparison to cement pastes without SP. It should be noted, that there is a difference in w/c 0.27 and 0.4. It could also be the reason for the increased hysteresis loop surface.

The biggest increase in the hysteresis loop surface due to SP addition (almost five-fold), was observed for cement paste CEM I. These cement pastes also have higher hysteresis loop surfaces than in case of cement pastes CEM II and CEM III.
It can be concluded that in cement pastes containing polycarboxylate SP the thixotropy phenomenon is more intensive than in cement pastes without SP. Analysis of the hysteresis loop surface of flowing curves, for cement pastes with SP at different temperatures (Figure 5), shows that with an increase of temperature to 25°C the hysteresis loop surface decreases, and thus thixotropy of cement paste is less intensive.

5. Conclusions

It was thus concluded:

- Generally the yield stress and plastic viscosity of cement pastes CEM I, CEM II, CEM III with and without superplasticizer grow over time (from 10 to 60 min) at measured temperatures: 15°C, 20°C and 25°C.
- The flow curves of cement pastes CEM I, CEM II, CEM III with and without superplasticizer demonstrated thixotropy phenomenon.
- It has been demonstrated, on the basis of hysteresis loop area measurement of flow curves for cement paste, that thixotropy tends to appear to a greater degree in cement pastes with superplasticizer.
- A temperature increase from 20°C to 25°C causes thixotropy drop in cement pastes containing superplasticizer.

References

[1] Wallevik OH, Wallevik JE. Rheology as a tool in concrete science: The use of rheographs and workability boxes. Cement and Concrete Research 2011;1279–1288.
[2] Roussel N, Lemaître A, Flatt R J, Coussot P. Steady state flow of cement suspensions: A micromechanical state of the art. Cement and Concrete Research 2010;77–84.
[3] Janowska-Renkas E. The superplasticizer’s structure and efficiency of its effects on cement paste properties. Warsaw; 2013 (in Polish).
[4] Banfill P. The rheology of fresh cement and concrete - a review. Paper accepted for publication in Proceedings of the 11th International Cement Chemistry Congress, Durban; 2003.
[5] Banfill P. Rheology of fresh cement and concrete. Rheology Reviews 2006;61–130.
[6] Möller PCF, Mewis J, Bonn D. Yield stress and thixotropy: on the difficulty of measuring yield stresses in practice. Soft Matter 2006;2:274-283.
[7] Grzeszczyk S. Rheology of cement pastes. Warsaw; 1999 (in Polish).
[8] Mewis J, Wagner NJ. Thixotropy. Advances in Colloid and Interface Science, 2009;214–227.
[9] Wallevik JE. Rheological properties of cement paste: Thixotropic behavior and structural breakdown. Cement and Concrete Research 2009;14–29.
[10] Kemblowski Z, Petera J. Rheological characterization of thixotropic fluids. Rheological Acta, 1979;18:702–710.