The study of magnetorheological fluids sedimentation behaviors based on volume fraction of magnetic particles and the mass fraction of surfactants

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Abstract
Magnetorheological fluids (MRFs) is composed of carbonyl iron (CI) powder distributed in carrier fluid. This paper studied the sedimentation behavior of MRFs in a cylindrical column by using direct visual observation (VO). In order to obtain the settlement law of MRFs with respect to particle concentration and surfactant contents, MRF samples with different particles volume fractions (i.e., 4, 10, 20 and 28 vol\%) and with different surfactant mass fractions (i.e., none, 2, 4 and 5 wt\%) were prepared, separately. And the commercial MRFs with the same magnetic particles volume fraction was used as the control group. In addition, the morphology of bare CI and surface modified CI particles samples were measured, experimentally, by light microscope. At last, three different settling velocity models (Vesilind model, Dick model, and Richardson and Zaki model) were considered to acquire the sedimentation velocity of magnetic particle concentration of MRF samples. Results present Dick model is more suited to the sedimentation rule of MRF sample in our study. The propagation velocity formula of the volumetric concentration of particles was also established on the basis of sedimentation velocity of particles and the particle setting velocity equation with the variational surfactant contents was also obtained.

1. Introduction
Magnetorheological fluids (MRFs) are a mixed solution consisted of micrometer magnetic particles diffusely distributed in a nonmagnetic carrier fluid and surfactants or other additives \cite{1–5}, such as antioxidant \cite{2} or anti-wear agents \cite{6} are often added to this suspension. The suspensions change from liquid like phase to solid like phase in millisecond in the presence of an external magnetic field and show a non-Newtonian fluid behavior in suspension and the magnetic particles are formed chain-like structure aligned parallel to the external field \cite{7, 8}. In the absence of external magnetic, the mixed solution is a Newtonian fluid. And the change process is reversible. The feature of MRFs ensures the applications in a variety of engineering \cite{9–11}.

Although owning the great progress of engineering, the sedimentation stability of particles in MRFs that this article focuses on is still a crucial problem with regard to their efficient long-term application in practice. Due to the importance and application of MRFs in practical engineering, the sedimentation properties of MRFs have been widely studied by many researchers through theoretical and experimental method \cite{12–15}. However, most of the researches are focused on how to improve the stability of MRFs, while the study which directed at the settlement laws of MRFs is very few. At present, some scholars have given the theoretical model of the settlement laws of MRFs at some conditions. The settling regulation of dilute solution of MRFs in a vertical column was in agreement with Stokes’ law \cite{16} when the magnetic particle volume concentration of MRFs is less. But Stokes’
law can’t explain the settling rule of large concentration of solution. Kynch [13] had proposed the speed of particles’ fall based on assumption that the settling velocity of particles was only a decision for the local volume concentration of particles and the distribution of particle concentration was homogeneous across any horizontal layer. Then, the sedimentation rate of particles had been given by Vesilind [17], Dick [18], and Richardson & Zaki [19], respectively.

The above studies on sedimentation of MRFs were always only based on one constant carrier fluid, lacking of whole and systemic study. In this study, silicon-oil-based MRFs with different volume fraction of CI particles were prepared. And commercial MRFs were purchased from Chongqing Materials Research Institute Co., Ltd, individually. The sedimentation experiments of diverse MRFs were systematically carried out to evaluate the settling performance of homemade MRFs prepared in our laboratory. At last, the general subsidence rule of magnetic particles in MRFs suspension was obtained through different settling models.

2. Experiment

2.1. Materials

Carbonyl iron (CI, particle diameter of 5-10 μm) was used as a dispersed phase. Particle shape of CI amplified 100 times and 200 times, respectively, were confirmed via a light microscope at room temperature and the photos are shown in figures 1(a) and (b). Oleic acid (OA) was used as surfactant. And silicone oil (SO) was applied as carrier liquids in the preparation of MRFs. MRF-G28 was purchased from Chongqing Materials Research Institute Co., Ltd Anhydrous alcohol was devoted as solvent in the coating process of CI particles. All materials were used as receiving without further purification.

2.2. Modification of CI micro-particles

Firstly, magnetic CI particles, OA and anhydrous alcohol were added in a beaker and stirred continuously in a water bath calefaction for 1 h. Then, the modified particles were washed by deionized water until the pH value
approximately was 7. Finally, the modified CI particles were dried from water at 60°C in a vacuum drying oven for 12 h to remove physical adsorbed water on the surfaces. As the result of the preceding procedure, modified CI particles with OA group were obtained. The schematic diagram of the adsorption process between CI particle and surfactant is presented in figure 2 and the morphology of modified CI particle characterized by light microscope is displayed in figures 1(c) and (d).

### 2.3. Preparation of MRFs samples

The surface modification particles were added in silicone oil. Then, in order to ensure the required homogeneity of MRFs, these samples were dispersed by ultrasonic oscillation for 1 h and milled by using a high-speed ball mill for 12 h. At last, MRFs samples were separated from balls mill. The detailed preparation process of MRFs samples is presented in figure 2(b). Table 1 lists the different samples of MRFs compositions.

| Name         | The volume fraction of modified CI (%) | The mass percent of surfactant (%) |
|--------------|---------------------------------------|-----------------------------------|
| MRF-SO10_4   | 10                                    | 4                                 |
| MRF-SO20_4   | 20                                    | 4                                 |
| MRF-SO28_4   | 28                                    | 4                                 |
| MRF-SO04_4   | 4                                     | 4                                 |
| MRF-SO28_0   | 28                                    | 0                                 |
| MRF-SO28_2   | 28                                    | 2                                 |
| MRF-SO28_5   | 28                                    | 5                                 |

### 3. Sedimentation theory

To quantify the sedimentation properties of fluids, both the degree to which the particles settled, the percentage of sedimentation, and the sedimentation rate were examined. The percentage of sedimentation is given by
\[
\frac{V_s}{V_t} \times 100\% = \frac{\text{The volume of supernatant}}{\text{Total volume}} \times 100\% \tag{1}
\]

Where, \(V_s\) is the volume of supernatant and \(V_t\) is the total volume of MRFs sample.

The layered sedimentation observation technique is one of the simplest analyses, pointing out some pivotal problems to gain favorable effect. But in order to get the settlement laws of magnetic particles, the dilute solution and concentrated solutions of MRFs are studied in the subsequent study.

When the magnetic particle volume concentration of MRFs is less than 5% of the mixing solution and the particle diameter is much lesser than the distance between particles, the particles’ sedimentation rate in the carrier fluid is mainly influenced and controlled by the density difference between magnetic particle and carrier fluid. The settling regulation of dilute solution of MRFs in a vertical column was in agreement with Stokes’ law [16].

\[
\nu = \frac{2r^2(\rho_p - \rho_f)g}{9\eta} \tag{2}
\]

Where, \(\eta\) and \(\rho_f\) is the viscosity and density of MRFs, respectively. And \(r\) and \(\rho_p\) is the radius and density of magnetic particle.

When considering a mechanical interaction between particles and thus to analysis the effects of particles volume concentration on suspension, Steinour [20] offered an empirical approach to explain the effect of particles volume concentration and Batchelor [12] gave a theoretical model. Thus two models give the following expression:

Steinour model:

\[
\nu(\phi) = \left[ v_0(1 - \phi)^2 \right] \left( 10^{-1.82\phi} \right) \tag{3}
\]

Batchelor model:

\[
\nu(\phi) = v_0(1 - k\phi) \tag{4}
\]

When the MRFs concentrations were relatively large, Stokes’ law couldn’t interpret the experimental results of settling rule. This was because interaction force between particles increased with the decreased distance of particles, thus particles aggregated together and settled to the bottom. Kynch [13] had proposed the speed of particles’ fall based on assumption that the settling velocity of particles was only a decision for the local volume concentration of particles and the distribution of particle concentration was homogeneous across any horizontal layer. According to Kynch’s analysis, combined with Holdich’s definition of the solids flux [16], Young-Tai Choi et al [21] had defined the spread speed of the volumetric concentration of particles.

\[
\frac{\partial h}{\partial t} = \frac{\partial(\phi v_s(\phi))}{\partial \phi} = v_c(\phi) \tag{5}
\]

Where, \(h\) is the distance between solution levels and mudline, \(t\) is propagation time, \(v_s(\phi)\) is the sedimentation velocity of particles and \(v_c(\phi)\) is the propagation velocity of the volumetric concentration of particles.

The sedimentation rate of particles had been given by Vesilind [17], Dick [18], and Richardson & Zaki [19], respectively.

Vesilind model:

\[
|v_s(\phi)| = v_0 e^{-k\phi} \tag{6}
\]

Dick model:

\[
|v_s(\phi)| = V_0 \phi^k \tag{7}
\]

Richardson & Zaki model:

\[
|v_s(\phi)| = v_0(1 - \phi)^k \tag{8}
\]

Where, \(v_0\) is the free settling velocity of particles in dilute concentration, which can be calculated by Steinour model or Batchelor model, \(k\) and \(V_0\) are constants that can be determined by experience.

4. Results and discussion

4.1. Sedimentation of self-made and commercial silicon-oil based MRFs

Figure 3 displays the mudline position change and settling percentage of self-made and commercial silicon-oil based MRFs samples with the same particles volume fraction in different test tubes, which were observed and documented directly for every 12 h, and the total time was 144 h. While, mudline is the boundary between the
upper supernatant and the underlying MRFs suspension. Mudline location change and settling percentage were measured and calculated in this study, and the precipitation of magnetic particles increases linearly with time in inception stage. They also demonstrate that the subsidence of commercial MRFs is faster and more than homemade MRFs during the first 100 h.

4.2. The influence of particle volume fraction

Figure 4 presents the mudline location changes and the particles setting percentage of different volume fraction of silicon-oil-based MRFs. Different volume fractions of MRFs were used to make solution for $v_0$ and $V_0$. The sedimentation velocity of particles was calculated from the curves of the mudline location change of four different particles volume concentrations of MRFs with over time, and the mudline location and settling percentage curves are shown in figure 4(a). The magnetic particles settlement increases linearly for the first ten minutes and reaches dynamic balance at last, and the proportion between supernatant fluid and initial fluid also increased with time obviously. Taking the slope of the initial linear stage as the settling velocity of particles in settling process to calculate sedimentation velocity $v_1(\phi)$ of particles concentration $v_1(\phi)$ according to Formula (5). Figure 4(b) gives the photograph of different volume fraction of MRFs samples when stable.

Figure 5 shows the particle setting velocity decreased exponentially with the increase of particles concentration of MRFs. According to the experimental data shown in figure 5, the relationship between the particles volume concentration of MRFs and particle setting velocity was fitted with least square method on the basis of sedimentation rate models. The models were as follows:

Vesilind model: $|v_1(\phi)| = 18.066e^{-27.085\phi}$

Dick model: $|v_1(\phi)| = 0.030\phi^{-1.655}$

Figure 3. The mudline location and settling percentage of self-made and commercial MRFs samples over time (solid is mudline location and hollow is sedimentation percentage).

Figure 4. (a) The settlement curves of different volume fraction MRFs samples with time (solid is mudline location and hollow is sedimentation percentage), (b) The photo of mudline location with different volume fraction of MRFs samples at stable.
Richardson & Zaki model: \[ v_c(\phi) = 17.407(1 - \phi)^{2.613} \]

As displayed in figure 5, Dick model shows the closest agreement with the experimental results as a whole, while Vesilind model and Richardson & Zaki model are in good agreement with the experimental data at low concentration stage and present the least effective between particles settlement velocity and concentration in this study. Based on the foregoing analysis of particles settlement, Dick model was used as the particle settling velocity function to establish the propagation velocity formula of the volumetric concentration of particles, separately, in this study, see the following formula:

\[
 v_c(\phi) = \frac{\partial H(\phi^{0.030\phi^{-1.655}})}{\partial \phi} = -0.0197\phi^{-1.655}
\]

According to Formula (2) and the material parameters, the settling velocity of dilute solution of MRFs could be calculated. The value ranges from 1.699 mm h\(^{-1}\) (particle radius of 2.5 \(\mu\)m) to 6.795 mm h\(^{-1}\) (particle radius of 5 \(\mu\)m). But depending on Vesilind model and Richardson & Zaki model, the free settling velocity of particles in dilute concentration is 18.066 mm h\(^{-1}\) and 17.407 mm h\(^{-1}\), respectively, which is much greater than the theoretical value. Perhaps the reason for this had the existence of chain-like structure in MRFs samples, as shown in figure 1, increasing the radius of the magnetic particles and resulting the addition of settling velocity of dilute solution.

4.3. Surfactant influence on sedimentation behaviors of MRFs

According to the study above, the MRFs sample with the volume fraction of 28% was selected as a comparing group, and the MRFs samples with the same particles volume fraction differing in surfactant mass percent (i.e. 0, 2% and 5%) were chosen as researching groups. And the mass percent of surfactant of the comparing sample was 4%. As shown in figure 6, it indicates that the settlement proportion of magnetic particles increases over time. And the precipitation of particles decreases with the content of surfactants increasing when the mass percent of surfactant is not greater than 2%. Presumably it is due to lesser content of surfactant and therefore they couldn’t completely cover the surface of magnetic particles. And magnetic particles in MRFs are active and steric repulsion can’t stop the contact between particles. Finally, the sedimentation behavior of magnetic particles will set off by the mutual gathering of particles. As for the MRFs containing more surfactant, the surfaces of magnetic particles can absorb large amounts of surfactants, so therefore there will provide enough resistance to prevent the aggregation between particles. However, that obvious rise of the content of the sedimentation particle has been visible when the gradient is more than 2%. This could be due to as the surfactant content in the particles increased, the individual particle mass and the interaction between magnetic particles is increasing, causing the particles to accumulate mutually and then setting down. The results also illustrate that the steric hindrance between particles exists even for the MRFs suspension with high surfactant content.

By using the initial tangent slop of figure 6 as the settling rate of MRFs samples with different surfactant contents, the variation relations between particle setting velocity and surfactant mass percent can be obtained, shown in figure 7. The particle settling velocity was gained by linear fitting the initial experimental data, as shown in figure 6. Carries on the data fitting to the experimental findings, the particle setting velocity equation with the variation surfactant contents was given by polynomial fitting, as follow:
Where, \( \phi \) is the mass fraction of surfactants in the magnetic particles.

5. Conclusions

The sedimentation process of homemade MRFs is more stable than commercial MRFs with the same particles volume fraction. The sedimentation velocity of particles decreased exponentially with the increase of particles concentration of MRFs. The magnetization intensity of CI particles modified by surfactants had good ability to disperse in carrier fluids and to prevent the aggregation of particles when the mass percent of surfactant is less than 2%. The relationship between the particles volume concentration of MRFs and particle setting velocity was obtained by using least square fitting method on the basis of mechanical interaction of particles. Dick model has the closest agreement with the experimental results as a whole, while Vesilind model and Richardson & Zaki model are in good agreement with the experimental data at low concentration stage. And the sedimentation velocity equation considering the variation surfactant contents was also gained. According to the sedimentation velocity of particles, the propagation velocity formula of the volumetric concentration of particles finally was established. Within the bounds of study, the MRFs sample consisting of 28 vol% of the modified particles with the surfactant mass fraction of 2% exhibited good sedimentation behavior promising MRFs suitable for real applications in industry.

\[ v(\phi) = -27.156\phi + 1512.816\phi^2 - 19173.18\phi^3 \]  

(9)
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