Possibilities of fly ash as responsive additive in magneto-rheology control of cementitious materials

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Abstract

Active rheology control, by means of pre-adding responsive additives and applying a trigger signal, is a potential approach to meet the contradicting requirements of concrete properties in different casting processes. In the present study, the possibilities of fly ash as responsive additive in magneto-rheology control of cementitious materials are examined from the viewpoint of early structural build-up of cement paste. Four different fly ashes with various particle sizes and magnetic properties are utilized. The magnetic properties of fly ash, characterized by saturation magnetization and magnetic fraction, are determined. Results reveal that the cement pastes containing fly ash exhibit apparent rheological response to an external magnetic field. The degree of the response depends on the magnetic properties and physical characteristics of the incorporated fly ash. Under the same volumetric replacement, the saturation magnetization of original fly ash is a useful parameter to describe the magneto-rheological effect of fly ash incorporated cement pastes. In comparison with the magneto-rheological response of cement paste with nano-Fe3O4 particles, the fly ash incorporated cement paste shows a longer period of dominating liquid-like properties. It is concluded that fly ash can be used as a responsive additive to improve the rheology of cement paste by applying magnetic field.

Keywords:
- Cement paste
- Fly ash
- Active rheology control
- Structural build-up
- Magnetic field

1. Introduction

Active rheology control is a ground-breaking approach to satisfy the contradicting requirements of rheological properties during the pumping and casting process for the same concrete mixture [1–3]. It is also beneficial to strike a balance between rheological properties, pumpability, extrudability, and buildability in 3D concrete printing [4–6]. The active rheology control can be achieved by activating an external trigger signal to a cementitious mixture with responsive additives [7,8]. One potential approach is the addition of magnetic particles in combination with applying an external magnetic field. From theoretical and lab-scale points of view, ferromagnetic particles with high magnetic properties such as carbonyl iron particles [9,10] and nano-Fe3O4 particles [11,12] can be used as the magnetizable additives in cementitious materials. Due to the high costs, however, the extensive usage of ferromagnetic particles in engineering applications of cementitious materials is probably not the first option, especially for mortar and concrete. In this case, traditional available mineral additives or waste materials with magnetic properties might provide better alternatives to achieve the magneto-rheology control of cementitious materials.

As the main by-product of coal-fired power plants, fly ash is an aluminosilicate material widely used in cement and concrete with economic, technical and ecological benefits [13–16]. From the viewpoint of element, Si and Al are the main elements of fly ash. Furthermore, fly ash also contains a small amount of Ca, Fe, Na,
Mg and K. From the perspective of chemical composition, fly ash typically consists of large amounts of quartz, mullite and anhydrite, as well as a small amount of hematite, magnetite and maghemite [17,18]. Depending on the nature of the coal source, the iron oxides in fly ash typically range from 2% to 20%. Due to the presence of the ferromagnetic spinel structures, i.e., magnetite and maghemite, fly ash particles are highly magnetic. It is well recognized that the magnetic properties of fly ash (such as magnetic susceptibility and saturation magnetization) show a linear correlation with the content of iron oxides [19–22]. Note that the Fe in the spinel structures could be substituted by Al, Mg, Mn or Ti, resulting in a decrease in the magnetic properties of fly ash [23,24].

Owing to the magnetic properties, fly ash can be separated into non-magnetic and magnetic fractions by passing through an external magnetic field [20,25–27]. Dry and wet separation methods are generally utilized. The dry separation method is less effective than the wet separation method, because of the strong electrostatic attractions between solid particles [20]. The iron content in magnetic fly ashes is significantly higher than that in non-magnetic ones. Kukier et al. [20] pointed out that the iron concentration in magnetic and non-magnetic fly ash particles were 22.3–31.1% and 1.5–4.43%, respectively. Besides, the crystalline structures of fly ash particles with different magnetic properties exhibit distinct differences. It is revealed that both non-magnetic and magnetic fly ash contain quartz and mullite, while obvious peaks of magnetite and hematite can be observed in the XRD patterns of magnetic fly ash [20,22,27]. Furthermore, the peak intensity of magnetite is generally more significant than the hematite peak intensity.

The magnetic properties of fly ash have attracted some attention in cement and concrete materials. Payá et al. [25] found that mortars with magnetic fly ash exhibited similar or lower flowability than those with non-magnetic fractions. Compared to mortars with magnetic fly ash, mortars containing non-magnetic fly ash showed faster compressive strength development due to the greater pozzolanic activity. Presuel-Moreno and Sagués [28] stated that the chemical hydration and carbonation of concrete had less influence on the magnetic response of a given fly ash inside the concrete. Based on the linear relationship between magnetic susceptibility and fly ash volume fraction in concrete, the authors pointed out that the chloride diffusivity of concrete can be determined by using magnetic measurements. Similarly, Gopalakrishnan et al. [29] indicated that the magnetic susceptibility was a good indicator to describe the chemical reactions between water and fly ash in cement paste. Furthermore, Garcés et al. [27] found that both non-magnetic and the magnetic fly ash showed an increased effect on the chloride ingress resistance of mortars, but the non-magnetic fly ash had higher efficiency.

As magnetic fly ash exhibits a response to an external magnetic field, it could be used as a potential responsive additive in the concept of active rheology control of cementitious materials. In the present study, the effect of external magnetic field on the early structural evolution of cement pastes with fly ash is investigated by using small amplitude oscillatory shear (SAOS) technique. Four different fly ashes with various particle sizes and magnetic properties are utilized. The correlations between the magnetorheological effect and the magnetic properties of the incorporated fly ash are established. The heat of hydration of cement pastes with fly ash is measured to qualitatively reveal the possible effect of chemical hydration on the early structural evolution. The magneto-rheological responses of fly ash and nano-Fe₃O₄ particles in cementitious suspension are also compared. This research offers an opportunity for potential active rheology control of cementitious materials with common materials. Note that the origins of magnetic properties of fly ash, which have been clearly investigated by many researchers [20–22,24,30], are beyond the scope of this study.

2. Experimental program

2.1. Materials and sample preparation

CEM I 42.5 N Portland cement (OPC) complying with EN 196–1 [31] is used. Four fly ashes obtained from different power plants, denoted as FA1, FA2, FA3 and FA4 according to the median size D₅₀, are utilized. The chemical composition and physical properties of the used powders are presented in Table 1. The particle size distributions of the cement and fly ashes are shown in Fig. 1. All cement pastes are prepared using de-ionized water.

The water-to-cement mass ratio (w/c) of reference cement paste was 0.35, corresponding to a volume ratio of 1.10. For the binary cement pastes, the replacements of fly ash were 25% and 50% by volume of cement. The mixture proportions of the prepared cement pastes are listed in Table 2. All samples were prepared using a rotational rheometer (MCR 52, Anton Paar) with a helix-shaped rotator. The geometric parameters of the rotator and the mixing procedure are to the same as described in [8,11]. Specifically, the shear rate of the helix rotator was increased from 0 min⁻¹ to 3000 min⁻¹ within 30 s, and then kept mixing at speed of 3000 min⁻¹ for 120 s. This high rotational speed provides a repeatable initial state of paste samples for the same mixture proportion.

2.2. Testing methods

The magnetic fly ashes were separated using a permanent magnet. After preparing a water slurry of fly ash with water-to-fly ash mass ratio of 20, a permanent magnet was placed into the slurry and then stirred vigorously. The magnetic particles that adhered to the magnet were afterwards separated and rinsed with water. This procedure was repeated until no obvious magnetic particles further adhered to the magnet. The magnetic fractions and non-magnetic fractions were dried in an oven with temperature of 40 °C for 72 h, yielding two dried fly ash samples for each one designated as NFAx (non-magnetic part) and MFAx (magnetic part), ready for weighing and analyzing.

The particle morphology of the cement and fly ash was determined by a scanning electron microscopy (SEM) (PHILIPS 505) equipped with energy dispersive X-Ray (EDX) spectroscopy. The magnetic properties of the cement and fly ash were measured by a vibrating sample magnetometer (VSM-550, Dexing Magnet) at room temperature.

A rotational parallel plate rheometer (MCR 102, Anton Paar) with magneto-rheological device (MRD) was used for the magneto-rheological test. The effective diameter of the plate is 20 mm and the gap between the upper and lower plates is fixed at 1 mm. The testing protocol for evaluating the structural build-up of the cement pastes includes pre-shearing, strain-sweep and time-sweep tests, as presented in Table 3. The strain-sweep test is used to evaluate the viscoelastic properties without magnetic field, and meanwhile, determine the linear viscoelastic range (LVER). An external magnetic field with 0 T or 0.5 T was applied at the beginning of the time-sweep test, where the shear strain was fixed at 0.01% (within the LVER) and the frequency was 2 Hz. An additional flow curve test was conducted using fresh samples to evaluate the rheological parameters of cement pastes in the absence of magnetic field. After pre-shearing the sample with a shear rate of 100 s⁻¹ for 30 s, the shear rate linearly decreased from 100 s⁻¹ to 0.1 s⁻¹ within 100 s. The shear stress and shear rate were recorded every second. The rheological tests were repeated three times using fresh samples. During the rheological tests, the temperature of all samples was controlled at 20 ± 0.5 °C.
Cement pastes with w/c of 0.4 and fly ash replacement of 50 wt% were prepared to determine the heat of hydration by using a TAM Air calorimeter. 14 g samples were used for each calorimetric measurement. After hand-mixing homogeneously, the samples were placed into the chamber of the calorimeter immediately. The data started to record about 5 min after the first contact of water with the particles. The temperature of the calorimeter was controlled at 20°C, and all the tests lasted for 72 h.

### 3. Results and discussion

#### 3.1. Physical and chemical properties of fly ashes

The magnetization versus magnetic field strength curves of the cement and original fly ashes obtained from VSM measurement are shown in Fig. 2. The corresponding magnetic parameters are summarized in Table 4. It can be seen that the saturation magnetization of all the particles is achieved at magnetic field strength around 0.2 T. All the fly ashes exhibit higher saturation magnetization compared to the Portland cement particles. This can be attributed to the presence of ferromagnetic structures in the fly ash particles such as magnetite and maghemite [20–22]. The order of the saturation magnetization of the fly ash particles is FA4 < FA2 < FA1 < FA3. The remnant magnetization, which is the magnetization left behind in a material after removal of the magnetic field, and the coercivity defined as the ability of a material withstanding a magnetic field without becoming demagnetized are also recorded. The results show that all the fly ash particles exhibit slightly higher remnant magnetization and coercivity than the Portland cement particles. This indicates that some residual magnetic clusters or structures formed under magnetic field might be present in cementitious suspensions after removal of the magnetic field.

The separated magnetic fraction by mass for every fly ash is presented in Fig. 3. The saturation magnetization of original fly ash is also plotted as a comparison. Generally, fly ash with higher saturation magnetization has higher magnetic fraction. FA3 has the highest saturation magnetization and the largest magnetic fraction, whereas FA2 has saturation magnetization and magnetic fraction comparable to FA4. From the viewpoint of magnetic properties, cement paste with FA3 could possibly have the highest rheological response to an external magnetic field. It should be mentioned that the non-magnetic fraction of the studied fly ashes is significantly higher than the magnetic fraction, indicating that a large amount of fly ash in cement paste shows negligible response to a magnetic field.

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### Table 2

Mixture proportions of the cement pastes (vol.%).

| Mix. | OPC | Water | FA1 | FA2 | FA3 | FA4 |
|------|-----|-------|-----|-----|-----|-----|
| Ref  | 1   | 1.10  | -   | -   | -   | -   |
| 2SFA1| 0.75| 1.10  | 0.25| -   | -   | -   |
| 5SFA1| 0.50| 1.10  | 0.50| -   | -   | -   |
| 2SFA2| 0.75| 1.10  | -   | 0.25| -   | -   |
| 5SFA2| 0.50| 1.10  | -   | 0.50| -   | -   |
| 2SFA3| 0.75| 1.10  | -   | -   | 0.25| -   |
| 5SFA3| 0.50| 1.10  | -   | -   | 0.50| -   |
| 2SFA4| 0.75| 1.10  | -   | -   | -   | 0.25|
| 5SFA4| 0.50| 1.10  | -   | -   | -   | 0.50|
with various sizes, regardless of the magnetic and non-magnetic fraction. This indicates that the magnetic separation procedure has less influences on the shape of fly ash particles, which is consistent with [20,27]. By contrast, both magnetic and non-magnetic fractions of FA4 have irregular shape and porous surface. It seems that more spherical small particles are present in the magnetic fractions of FA4 compared to the non-magnetic fractions. This is in agreement with [30], which shows that the magnetic fractions of fly ash tend to be more spherical. It should be noted that the wet separation has insignificant influence on the particle morphology of FA4 particles, in spite of the high CaO content, as the SEM images of the original FA4 still show irregular shape.

The EDX spectrum of the cement reveals the presence of Ca, O, Si, Fe, Al, S and Mg. However, the amount of Fe is extremely low, which agrees with the chemical composition in Table 1. For the fly ash particles, the Fe element amount in the magnetic fractions is larger than that in the non-magnetic fractions, regardless of the fly ash types, as can be clearly observed from Table 5. It should be mentioned that the EDX spectra taken at different spot areas, at least three areas for each fly ash, are in general agreement with the aforementioned statement. In spite of the semi-quantitative nature of this method, the EDX spectra show good coincidence with the fact that the magnetic fractions of fly ash have higher magnetic properties than that of non-magnetic ones.

### 3.2. Rheological properties of cement pastes without magnetic field

For the sake of simplicity, the influence of fly ash volume fraction is discussed by focusing on the cement pastes with FA1. Cement pastes with 50 vol% fly ash are selected to evaluate the effect of fly ash type on the rheological properties. In the absence of external magnetic field, the strain-sweep curves and flow curves of the cement pastes are presented in Fig. 5 (a) and (b), respectively. It can be seen that the critical strain of the studied fly ash incorporated cement pastes is around 0.01%, regardless of the cementitious compositions. The volumetric replacement of cement by fly ash reduces the storage modulus at LVER, i.e., stiffness, except for the mixture of 50%FA4, which shows comparable storage modulus to the reference cement paste. From Fig. 5 (b), it can be observed that all the cement pastes exhibit shear thinning behavior in the entire shear rate range. The measured shear stresses of the cement pastes differ with the mixture proportions. With increasing volume fraction of FA1, the measured shear stress shows a gradual reduction trend. At the same replacement of 50%, the addition of FA1, FA2 and FA3 reduces the measured shear stress, while the incorporation of FA4 exhibits an opposite behavior. This is in good agreement with the oscillatory strain sweep test results. To understand the influence of fly ash volume and type on the viscoelastic and rheological properties more clearly, the storage modulus at linear viscoelastic region $G'$ (LVER), the elastic limit yield stress $\gamma_{c,ys}$, as calculated by Eq. (1), and the viscosity of the cement pastes at linear low shear rates $\eta_{pl}$ (e.g., $1-5$ s$^{-1}$) are listed in Table 6.

$$\gamma_{c,ys} = \frac{\tau_{c,ys}}{G}$$

where $\tau_{c,ys}$ is the elastic limit yield stress (Pa), $\gamma_c$ is the critical strain (%), and $G$ is the storage modulus at critical strain (Pa).

From the viewpoint of fly ash (FA1) volume fraction, the storage modulus at LVER, elastic limit yield stress and viscosity at linear low shear rates decrease with the increase of fly ash volume fraction. The lower the viscosity, the easier the solid particles can move if an additional small stress is applied. The results are consistent with [32,33], which can be attributed to the dilution effect, ball bearing effect and filling effect of the spherical fly ash particles. Under the same replacement of 50 vol%, the storage modulus at
LVER of the cement pastes gradually decreases with increasing fly ash particle size from the perspectives of FA1, FA2 and FA3. The viscosity also shows similar trend. This is in conformity with [34], which possibly can be attributed to the magnified ball bearing effect of spherical particles as the particle size distribution becomes broader. Despite the highest median particle size of FA4, 50%FA4 shows the highest stiffness and viscosity in the considered four types of fly ashes. This is in good agreement with the measured shear stress in Fig. 5 (b). The influence of fly ash on rheological properties of cement-based materials depends on the particle size, shape, morphology, reactivity, etc. [35]. The high stiffness and viscosity of 50%FA4 are possibly because of the morphology and particle shape of the fly ash. Indeed, FA4 particles are more angular and rougher than other fly ashes, as shown in Fig. 4 (h) and (i). This increases the friction and adhesion between solid particles. Moreover, the porous surface of the fly ash particles increases the water requirement and thus decreases the free water with lubrication effect. As a result, the replacement of cement by FA4 has limited increased effect on the viscoelastic and rheological properties of cement pastes.

**Fig. 4.** Typical SEM images and corresponding EDX spectra of (a) OPC, (b) NFA1, (c) MFA1, (d) NFA2, (e) MFA2, (f) NFA3, (g) MFA3, (h) NFA4, and (i) MFA4, where NFAx is the non-magnetic part and MFAx is the magnetic part. Red spots are the area where EDX spot analysis was taken. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3.3. Structural build-up of cement pastes under magnetic field

3.3.1. Influence of fly ash volume fraction

The influence of fly ash volume fraction on the structural build-up of cement pastes under magnetic field of 0 T and 0.5 T, characterized by the evolutions of storage modulus, loss modulus and phase angle, is presented in Fig. 6. The increase rate of the storage modulus at time scale of 200–300 s ($\Delta\sigma'$) is calculated as an indicator to describe the structural build-up rate of cement paste at steady state. The main magneto-rheological parameters of the

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**Fig. 6 (continued)**

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Cement pastes with various fly ash volume fractions are summarized in Table 7. In the absence of magnetic field, the volumetric replacement of cement with fly ash reduces the intensity and rate of structural build-up of the cement pastes, especially at higher fly ash volume fraction. More specifically, the incorporation of fly ash slightly prolongs the percolation time, possibly due to the increase of interparticle distance contributed by the lower density and finer particle size of the fly ash (FA1) particles compared to cement. The storage modulus at 300 s and the structural build-up rate at steady state are 95 kPa, 83 kPa, 30 kPa and 0.24 kPa/s, 0.21 kPa/s, 0.08 kPa/s for the cement pastes with fly ash volume fraction of 0%, 25% and 50%, respectively. The slowdown of the structural build-up of cement paste with fly ash agrees with [33,36]. This probably can be attributed to the reduced cation precipitations, as reflected by the retardation effect in the hydration process of the cement paste by replacing cement with fly ash, as shown in Fig. 12 (see later).

Under the magnetic field of 0.5 T, the fly ash incorporated cement pastes exhibit obvious rheological responses. The rheological responses of the fly ash incorporated cement pastes to an external magnetic field are generally similar to that of cementitious paste containing nano-Fe₃O₄ particles [37]. Specifically, the loss modulus is higher than the storage modulus and the phase angle is higher than 45° right after applying the magnetic field, indicating the predominance of viscous behavior at that moment. Both the storage modulus and the loss modulus increase with elapsed magnetization time. Meanwhile, the phase angle gradually decreases. This points to a higher increase rate of the storage modulus than the loss modulus, indicating the transition of the cement paste from liquid-like state to semi-solid state. With further increasing magnetization time, the loss modulus reaches a peak and the storage modulus (or phase angle) continuously increases (or decreases). After a sufficiently long period of magnetization, the storage modulus, loss modulus and phase angle arrive at stable state. Interestingly, applying the external magnetic field of 0.5 T shows less influences on the structural build-up rate at steady state, as reflected by the little difference of the increase rate of storage modulus at time scale of 200–300 s between 0 T and 0.5 T (i.e., ΔG'). This to a certain extent indicates that applying an external magnetic field has little influence on the early chemical hydration of cement paste, which is consistent with the results of nano-Fe₃O₄ incorporated cement paste [11].

The obvious rheological response of the cement paste with fly ash to an external magnetic field can be attributed to the magnetic properties of the fly ash particles. As can be observed from Fig. 3, the saturation magnetization of the OPC and FA1 is 0.59 emu/g and 1.74 emu/g, respectively. The magnetic fraction of FA1 is around 11%. In the presence of an external magnetic field, the magnetic fly ash particles are magnetized, and have a tendency to fol-

![Table 5](image1)

Typical EDX spot analysis of cement and fly ash particles (wt.%).

| Element | OPC | NFA1 | NFA2 | NFA3 | MFA1 | MFA2 | MFA3 | MFA4 |
|---------|-----|------|------|------|------|------|------|------|
| Ca      | 71.3| 1.4  | -    | 0.8  | 15.7 | 2.2  | 3.5  | 6.2  | 9.9  |
| O       | 24.6| 47.8 | 50.2 | 64.7 | 45.9 | 43.9 | 25.9 | 28.6 | 33.7 |
| Si      | 1.9 | 28.3 | 23.6 | 38.3 | 22.1 | 18.2 | 2.5  | 29.2 | 15.6 |
| Fe      | 1.2 | 6.0  | 0.6  | 5.6  | 0.9  | 24.2 | 65.2 | 24.5 | 23.3 |
| Al      | 0.4 | 11.5 | 22.7 | 5.9  | 12.1 | 9.1  | 2.6  | 6.6  | 15.0 |
| S       | 0.4 | -    | -    | -    | 0.5  | -    | -    | -    | -    |
| Mg      | 0.3 | 1.0  | -    | 2.5  | 1.5  | 1.2  | -    | 3.1  | 1.8  |
| Na      | -   | 2.3  | 1.1  | -    | -    | -    | -    | -    | -    |
| K       | -   | 1.2  | 1.8  | 1.4  | 1.0  | 0.6  | -    | 1.2  | 0.5  |
| Ti      | -   | 0.4  | -    | 0.7  | 0.3  | 0.5  | -    | 0.6  | 0.4  |

![Table 6](image2)

Rheological parameters of fly ash incorporated cement pastes without magnetic field.

| Mix. | G’ (LVER) (Pa) | τc,ys (Pa) | ηb (Pa.s) |
|------|----------------|------------|-----------|
| Ref  | 11,100         | 1.43       | 6.61      |
| 25%FA1 | 8310       | 0.88       | 5.41      |
| 50%FA1 | 8120       | 0.86       | 3.61      |
| 50%FA2 | 7180       | 0.76       | 3.62      |
| 50%FA3 | 5230       | 0.67       | 1.85      |
| 50%FA4 | 11,500     | 1.48       | 4.58      |

(a) Strain-sweep curves

(b) Flow curves

Fig. 5. (a) Strain-sweep curves and (b) flow curves of fly ash incorporated cement pastes without magnetic field.

In the absence of magnetic field, the volumetric replacement of cement with fly ash reduces the intensity and rate of structural build-up of the cement pastes, especially at higher fly ash volume fraction. More specifically, the incorporation of fly ash slightly prolongs the percolation time, possibly due to the increase of interparticle distance contributed by the lower density and finer particle size of the fly ash (FA1) particles compared to cement. The storage modulus at 300 s and the structural build-up rate at steady state are 95 kPa, 83 kPa, 30 kPa and 0.24 kPa/s, 0.21 kPa/s, 0.08 kPa/s for the cement pastes with fly ash volume fraction of 0%, 25% and 50%, respectively. The slowdown of the structural build-up of cement paste with fly ash agrees with [33,36]. This probably can be attributed to the reduced cation precipitations, as reflected by the retardation effect in the hydration process of the cement paste by replacing cement with fly ash, as shown in Fig. 12 (see later).
low the lines of magnetic field to form magnetic clusters. Their movement and assemblage result in the rheological responses of the suspensions to the external magnetic field. The magneto-rheological effect amplifies with the increase of fly ash volume fraction. For example, the difference of the storage modulus at 300 s between 0 T and 0.5 T (D-value) is 49 kPa and 122 kPa for the cement paste with fly ash of 25% and 50%, respectively. Besides, the liquid-like properties dominating duration (\( t_{G'}=G'' \)) and the percolation time (\( t_{\text{perc}} \)) increase from 6 s to 40 s and from 105 s to 170 s with increasing fly ash replacement from 25% to 50%, respectively. The increased magneto-rheological effect can be explained by the increasing concentration of the magnetic fly ash particles. Increasing the magnetic fly ash content has a positive effect on the enhancement of the magnetic structures and thus the improvement of the magneto-rheological responses. Furthermore, higher fly ash replacement reduces the magnitude of storage modulus and increases the viscous behavior, which makes the storage modulus become more sensitive to the change of internal microstructures due to the formation of magnetic clusters. Consequently, more obvious magneto-rheological effect is obtained at higher fly ash volume fractions.

### 3.3.2. Influence of fly ash type

At the same volumetric replacement of 50%, the influence of fly ash type on the magneto-rheological response of cement paste is presented in Fig. 7. The main rheological parameters of the cement pastes are summarized in Table 8. It can be observed that the structural evolution of the cement pastes depends on the type of fly ash, regardless of the application of the magnetic field. Without the external magnetic field, 50%FA1 and 50%FA4 show similar structural build-up, while 50%FA2 and 50%FA3 have relatively higher intensity and rate of structural evolution. Indeed, the storage modulus at magnetization of 300 s is around 30 kPa and 58 kPa for the mixtures of 50%FA1 and 50%FA4, respectively. The corresponding
The increase rate of the storage modulus at steady state is 0.08 kPa/s and 0.15 kPa/s for these two mixtures, respectively. This can be explained by the morphology and chemical activity of the fly ash particles. The particles of FA1, FA2, and FA3 are spherical, while FA4 has irregular shape. The chemical activity of FA4 is higher than that of FA1, FA2, and FA3, as reflected by the relatively high CaO content in Table 1 as well as the calorimetric testing results in Fig. 12 (see later). Consequently, 50%FA4 shows slightly higher structural build-up rate comparing with 50%FA1 and 50%FA3. The higher structural build-up of the cement paste with FA2 is possibly due to the high specific surface area of the fly ash, as shown in Table 1.

In the presence of an external magnetic field of 0.5 T, 50%FA2 exhibits lower magneto-rheological response than 50%FA1. More specifically, 50%FA2 shows significantly shorter liquid-like properties dominating duration and percolation time than 50%FA1. The D-value of G’ between 0.5 T and 0 T is 122 kPa/s and 50 kPa/s for the mixtures of 50%FA1 and 50%FA2, respectively. This is in good agreement with the relatively low saturation magnetization and magnetic fraction of FA2 as compared to FA1. Comparing with 50%FA1, 50%FA3 exhibits more obvious magneto-rheological response, characterized by the faster structural build-up (i.e., higher D-value and D_G”), which can be attributed to the high magnetic properties of FA3 and thus the high interparticle connections between magnetic particles. In spite of the higher magneto-rheological response, 50%FA3 has similar liquid-like properties dominating duration and slightly shorter percolation time than 50%FA1. This indicates that the solid particles in the suspension of 50%FA3 can easily reach their equilibrium positions after applying the external magnetic field. This is probably because of the coarser particles of FA3 than FA1. In the case of 50%FA4, the suspension shows a relatively high structural build-up rate compared

| Mix. | 0 T | ΔG’ (kPa/s) | t_G’ (s) | t_G’ peak (s) | G’ peak (kPa) | t_perc (s) | ΔG” (kPa/s) | D-value (kPa) |
|------|-----|-------------|---------|---------------|--------------|------------|-------------|--------------|
| Ref  | 15  | 0.24        | –       | –             | –            | 15         | 0.25        | 2            |
| 50%FA1| 20  | 0.08        | 40      | 95            | 44           | 170        | 0.51        | 0.06         | 122          |
| 50%FA2| 20  | 0.14        | 13      | 80            | 27           | 125        | 0.41        | 0.12         | 50           |
| 50%FA3| 15  | 0.09        | 44      | 60            | 55           | 125        | 1.32        | 0.10         | 145          |
| 50%FA4| 20  | 0.15        | 13      | 48            | 48           | 90         | 1.20        | 0.31         | 107          |

Note: t_perc is the percolation time when phase angle reduces to steady state, ΔG’ is the increase rate of storage modulus at time scale of 200–300 s, t_G’ peak is the peak loss modulus, ΔG” is the increase rate of loss modulus at very early age (e.g., 2–20 s), and D-value is the difference of storage modulus at 300 s between 0 T and 0.5 T.
with other suspensions, possibly due to the higher chemical hydration. Interestingly, 50%FA4 has quite higher magneto-rheological response than 50%FA2. This can be attributed to the morphological effect of the magnetic particles, which increases the friction and connection between magnetic clusters [39,40].

3.3.3. Relationship between magneto-rheological effect and magnetic properties of FA

To correlate the magneto-rheological effect of cement pastes with the magnetic properties of fly ash, the D-value of storage modulus at 300 s is used to quantitatively describe the magneto-rheological effect. The saturation magnetization of original fly ash, effective magnetic fraction and effective magnetization (defined as the product of the effective magnetic fraction and the saturation magnetization of the magnetic fraction, see later) are respectively selected to characterize the magnetic properties of fly ash.

The points of D-value versus saturation magnetization of original fly ash are plotted in Fig. 8. It can be seen that at the same volumetric replacement, the magneto-rheological effect has a considerable linear proportional relationship with the saturation magnetization of the original fly ash, with the coefficient of determination $R^2$ higher than 0.97, except for the mixture of 50%FA4. The results infer that the saturation magnetization of original fly ash could be used as an effective parameter to evaluate the magneto-rheological properties of fly ash incorporated cement pastes. The aberrant point of 50%FA4 is possibly due to the surface texture, irregular shape and high chemical reactivity of the fly ash, increasing the inter-particle frictions between magnetic fly ash clusters. In the case of cementitious paste with nano-Fe$_3$O$_4$ particles, the particle size of the nanoparticles plays a significant role in dominating the viscoelastic properties without magnetic field, while the response of the cementitious paste to an external magnetic field is mainly determined by the magnetic properties and crystalline structures of the nanoparticles [8,41]. For the fly ash incorporated cement pastes, the median size of the used fly ash only varies from 8 μm to 15 μm. In the presence of a magnetic field, the structural evolution of fly ash incorporated cement pastes is mainly determined by the magnetic properties of the fly ash, rather than the particle size. Although more data is required, it is reasonable to correlate the magneto-rheological effect with the saturation magnetization of original fly ash.

Each fly ash can be separated into magnetic and non-magnetic parts. Assuming that all the Portland cement particles with low magnetic properties are non-magnetic, the effective fraction of magnetic particles in each suspension can be calculated as:

$$F_{eff, MF} = \frac{m_{FA} \cdot m_{FA}}{m_C + m_{FA}} \cdot 100\%$$

(2)

where $F_{eff, MF}$ is the magnetic fraction of the used fly ash (%), $m_C$ and $m_{FA}$ are the content of cement and fly ash in each mixture (kg), respectively. The effective magnetic fraction indicates the concentration of magnetic fly ash particles in each suspension, providing an indication of magnetic particles in cement paste with various fly ash replacements. The relationship between the effective magnetic fraction and the D-value for all the studied cement pastes is presented in Fig. 9. It can be observed that the D-value of the storage modulus shows a general rough linear relationship with the effective magnetic fraction (except the point of 50%FA4). This indicates higher magneto-rheological responses of cement paste with higher content of magnetic particles. Nevertheless, some contradictory points can be observed. For example, 25%FA3 has a higher effective magnetic fraction than 50%FA1, while the corresponding magneto-rheological effect shows an opposite trend. This probably can be attributed to the different magnetic properties of the magnetic fraction of each fly ash, as shown in Fig. 10. Compared to the saturation magnetization of original fly ash, the effective magnetic fraction is a less effective parameter to describe the order of magneto-rheological effect of fly ash incorporated cement pastes.

Both the saturation magnetization and concentration of magnetic fraction of fly ash play important roles in determining the rheological response of fly ash incorporated cement paste to an external magnetic field. Therefore, a modified parameter characterizing the coupled effect of the magnetic fraction and the corresponding saturation magnetization, defined as effective magnetization ($M_{eff, s} = F_{eff, MF} \cdot M_{s, MFA}$ where $M_{s, MFA}$ is the saturation magnetization of the magnetic fraction), is attempted to correlate with the magneto-rheological effect, as presented in Fig. 11. It can be seen that the D-value of the storage modulus exhibits a linear correlation with the effective magnetization of cement paste if excluding the mixture of 50%FA4. This means that a cement paste with higher magnetic fraction and higher corresponding saturation magnetization shows more obvious magneto-rheological response. The drawback of this modified parameter is that fly ash is required to be separated. Overall, the saturation magnetization of original fly ash is a simple and effective indicator to describe the
magneto-rheological properties of fly ash incorporated cement paste.

3.4. Heat of hydration

The early structural build-up of cement paste is a physicochemical process with a combined result of colloidal interactions and chemical hydration. The calorimetric results of cement paste are helpful to understand the possible chemical influence on the structural build-up. The curves of hydration heat evolution, normalized to the amount of cement, are shown in Fig. 12. The main parameters obtained from the heat evolution curves, including the ending time of so-called induction period, the time and hydration rate of the second exothermic peak, and the total heat of hydration (1 h, 2 h, 12 h and 36 h), are listed in Table 9. For the pure cement paste mixture, a sharp exothermic peak appears a few minutes after the first contact of cement with water, due to the presence of complex reactions during the wetting process, where free lime hydrates and C-S-H with low Ca/Si and ettringite are formed. The heat hydration rate afterwards decreases rapidly, and then the induction period associated with C-S-H gel nucleation and calcium hydroxide (CH) supersaturation appears. The ending time of the induction period is about 1.47 h for the pure cement paste. This is followed by the acceleration period with rapid hydration of C3S and fast formation of C-S-H gel and CH.

The cement pastes with fly ash show similar trend but different intensity of hydration heat evolution. It can be seen that FA1, FA2 and FA3 almost have similar effect on the hydration rate evolution, with a prolongation in the induction period duration. This indicates that the addition of FA1, FA2, and FA3 exhibits a retarding effect on the cement hydration. This is in agreement with [32,42], which can be attributed to the effect of spherical fly ash particles on the adsorption of Ca²⁺. The heat release rate of cement at the second exothermic peak apparently increases and the corresponding time is slightly prolonged after adding fly ash. Furthermore, there is a weak exothermic effect in the later period due to the pozzolanic reaction of fly ash. From the total heat release curves, it can be observed that the addition of FA2 and FA3 shows similar influence on the hydration heat of cement, which is lower within the first 24 h but higher beyond 24 h compared to the values of pure cement. However, the mixture with FA1 shows comparable total cement hydration heat to the pure cement at first hours after mix-
ing the binder with water. The cement paste with FA4 shows distinct hydration heat behavior compared with other mixtures. After the first exothermic peak, the heat of hydration rate decreases slowly and the heat release rate is significantly higher than that of pure cement within the first few hours. This indicates that the addition of FA4 shows an accelerating effect on the early chemical hydration of cement, probably due to the presence of free lime (as can be reflected by the high CaO content in Table 1). The total hydration heat at 1 h slightly increases from 1.40 J/g(cement) to 1.57 J/g(cement). Replacing cement by FA4 prolongs the induction period but increases the corresponding hydration heat evolution rate. Compared to the pure cement, the peak value of the accelerated period increases, and there is no third exothermic peak in the curve of hydration heat rate. Moreover, the total released hydration heat of 50%FA4 is far higher than that of other cement pastes. In a word, the addition of FA1, FA2 and FA3 exhibits a slight retarding effect, while FA4 has an acceleration effect on the cement hydration.

3.5. Comparison of magneto-rheological response between nano-Fe₃O₄ and fly ash

The magneto-rheological responses of fly ash and nano-Fe₃O₄ particles in cementitious suspensions are compared. The fly ash is represented by FA1, and the mixture with 50% fly ash is selected, designated as 0.35_50%FA1. The nano-Fe₃O₄ particles (MNPs) with particle size of 20–30 nm are selected. Detailed information of the nano-Fe₃O₄ particles is referred to [37,43]. The w/c and MNPs content of the cement paste with nano-Fe₃O₄ particles (0.4_3%MNPs) are 0.4 and 3%, respectively. The evolutions of storage modulus and phase angle of 0.35_50%FA1 and 0.4_3%MNPs under magnetic field of 0 T and 0.5 T are presented in Fig. 13. In the absence of external magnetic field, 0.35_50%FA1 shows significantly lower storage modulus but higher phase angle than that of 0.4_3%MNPs, indicating the higher viscous-liquid properties of 0.35_50%FA1 than 0.4_3%MNPs. It should be mentioned that the statement about the structural build-up without magnetic field is as a basis for comparing the intensity of magneto-rheological response. There is no point in comparing their absolute values due to the differences of w/c and solid volume fraction.

In the presence of an external magnetic field of 0.5 T, both 0.35_50%FA1 and 0.4_3%MNPs immediately exhibit liquid-like properties domination over solid-like properties. However, the internal microstructure of 0.4_3%MNPs consolidates much faster than 0.35_50%FA1, exhibiting a significant increase in the storage modulus and rapid decrease in the phase angle to steady state. In other words, 0.35_50%FA1 requires longer time for the solid particles to reach their final equilibrium after applying the external magnetic field. From the viewpoint of the difference of the storage modulus at steady state, 0.4_3%MNPs shows more obvious magneto-rheological effect than 0.35_50%FA1, with the storage modulus at 300 s increasing from 400 kPa to 940 kPa and from 30 kPa to 180 kPa, respectively. It should be noted that the intensity of the structural build-up of 0.35_50%FA1 under the magnetic field of 0.5 T is still lower than that of 0.4_3%MNPs without external magnetic field. Overall, under external magnetic field of 0.5 T, the fly ash incorporated cement paste has a long period of liquid-like properties domination, revealing that magnetic fly ash could be used as a responsive additive to improve the rheology of cement paste by applying magnetic field.

4. Conclusions

In the present study, the magneto-rheological properties of cement pastes containing fly ash are investigated. The relationship between magneto-rheological effect and magnetic properties of

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**Table 9**

Parameters derived from hydration rate curves of the cement pastes.

| Mix. | Ending time of induction period (h) | Second heat hydration peak | Total heat release (J/g(cement)) |
|------|----------------------------------|---------------------------|---------------------------------|
|      |                                  | Time(h)                   | Rate (J/g(cement)h) 1 h 2 h 12 h 36 h |
| Ref. | 1.47                             | 13.97                     | 7.93                           | 1.40 2.79 24.99 89.18 |
| 50FA1 | 2.82                             | 16.58                     | 8.64                           | 1.35 2.70 18.97 103.7 |
| 50FA2 | 2.35                             | 16.18                     | 8.68                           | 0.41 0.82 20.44 103.3 |
| 50FA3 | 2.18                             | 15.23                     | 8.41                           | 0.36 0.71 21.18 100.9 |
| 50FA4 | 4.42                             | 15.55                     | 9.25                           | 1.57 3.14 36.01 124.6 |

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*Fig. 13.* Magneto-rheological responses of 0.35_50%FA1 and 0.4_3%MNPs.
the incorporated fly ash is established. Based on the results and discussion, the main conclusions can be summarized as follows:

1. The volumetric replacement of cement with spherical fly ash decreases the storage modulus and measured shear stress, and slows down the structural build-up of cement paste. By contrast, fly ash with irregular shape and high chemical activity has limited increased effect on the viscoelastic and rheological properties of cement paste.

2. All the studied cement pastes containing fly ash with magnetic properties higher than the used cement exhibit apparent magneto-rheological response. The magneto-rheological effect increases with the volume fraction of fly ash, due to the increased concentration of magnetic fly ash particles and the reduced storage modulus without magnetic field.

3. The magneto-rheological response depends on the magnetic properties and physical characteristics of fly ash. Spherical fly ash with higher saturation magnetization and magnetic fraction generally shows higher magneto-rheological response to an external magnetic field in cement suspension. Irregular fly ash with relatively low magnetic properties can show unexpectedly obvious magneto-rheological response, possibly because of the morphological effect of the particles.

4. Under the same volumetric replacement, the saturation magnetization of original fly ash has a considerable linear proportional relationship with the magneto-rheological effect, which can be used as an effective and simple indicator to describe the magneto-rheological properties of fly ash incorporated cement paste.

5. In comparison with the magneto-rheological response of nano-Fe3O4 incorporated cementitious paste, cement paste with fly ash has a longer period of dominating liquid-like properties, whereas the increase of stiffness at steady state is not significant. Magnetic fly ash could be used as a responsive additive to improve the rheology of cement paste by applying magnetic field.

CRediT authorship contribution statement

Dengwu Jiao: Methodology, Formal analysis, Investigation, Visualization, Writing - original draft. Karel Lesage: Conceptualization, Methodology, Resources, Supervision, Writing - review & editing. Mert Yucel Yardimci: Supervision, Writing - review & editing. Geert De Schutter: Conceptualization, Methodology, Formal analysis, Supervision, Project administration, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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