Estimation of Magnetic Force between Micrometer-Sized Fly-Ash Particles in Cementitious Suspensions

Dengwu Jiao, Ph.D.[1]; Caijun Shi[2]; and Geert De Schutter[3]

Abstract: Magnetic fly ash is a potential alternative responsive additive to achieve magneto-rheology control of cementitious materials; it reduces the cost of magnetic particles and also is beneficial to preparing sustainable binder materials. This paper estimates the magnetic force between micrometer-sized fly-ash particles in cementitious suspensions. Four cases, regarding different selections of particle distance and different characterizations of magnetic properties of fly ash, are considered. The correlations between theoretical calculated parameters and experimental rheological properties are discussed. Results show that fly ash should be separated into magnetic and nonmagnetic parts to better estimate the magnetic force between particles. For the case of two neighboring magnetic fly-ash particles in cementitious suspensions, the estimated magnetic yield parameter, describing the relative magnitude of magnetic force to the resistance of the suspension, can be used as an indicator to describe whether the fly-ash cement paste shows rheological response to an external magnetic field. The intensity of the magneto-rheological response can be correlated to the average magnetic force calculated by considering the even distribution of magnetic fly-ash particles in nonmagnetic solid suspensions. **DOI: 10.1061/(ASCE)MT.1943-5533.0004594.**

Author keywords: Magnetic force; Fly ash; Active rheology control; Magnetic field; Cement paste.

Introduction

Active rheology control is an innovative concept aimed at overcoming the contradicting requirements of properties during different concrete construction processes (De Schutter and Lesage 2018; Sanjayan et al. 2021), such as flowability requirements in pumping and formwork casting (Roussel 2007; Jiao et al. 2021a), or yield stress demand in extruding and after extrusion in three-dimensional (3D) concrete printing (Yuan et al. 2019; Tao et al. 2021). Magneto-rheology control, an integration of magneto-responsive additives and employing an external magnetic field, is a potential approach to achieve the target of controllable rheology of cementitious materials (Nair and Ferron 2014; De Schutter et al. 2018). The theoretical foundation of controlling rheology by magnetic field comes from the concept of magneto-rheological fluid, a smart material consisting of magnetic particles and nonmagnetic carrier fluid, which exhibits solid-like properties under a magnetic field while recovering to a liquid reversibly after removal of the magnetic field (Rabinow 1948; Felt et al. 1996). Active rheology control by magnetic field is a possible solution to manipulate the evolution of structural buildup and adjust the rheological properties of postmixing cementitious materials with the same mix proportions, which is in favor of improving the construction efficiency of pumping and casting processes and even 3D printing (Chibulu et al. 2021; Deshmukh et al. 2021; Jiao et al. 2021g).

Successful magneto-responsive additives used in cementitious materials, from the viewpoint of lab-scale experiments, are ferromagnetic particles such as carbonyl iron powder (Nair and Ferron 2016), FeO particles (De Schutter et al. 2018) and nano-Fe_3O_4 particles (Jiao et al. 2019). It was revealed that applying an external magnetic field promotes the movement of magnetic particles in cementitious suspensions to form magnetic chains and/or clusters, resulting in an increase in the liquid-like behavior at very early age and an enhancement in the solid-like properties after longer magnetization time. To verify the movement of magnetic particles under magnetic field, Jiao et al. (2021c, e) derived the conceptual equations of magnetic force between neighboring nano-Fe_3O_4 particles assumed to be distributed evenly in the voids between cement particles, and proposed an indicator, defined as the magnetic yield parameter, to characterize the relative magnitude of magnetic force to the resistance of the suspension. The clustering of nano-Fe_3O_4 particles in cementitious paste is also quantified by converting a Fe-element energy dispersive X-ray (EDX) map into the distribution of Fe-element numbers using the image analysis technique to provide an experimental validation of the formation of magnetic clusters in cement suspensions (Jiao et al. 2021b).

Despite the obvious responses of ferromagnetic particles in cementitious suspensions, the high cost restricts the further investigation of magneto-rheology control in mortar and concrete materials, as well as its extensive applications such as real pumping and 3D concrete printing. In this context, traditional waste materials with magnetic properties are good alternative economical magnetic additives in magneto-rheology control. As a result of the presence of magnetite and maghemite, fly-ash particles can be highly magnetic (Gomes et al. 1999; Presuel-Moreno and Sagüés 2009; Bhattacharjee et al. 2013; Liu et al. 2018). The fraction of magnetic particles in fly ash can reach up to 35% by weight

[1]Postdoctoral Researcher, Magnel-Vandepitte Laboratory, Dept. of Structural Engineering and Building Materials, Ghent Univ., Ghent 9052, Belgium. ORCID: https://orcid.org/0000-0002-8943-757X. Email: jiaodengwu@hnu.edu.cn

[2]Professor, Key Laboratory for Green and Advanced Civil Engineering Materials and Application Technology of Hunan Province, College of Civil Engineering, Hunan Univ., Changsha 410082, China. Email: cshi@hnu.edu.cn

[3]Professor, Magnel-Vandepitte Laboratory, Dept. of Structural Engineering and Building Materials, Ghent Univ., Ghent 9052, Belgium (corresponding author). ORCID: https://orcid.org/0000-0001-5603-2616. Email: Geert.DeSchutter@UGent.be

Note. This manuscript was submitted on February 15, 2022; approved on May 23, 2022; published online on November 29, 2022. Discussion period open until April 29, 2023; separate discussions must be submitted for individual papers. This paper is part of the ***Journal of Materials in Civil Engineering***, © ASCE, ISSN 0899-1561.

(Prakash et al. 2001; Jiao et al. 2021f). Considering fly ash as a magneto-responsive additive, experimental results in Jiao et al. (2021f) show that the storage modulus of fly-ash cement paste under an external magnetic field of 0.5 T for 300 s can increase from ~30 to ~170 kPa, i.e., by a factor of 5.7. The rheological response depends on the volume fraction and magnetic properties of fly ash. It is found that the intensity of magneto-rheological response shows an empirical linear relationship with the saturation magnetization of original fly ash. However, no further study on the calculation of magnetic force between fly-ash particles is available. This is because the assumption in the calculation of magnetic force that nanoparticles are randomly distributed in the voids of cement particles cannot be directly applied to fly-ash cement paste because of the comparable particle size of fly ash to cement. To further understand the particle interactions of cement paste with fly ash under a magnetic field, it is necessary to estimate the theoretical magnetic force between micrometer-sized fly-ash particles in cementitious suspensions.

The present study attempted to extend the conceptual equations of magnetic force between magnetic nanoparticles in cementitious suspensions, derived by Jiao et al. (2021c), to cement pastes with micrometer-sized magnetic fly ash. For this purpose, different cases regarding the selection of particle distance and the characterization of magnetic properties of fly ash were considered. The magnetic force and magnetic yield parameter of the fly-ash cement pastes studied in Jiao et al. (2021f) were then calculated, and their relationship with the magneto-rheological behavior was established. This study provides theoretical support to understand the rheological response of cementitious paste with fly ash to an external magnetic field, and it is also beneficial to the estimation of magnetic force between micrometer-sized magnetic particles in cementitious suspensions.

Calculations of Magnetic Force between Micrometer-Sized Fly Ashes

Conceptual Equations

A cementitious suspension containing magnetic particles can be regarded as a stable magneto-rheological fluid. Immediately after applying a sufficiently strong magnetic field, the magnetic particles will move inside the cement paste to form magnetic chains or clusters (Jiao et al. 2020). The magnetic force between two neighboring magnetic particles aligning along the direction of the magnetic field can be estimated by (Rich et al. 2012; Jiao et al. 2021c)

$$F_m = \frac{\pi d^2 \mu_0 (\rho M)^2}{24} \cdot \left(\frac{d}{r}\right)^4 \tag{1}$$

where F_m = magnetic force (N); d and ρ = average particle size (m) and density (kg/m^3) of magnetic particles, respectively; μ_0 = magnetic permeability of the medium (N/A^2); M = magnetization per unit mass of the magnetic particles (Am^2/kg); and r = center-to-center distance between two magnetic particles (m). The relative magnitude of the magnetic force and the resistance induced by the viscoelasticity of the suspension, defined as the magnetic yield parameter (Y_M), can be expressed as

$$Y_M = \frac{\mu_0 (\rho M)^2}{24 \tau_{c,ys}} \cdot \left(\frac{d}{r}\right)^4 \tag{2}$$

where $\tau_{c,ys}$ = viscoelastic yield stress (Pa), which is the product of the critical strain and the corresponding storage modulus in the small-amplitude oscillatory strain sweep curve (Jiao et al. 2021c). The magnetic yield parameter represents whether magnetic particles could move in the suspension. For example, $Y_M > 1$ indicates that the magnetic force between magnetic particles can overcome the resistance of the suspension. In this case, the magnetic particles can move to connect and form clusters, and the suspension will show rheological response to the external magnetic field. A higher magnetic yield parameter generally indicates a more obvious magneto-rheological response for cementitious suspensions with the same type but different concentrations of magnetic particles (Jiao et al. 2021d).

As mentioned in the "Introduction," for cementitious paste with magnetic nanoparticles, the interparticle distance can be determined by assuming the random distribution of nanoparticles in the voids between micrometer-sized cement particles (Jiao et al. 2021c). This assumption, unfortunately, is not applicable to the situation of micrometer-sized magnetic particles. To address this issue, the surface–surface distance between two solid particles (b) is estimated by Eq. (3) (Yammine et al. 2008)

$$b = -d\left(1 - \left(\frac{\varphi}{\varphi_M}\right)^{-1/3}\right) \tag{3}$$

where d = particle size (m); φ = volume concentration of the considered particles (%), and the selection of its value will be discussed in the following sections; and φ_M = maximum packing density of the fly ash (%), which can be calculated by

$$\varphi_M = 1 - 0.45\left(\frac{d_{\min}}{d_{\max}}\right)^{0.19} \tag{4}$$

where $d_{\min}$ and $d_{\max}$ = sieve sizes (m) corresponding to 10% and 90% from the particle size distribution curve (Hu and de Larrard 1996), respectively. The particle distance and/or maximum packing density of cement suspensions vary with the determination methods (Guo et al. 2017; Wong and Kwan 2007; Štefančič et al. 2017). This study aims to provide an estimation of magnetic force between micrometer-sized fly-ash particles, and thus only one representative calculation approach based on the physical properties of raw materials was selected.

Determination of Interparticle Distance and Magnetic Properties of Fly Ash

Under the same magnetic field, it can be observed from Eqs. (1) and (2) that the estimated magnetic force depends on the physical properties of the magnetic particles (i.e., particle size, magnetic properties, and density) and the nature of the suspension (i.e., interparticle distance). The magnetic yield parameter is further related to the viscoelastic stress of the suspension. With regard to fly ash, the fraction of nonmagnetic part (NFA) is generally higher than the magnetic fraction (MFA) when separated by a permanent magnet (Kukier et al. 2003; Prakash et al. 2001). This is also the case for the fly ashes studied in Jiao et al. (2021f), as shown in Table 1. This means that a large amount of fly-ash particles in cement paste will not directly show a response to an external magnetic field. To calculate the magnetic force between fly-ash particles, two key parameters, i.e., the particle concentration φ in Eq. (3) and the magnetic properties of fly ash M in Eqs. (1) and (2), should first be determined. As previously mentioned, fly ash can be regarded as its magnetic and nonmagnetic parts. It is possible that two neighboring solid particles in cement pastes are both fly ash, while it is also reasonable that fly-ash particles are randomly distributed in cementitious suspensions. Accordingly, four different cases regarding the selection of magnetic properties and interparticle

Table 1. Main physical properties of the cement and fly ash

Physical property	PC	FA1	FA2	FA3	FA4
Specific gravity	3.15	2.22	2.35	1.95	2.56
D_{10} (μm)	2.53	1.33	1.26	2.51	2.74
D_{50} (μm)	9.46	8.01	10.17	13.32	15.39
D_{90} (μm)	25.28	39.66	41.57	49.34	55.09
Saturation magnetization of original fly-ash particles, $M_{s,\mathrm{FA}}$ (Am^2/kg)	0.59	1.74	0.99	2.31	0.85
Magnetic fraction (%)	—	10.03	4.38	27.13	5.87
Saturation magnetization of magnetic part, $M_{s,\mathrm{MFA}}$ (Am^2/kg)	—	16.87	19.00	6.59	11.21

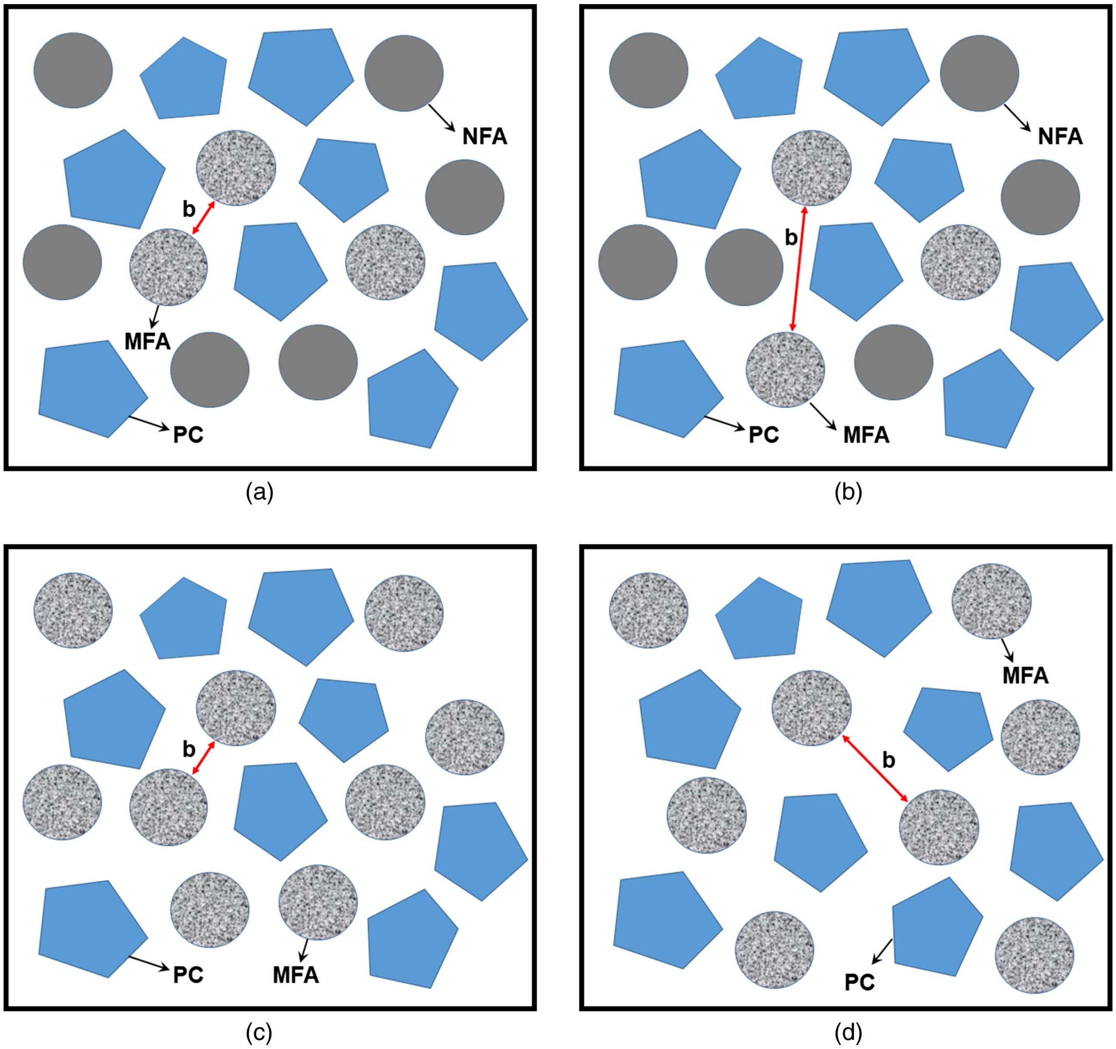

Fig. 1. Different cases for selecting the particle distance between magnetic fly ashes: (a) Case I; (b) Case II; (c) Case III; and (d) Case IV. PC = portland cement; MFA = magnetic fly ash; and NFA = nonmagnetic fly ash.

distance between fly ash, as shown in Fig. 1, are discussed in the following sections. All the cement particles are regarded as nonmagnetic, based on the fact that cement particles have extremely low saturation magnetization (less than 0.6 Am^2/kg) and plain cement paste shows insignificant rheological response to an external magnetic field (Jiao et al. 2021d; Nair and Ferron 2014).

Case I: Maximum Saturation Magnetization and Minimum Particle Distance

Fly ash is divided into magnetic and nonmagnetic parts, and it is postulated that two neighboring particles are both magnetic fly ashes, as shown in Fig. 1(a). This can also be regarded as the minimum particle distance between two magnetic fly-ash particles in the cementitious suspension. In this case, φ in Eq. (3) should be determined as the volume fraction of total solids in the cementitious suspension (φ_T), and the saturation magnetization of magnetic fly ash ($M_{s,\mathrm{MFA}}$) should be selected to represent the magnetic properties of fly ash in Eqs. (1) and (2).

Case II: Maximum Saturation Magnetization and Average Particle Distance

Fly ash is divided into magnetic and nonmagnetic parts, and magnetic fly-ash particles are randomly distributed in the suspension with nonmagnetic particles (i.e., cement and nonmagnetic fly ash). In this case, the surface–surface distance between magnetic fly-ash particles is considered as the average particle distance, which

J. Mater. Civ. Eng., 2023, 35(2): 04022421

shows relatively higher value compared to the one in Case I. Therefore, φ in Eq. (3) is selected as the volume fraction of magnetic fly ash (φ_{MFA}), and the saturation magnetization of magnetic fly ash ($M_{s,\mathrm{MFA}}$) is used to represent the magnetic properties of fly ash in Eqs. (1) and (2).

Case III: Average Saturation Magnetization and Minimum Particle Distance

All fly-ash particles in cement paste are assumed to be magnetic. In other words, the magnetic and nonmagnetic parts are not separated. In this case, the saturation magnetization of original fly ash ($M_{s,\mathrm{FA}}$) is selected to characterize the magnetic properties of fly ash M in Eqs. (1) and (2). With regard to the particle distance, it is postulated that two neighboring particles are both fly ashes. This means that φ in Eq. (3) is determined as the volume fraction of total solids in the cementitious suspension (φ_T), similar to Case I.

Case IV: Average Saturation Magnetization and Average Particle Distance

All fly-ash particles in cement paste are assumed to be magnetic, and all fly-ash particles are evenly distributed in the nonmagnetic cement suspensions. Therefore, the magnetic properties of fly ash in Eqs. (1) and (2) are represented by the saturation magnetization of original fly ash ($M_{s,\mathrm{FA}}$), and φ in Eq. (3) is selected as the volume fraction of fly ash in the cementitious suspension (φ_{FA}).

Experimental Program

Materials and Mixture Proportions

CEM I 42.5 N portland cement (PC) and four kinds of fly ash (FA1, FA2, FA3, and FA4) were utilized. The main physical properties of the cement and fly ashes are summarized in Table 1. The saturation magnetization of original fly-ash particles ($M_{s,\mathrm{FA}}$) was measured using a vibrating sample magnetometer, where the bulk (unseparated) materials were used as the sample. The magnetic fraction is the weight ratio of the magnetic part separated by a permanent magnet (Jiao et al. 2021f; Garcés et al. 2010; Kukier et al. 2003), and its magnetic properties were also measured, denoted as the saturation magnetization of magnetic part ($M_{s,\mathrm{MFA}}$).

The water-to-cement mass ratio of the reference cement paste was 0.35, corresponding to a volume ratio of 1.10. In the condition of keeping the water-to-binder volume ratio of 1.10 constant, the replacements of fly ash were 25% and 50% by the volume of cement. The mixture proportions of the cement pastes, similar to Jiao et al. (2021f), are presented in Table 2.

Testing Methods

The rheological response of the prepared cement pastes to an external magnetic field was evaluated by a rotational parallel plate rheometer (MCR 102, Anton Paar, Graz, Austria) equipped with a magneto-rheological device (MRD). The testing protocol includes flow curve test, strain sweep test, and time sweep test, and the details can be found in Jiao et al. (2021f). The strength of the external magnetic field used in this work includes 0 T and 0.5 T. The rheological results related to the theoretical calculations are summarized in Table 2.

Results and Discussion

According to the four situations described in Fig. 1, the calculated results of magnetic force and magnetic yield parameter for the studied fly-ash cement pastes are summarized in Table 3.

For the case of maximum saturation magnetization and minimum particle distance (Case I), it can be observed that the calculated magnetic yield parameter of all the fly-ash cement pastes is higher than 1. This indicates that neighboring magnetic fly-ash particles can overcome the resistance of the cementitious suspension to connect if applying an external magnetic field. In other words, all the fly-ash cement pastes should exhibit rheological response to the magnetic field, which agrees with the experimental results, because the situation that two adjoining particles are both magnetic fly ash happens in cementitious suspensions. The magnetic force calculated in this case can be regarded as the maximum value, which is significantly higher than the one obtained based on other cases for the same mixture, as can be observed from Table 3. However, the fly-ash volume fraction as well as the magnetic fraction were not taken into account in this case. Therefore, for the cement pastes with the same type but different volumetric replacements of fly ash, the calculated magnetic force was only determined by the saturation magnetization of the magnetic fly ash. This results in the calculated magnetic force do not change with the fly-ash volume fractions (Table 3). Besides, some calculated results may contradict the experimental observations. For example, cement pastes with FA3 exhibit the most obvious magneto-rheological response (as presented in Table 2), while the calculated magnetic force and magnetic yield parameter are relatively low (Table 3). This is because of the low magnetization of the magnetic part compared to other fly-ash particles, as shown in Table 1.

If taking the volume fraction of the magnetic part into account (i.e., Case II), all the calculated magnetic yield parameters are lower than 1, which can be attributed to the extremely low volume

Table 2. Mixture proportions and rheological testing results

Mix	PC (g)	FA (g)	Water (g)	$\tau_{c,ys}$ (Pa)[a]	$G'_{300\ \mathrm{s}}$ (0T) (kPa)[b]	$G'_{300\ \mathrm{s}}$ (0.5T) (kPa)[c]	$D-$value (kPa)[d]
Reference	20	0	7	1.43	96	97	1
25%FA1	15	3.52	7	0.88	86.9	126.65	39.75
25%FA2	15	3.73	7	0.91	67.1	86.35	19.25
25%FA3	15	3.10	7	0.94	55.4	136.05	80.65
25%FA4	15	4.06	7	0.83	91.75	103.75	12
50%FA1	10	7.05	7	0.86	30.05	148	117.5
50%FA2	10	7.46	7	0.76	49	91	42
50%FA3	10	6.19	7	0.67	31.5	175	143.5
50%FA4	10	8.13	7	1.48	59	167.5	108.5

Source: Data from Jiao et al. (2021f).

[a]$\tau_{c,ys}$ = viscoelastic yield stress of cementitious suspension obtained from small-amplitude oscillatory strain sweep curve (Jiao et al. 2021c).

[b]$G'_{300\ \mathrm{s}}$ (0T) = storage modulus at 300 s obtained from oscillatory time sweep curve in the absence of magnetic field.

[c]$G'_{300\ \mathrm{s}}$ (0.5T) = storage modulus at 300 s obtained from oscillatory time sweep curve in the presence of an external magnetic field of 0.5 T.

[d]$D-$value is the absolute difference of $G'_{300\ \mathrm{s}}$ (0.5T) and $G'_{300\ \mathrm{s}}$ (0T).

Table 3. Parameter selection and calculated results of fly-ash cement pastes

Case	Mix	φ (%)	φ_M (%)	b (μm)	M (Am^2/kg)	$\tau_{c,ys}$ (Pa)	Y_M	F_m (10^{-10} N)
I	25%FA1	0.476	0.764	1.549	16.87	0.88	44.360	100.443
	25%FA2	0.476	0.768	1.763	19.00	0.91	60.509	178.919
	25%FA3	0.476	0.744	2.145	6.59	0.94	5.063	26.526
	25%FA4	0.476	0.746	2.488	11.21	0.83	28.527	176.181
	50%FA1	0.476	0.764	1.548	16.87	0.86	45.405	100.474
	50%FA2	0.476	0.768	1.763	19.00	0.76	72.452	178.917
	50%FA3	0.476	0.744	2.146	6.59	0.67	7.101	26.518
	50%FA4	0.476	0.746	2.487	11.21	1.48	16.003	176.230
II	25%FA1	0.012	0.764	27.172	16.87	0.88	0.325	0.736
	25%FA2	0.005	0.768	43.570	19.00	0.91	0.147	0.435
	25%FA3	0.032	0.744	24.586	6.59	0.94	0.140	0.735
	25%FA4	0.007	0.746	57.650	11.21	0.83	0.102	0.632
	50%FA1	0.024	0.764	19.688	16.87	0.86	0.840	1.859
	50%FA2	0.010	0.768	32.483	19.00	0.76	0.444	1.096
	50%FA3	0.065	0.744	16.780	6.59	0.67	0.495	1.848
	50%FA4	0.014	0.746	42.562	11.21	1.48	0.145	1.596
III	25%FA1	0.476	0.764	1.549	1.74	0.88	0.472	1.069
	25%FA2	0.476	0.768	1.763	0.99	0.91	0.164	0.486
	25%FA3	0.476	0.744	2.145	2.31	0.94	0.622	3.259
	25%FA4	0.476	0.746	2.488	0.85	0.83	0.164	1.013
	50%FA1	0.476	0.764	1.548	1.74	0.86	0.483	1.069
	50%FA2	0.476	0.768	1.763	0.99	0.76	0.197	0.486
	50%FA3	0.476	0.744	2.146	2.31	0.67	0.872	3.258
	50%FA4	0.476	0.746	2.487	0.85	1.48	0.092	1.013
IV	25%FA1	0.119	0.764	7.779	1.74	0.88	0.074	0.168
	25%FA2	0.119	0.768	8.773	0.99	0.91	0.026	0.076
	25%FA3	0.119	0.744	11.219	2.31	0.94	0.098	0.514
	25%FA4	0.119	0.746	12.996	0.85	0.83	0.026	0.159
	50%FA1	0.238	0.764	4.302	1.74	0.86	0.192	0.424
	50%FA2	0.238	0.768	4.865	0.99	0.76	0.078	0.193
	50%FA3	0.238	0.744	6.166	2.31	0.67	0.346	1.293
	50%FA4	0.238	0.746	7.132	0.85	1.48	0.037	0.402

fractions of magnetic fly ash in cementitious suspensions and thus the large surface–surface distance between magnetic particles. This does not necessarily mean the cement pastes cannot show rheological response to the external magnetic field because the calculated magnetic force based on this case can be regarded as an average magnetic force between magnetic fly-ash particles, which should be significantly lower than that calculated according to Case I. The results indicate the magnetic yield parameter calculated from the average magnetic force cannot be used to perfectly describe the rheological response of fly-ash cement paste to an external magnetic field. This can also be concluded from the very poor correlation between the magnetic yield parameter and the D-value, as shown in Fig. 2(a). However, from the D-value versus estimated magnetic force graph in Fig. 2(b), it can be observed that fly-ash cement paste with higher magnetic force generally shows higher magneto-rheological response, which is consistent with the fact that increasing the magnetic force increases the connections between magnetic particles and thus improves the intensity of the rheological response. This means the estimated average magnetic force, concerning the volume fraction of both total fly ash and magnetic part, as well as the magnetization of magnetic fraction show a rough proportional correlation with the magneto-rheological response of cement paste with magnetic fly ash, yielding the correlation of determination (R^2) of 0.78 and Prob $> F$ of 0.002; the value is less than 0.05, meaning the model terms are statistically significant at the 95% confidence level.

For Case III, the calculated magnetic yield parameter of all the cement pastes is lower than 1, indicating the magnetic force between neighboring fly-ash particles, if considering all fly-ash particles are magnetic, cannot overcome the resistance of the suspension. This means that fly-ash cement paste will show unapparent response to the external magnetic field, which obviously contradicts the rheological experimental observations. The calculation results conversely reveal that not all the fly-ash particles are magnetic, agreeing with the magnetic separation results of fly ash in Table 1. Another drawback of the assumption in Case III is that the (magnetic) fly-ash volume fraction is not considered, similar to Case I, resulting in cement pastes with the same fly ash obtaining similar calculated magnetic force, regardless of the fly-ash replacements. With regard to Case IV, it can be expected that the magnetic yield parameter is lower than that obtained based on Case III because of the increase in the surface–surface separation distance between fly-ash particles. The points of D-value versus magnetic yield parameter are plotted in Fig. 2(c). Despite the rough linear relationship if excluding the point of 50%FA4, the magnetic yield parameter estimated based on Case IV is not a good indicator to describe the magneto-rheological response of fly-ash cement pastes because the value is significantly lower than 1. From Fig. 2(d), it can be seen that the calculated magnetic force also shows an approximately linear relationship with the magneto-rheological effect with the correlation of determination (R^2) of 0.63 and Prob $> F$ of 0.011. Nevertheless, the slightly lower coefficient of determination in Fig. 2(d) compared to Fig. 2(b) indicates the magnetic force estimated by regarding that all fly-ash particles are magnetic is less effective to describe the magneto-rheological response of fly-ash cement pastes.

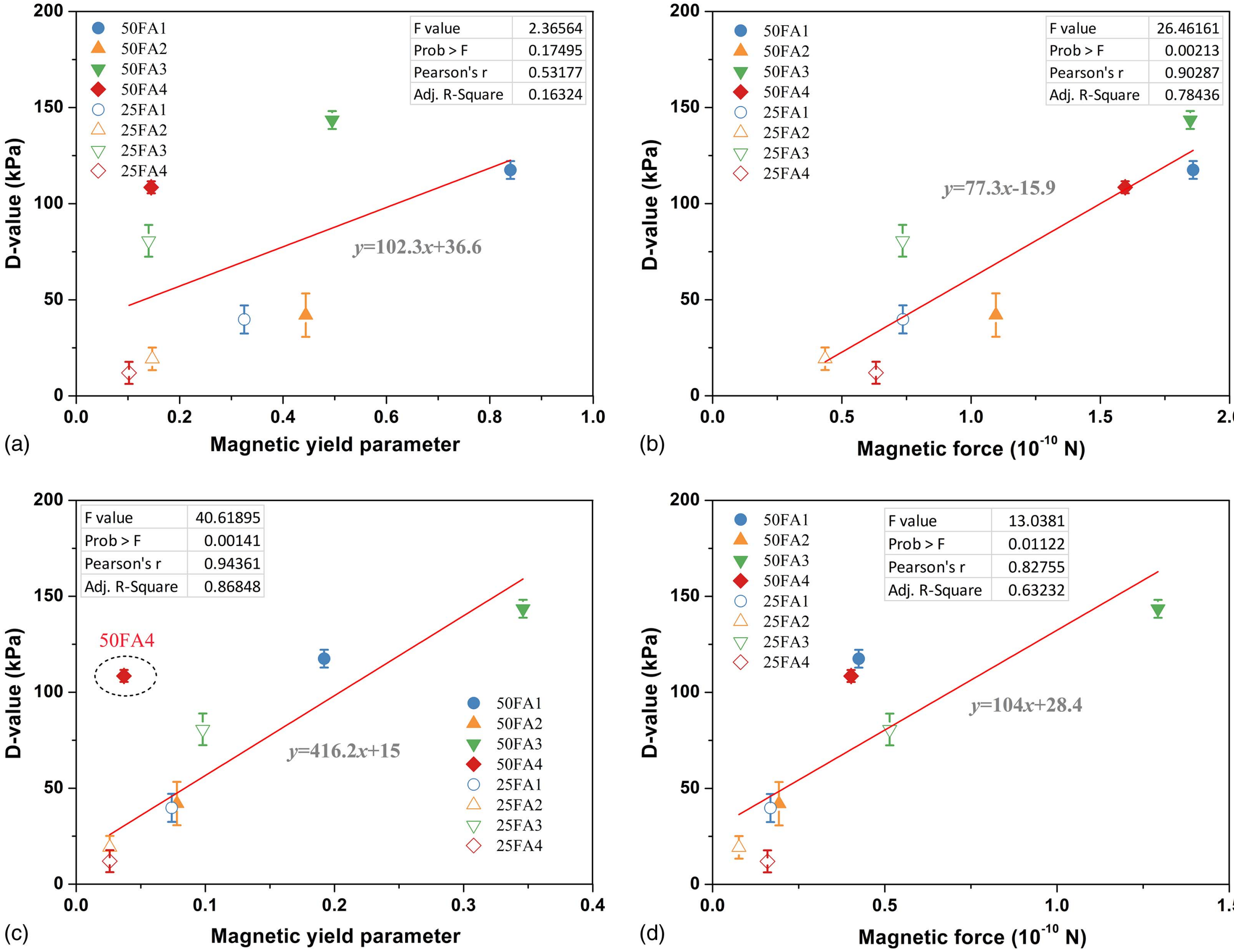

Fig. 2. Relationship between magneto-rheological response and estimated parameters: (a) magnetic yield parameter (Case II); (b) magnetic force (Case II); (c) magnetic yield parameter (Case IV); and (d) magnetic force (Case IV).

In summary, fly ash should be separated into magnetic part and nonmagnetic part to provide a better estimation of magnetic force between fly ash particles. Both the magnetic fraction and its saturation magnetization should be taken into account to describe the magneto-rheological response of fly-ash cement pastes. Furthermore, the interparticle distance between magnetic particles in cementitious suspensions should be carefully selected.

Conclusions

In the present study, the magnetic forces between fly-ash particles in cementitious paste were calculated. Different cases regarding the selections of particle distance and magnetic properties of fly ash were considered. The relationships between theoretically calculated parameters and experimentally measured rheological properties were discussed. Based on the results and discussion, the following conclusions can be reached:

- Not all fly-ash particles in cementitious suspensions can respond to an external magnetic field, neither from the viewpoint of experimental observations nor from the theoretical calculations. It is recommended to separate fly ash into magnetic and nonmagnetic parts to better estimate the magnetic force between fly-ash particles in cementitious suspensions.
- When two neighboring particles in cementitious suspensions are both magnetic fly ash, the calculated magnetic yield parameter can be used as an indicator to describe whether fly-ash cement paste shows rheological response to an external magnetic field. However, the estimated magnetic force does not change with the fly-ash volumetric replacements.
- Based on the assumption that magnetic fly-ash particles are evenly distributed in nonmagnetic solid suspensions, the magnetic yield parameter, showing values lower than 1 for all the tested pastes, cannot perfectly describe the magneto-rheological response of fly-ash cement paste. Nevertheless, the intensity of the response still shows a rough linear correlation with the calculated average magnetic force.

Data Availability Statement

All data, models, and code generated or used during the study appear in the published article.

Acknowledgments

The authors gratefully acknowledge the financial support from the European Research Council (ERC) Advanced Grant project SmartCast (693755).

References

Bhattacharjee, A., H. Mandal, M. Roy, J. Kusz, and W. Hofmeister. 2013. "Comparative study of the microstructural and magnetic properties of fly ashes obtained from different thermal power plants in West Bengal, India." *Environ. Monit. Assess.* 185 (10): 8673–8683. https://doi.org/10.1007/s10661-013-3203-6.

Chibulu, C., M. Y. Yardimci, D. Jiao, R. De Schryver, K. Lesage, and G. De Schutter. 2021. "Active stiffening control by magnetically induced blocking in confined flow of fly ash pastes." *Constr. Build. Mater.* 313 (Dec): 125485. https://doi.org/10.1016/j.conbuildmat.2021.125485.

De Schutter, G., and K. Lesage. 2018. "Active control of properties of concrete: A (p)review." *Mater. Struct.* 51 (5): 123. https://doi.org/10.1617/s11527-018-1256-2.

De Schutter, G., K. Lesage, V. Mechtcherine, V. N. Nerella, G. Habert, and I. Agusti-Juan. 2018. "Vision of 3D printing with concrete: Technical, economic and environmental potentials." *Cem. Concr. Res.* 112 (Oct): 25–36. https://doi.org/10.1016/j.cemconres.2018.06.001.

Deshmukh, A. S., R. T. Heintzkill, R. A. Huerta, and K. Sobolev. 2021. "Rheological response of magnetorheological cementitious inks tuned for active control in digital construction." *ACI Mater. J.* 118 (6): 263–274. https://doi.org/10.14359/51733128.

Felt, D. W., M. Hagenbuchle, J. Liu, and J. Richard. 1996. "Rheology of a magnetorheological fluid." *J. Intell. Mater. Syst. Struct.* 7 (5): 589–593. https://doi.org/10.1177/1045389X9600700522.

Garcés, P., L. G. Andión, E. Zornoza, M. Bonilla, and J. Payá. 2010. "The effect of processed fly ashes on the durability and the corrosion of steel rebars embedded in cement–modified fly ash mortars." *Cem. Concr. Compos.* 32 (3): 204–210. https://doi.org/10.1016/j.cemconcomp.2009.11.006.

Gomes, S., M. François, M. Abdelmoula, P. Refait, C. Pellissier, and O. Evrard. 1999. "Characterization of magnetite in silico-aluminous fly ash by SEM, TEM, XRD, magnetic susceptibility, and Mössbauer spectroscopy." *Cem. Concr. Res.* 29 (11): 1705–1711. https://doi.org/10.1016/S0008-8846(99)00133-7.

Guo, Y., T. Zhang, J. Wei, Q. Yu, and S. Ouyang. 2017. "Evaluating the distance between particles in fresh cement paste based on the yield stress and particle size." *Constr. Build. Mater.* 142 (Jul): 109–116. https://doi.org/10.1016/j.conbuildmat.2017.03.055.

Hu, C., and F. de Larrard. 1996. "The rheology of fresh high-performance concrete." *Cem. Concr. Res.* 26 (2): 283–294. https://doi.org/10.1016/0008-8846(95)00213-8.

Jiao, D., R. De Schryver, C. Shi, and G. De Schutter. 2021a. "Thixotropic structural build-up of cement-based materials: A state-of-the-art review." *Cem. Concr. Compos.* 122 (Sep): 104152. https://doi.org/10.1016/j.cemconcomp.2021.104152.

Jiao, D., K. El Cheikh, K. Lesage, C. Shi, and G. D. Schutter. 2020. "Structural build-up of cementitious paste under external magnetic fields." In *Rheology and processing of construction materials*, 36–42. Cham, Switzerland: Springer.

Jiao, D., K. El Cheikh, C. Shi, K. Lesage, and G. De Schutter. 2019. "Structural build-up of cementitious paste with nano-Fe_3O_4 under time-varying magnetic fields." *Cem. Concr. Res.* 124 (Oct): 105857. https://doi.org/10.1016/j.cemconres.2019.105857.

Jiao, D., K. Lesage, M. Y. Yardimci, K. El Cheikh, C. Shi, and G. De Schutter. 2021b. "Quantitative assessment of the influence of external magnetic field on clustering of nano-Fe_3O_4 particles in cementitious paste." *Cem. Concr. Res.* 142 (Apr): 106345. https://doi.org/10.1016/j.cemconres.2020.106345.

Jiao, D., K. Lesage, M. Y. Yardimci, K. El Cheikh, C. Shi, and G. De Schutter. 2021c. "Rheological behavior of cement paste with nano-Fe_3O_4 under magnetic field: Magneto-rheological responses and conceptual calculations." *Cem. Concr. Compos.* 120 (Jul): 104035. https://doi.org/10.1016/j.cemconcomp.2021.104035.

Jiao, D., K. Lesage, M. Y. Yardimci, K. El Cheikh, C. Shi, and G. De Schutter. 2021d. "Structural evolution of cement paste with nano-Fe_3O_4 under magnetic field—Effect of concentration and particle size of nano-Fe_3O_4." *Cem. Concr. Compos.* 120 (Jul): 104036. https://doi.org/10.1016/j.cemconcomp.2021.104036.

Jiao, D., K. Lesage, M. Y. Yardimci, C. Shi, and G. De Schutter. 2021e. "Flow behavior of cementitious-like suspension with nano-Fe_3O_4 particles under external magnetic field." *Mater. Struct.* 54 (6): 209. https://doi.org/10.1617/s11527-021-01801-y.

Jiao, D., K. Lesage, M. Y. Yardimci, C. Shi, and G. De Schutter. 2021f. "Possibilities of fly ash as responsive additive in magneto-rheology control of cementitious materials." *Constr. Build. Mater.* 296 (Aug): 123656. https://doi.org/10.1016/j.conbuildmat.2021.123656.

Jiao, D., C. Shi, and G. De Schutter. 2021g. "Magneto-rheology control in 3D concrete printing: A rheological attempt." *Mater. Lett.* 309 (Feb): 131374. https://doi.org/10.1016/j.matlet.2021.131374.

Kukier, U., C. F. Ishak, M. E. Sumner, and W. P. Miller. 2003. "Composition and element solubility of magnetic and non-magnetic fly ash fractions." *Environ. Pollut.* 123 (2): 255–266. https://doi.org/10.1016/S0269-7491(02)00376-7.

Liu, D., X. Wu, Y. Du, and L. Sun. 2018. "Experimental study on the magnetic characteristics of coal fly ash at different combustion temperatures." *Environ. Technol.* 39 (15): 1967–1975. https://doi.org/10.1080/21622515.2017.1345987.

Nair, S. D., and R. D. Ferron. 2014. "Set-on-demand concrete." *Cem. Concr. Res.* 57 (Mar): 13–27. https://doi.org/10.1016/j.cemconres.2013.12.001.

Nair, S. D., and R. D. Ferron. 2016. "Real time control of fresh cement paste stiffening: Smart cement-based materials via a magnetorheological approach." *Rheol. Acta* 55 (7): 571–579. https://doi.org/10.1007/s00397-016-0923-x.

Prakash, S., J. K. Mohanty, B. Das, and R. Venugopal. 2001. "Characterisation and removal of iron from fly ash of talcher area, Orissa, India." *Miner. Eng.* 14 (1): 123–126. https://doi.org/10.1016/S0892-6875(00)00167-9.

Presuel-Moreno, F. J., and A. A. Sagüés. 2009. "Bulk magnetic susceptibility measurements for determination of fly ash presence in concrete." *Cem. Concr. Res.* 39 (2): 95–101. https://doi.org/10.1016/j.cemconres.2008.11.004.

Rabinow, J. 1948. "The magnetic fluid clutch." *Electr. Eng.* 67 (12): 1167. https://doi.org/10.1109/EE.1948.6444497.

Rich, J. P., P. S. Doyle, and G. H. McKinley. 2012. "Magnetorheology in an aging, yield stress matrix fluid." *Rheol. Acta* 51 (7): 579–593. https://doi.org/10.1007/s00397-012-0632-z.

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.

Sanjayan, J. G., R. Jayathilakage, and P. Rajeev. 2021. "Vibration induced active rheology control for 3D concrete printing." *Cem. Concr. Res.* 140 (Feb): 106293. https://doi.org/10.1016/j.cemconres.2020.106293.

Štefančič, M., A. Mladenovič, M. Bellotto, V. Jereb, and L. Završnik. 2017. "Particle packing and rheology of cement pastes at different replacement levels of cement by α-Al_2O_3 submicron particles." *Constr. Build. Mater.* 139 (May): 256–266. https://doi.org/10.1016/j.conbuildmat.2017.02.079.

Tao, Y., A. V. Rahul, K. Lesage, Y. Yuan, K. Van Tittelboom, and G. De Schutter. 2021. "Stiffening control of cement-based materials using accelerators in inline mixing processes: Possibilities and challenges." *Cem. Concr. Compos.* 119 (May): 103972. https://doi.org/10.1016/j.cemconcomp.2021.103972.

Wong, H. H. C., and A. K. H. Kwan. 2007. "Packing density of cementitious materials: Part 1—Measurement using a wet packing method." *Mater. Struct.* 41 (4): 689–701. https://doi.org/10.1617/s11527-007-9274-5.

Yammine, J., M. Chaouche, M. Guerinet, M. Moranville, and N. Roussel. 2008. "From ordinary rhelogy concrete to self compacting concrete: A transition between frictional and hydrodynamic interactions." *Cem. Concr. Res.* 38 (7): 890–896. https://doi.org/10.1016/j.cemconres.2008.03.011.

Yuan, Q., Z. Li, D. Zhou, T. Huang, H. Huang, D. Jiao, and C. Shi. 2019. "A feasible method for measuring the buildability of fresh 3D printing mortar." *Constr. Build. Mater.* 227 (Dec): 116600. https://doi.org/10.1016/j.conbuildmat.2019.07.326.