Iron oxidation and its impact on MR behavior

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Abstract. The oxidation of particles in MR fluids and its impact on rheology are investigated. The oxidation of iron spheres in an aliphatic oil follows a linear growth law, suggesting that the oxide forms a nonadherent layer. The magnetic field-induced yield stress decreases with increasing extent of oxidation. The rheological behavior is consistent with that predicted using a core-shell model.

1. Introduction
The rheological properties of magnetorheological (MR) fluids change over time. Carlson [1] describes the phenomenon of “in-use-thickening,” or IUT, which refers to the increase in off-state viscosity of MR fluids over time during use. IUT can be quite significant, ultimately resulting in device failure, as the MR fluid becomes an unmanageable paste. The cause of this viscosity increase is believed to be spalling of the friable surface layer from the iron particles. This surface layer, composed of iron oxides, is brittle. When subjected to high inter-particle stresses, this surface layer fractures and breaks into small pieces that separate from the primary particle. These small nanometer-sized secondary particles have a large surface area to weight ratio and are less dense than pure iron. This increase in off-state viscosity may therefore be caused by the increase in solid volume, and perhaps colloidal forces acting between small particles.

Ulicny et al. [2] examined the behavior of an MR fan clutch subjected to durability tests performed over extended periods. The field-induced torque capacity, characterized by the maximum output fan speed as the electromagnet current is cycled up and down, decreased slowly with time. Prior to the durability test, the particles were composed of nearly pure iron, containing only 0.4 wt% oxygen. Following the durability tests, the particles were found to contain significantly more oxygen; the particles examined following a 540 hour durability test contained 7 wt% oxygen. The authors also examined the particles using scanning electron microscopy. Prior to the durability test, the particles appeared smooth and spherical, as depicted in Fig. 1. Following the durability test, the particles developed a core-shell structure, with the outer layer containing iron oxide, as illustrated in Fig 2. The authors speculated that the time-dependent decrease in fan speed observed during the durability test may be caused by the oxidation of the iron particles, because the particles’ magnetizability decreases with increasing iron oxide content.

In this study, we examine the oxidation of iron particles within MR fluids and its impact on the field-induced rheological properties. We employ experiments in which the particles are oxidized in a controlled environment. The effects of oxidation on rheological properties are examined experimentally and compared with predictions obtained from a model based on dipolar magnetized particles.
2. Experimental Methods
Iron particles (2 μm diameter; BASF HS) in an aliphatic oil (Spectrasyn 2C; ExxonMobil) were oxidized using a three-neck flask reactor. All oxidation reactions were carried out with 10 wt% suspensions. Air was fed into the flask at a rate of 0.3 liters per minute. A heating mantle was used to maintain the temperature of the reaction mixture at the desired value. A condenser was employed to prevent loss of oil during the reaction. The reaction mixtures were stirred continuously (at 480 rpm) during the reactions.

The extent of oxidation was determined by measuring the decrease in the weight of samples when reduced in hydrogen. The reduction reaction was carried out in a modified Gow-Mac gas chromatograph (GC). Oxidized iron powder was packed in a 0.25 in. I.D. brass tube, and connected to the hydrogen supply inside the GC oven. Glass wool was packed into the tube ends to keep the powder in place. Hydrogen was fed through the bed at a rate of 0.22 liters per minute. Reaction gas products were passed through a Drierite bed. The extent of oxidation determined from the weight loss of the iron particles agreed with that determined from the water weight gain of the Drierite. All reduction reactions were carried out at 400°C, and continued until the sample mass no longer changed with time.

The effect of oxidation on the field-induced rheological properties is determined using a Bohlin VOR rheometer modified for the application of large magnetic fields [3].

3. Results and Discussion
The extent of oxidation of 10 wt% iron suspensions is plotted as a function of oxidation time in Fig. 3 for different oxidation reaction temperatures. The oxygen content grows linearly with time, which suggests that the oxide layer is nonadherent [4]. The activation energy estimated from the results at different temperatures is 92 ± 36 kJ/mol, which is similar to that obtained for similar systems. Grosvenor et al. [5, 6] obtained an activation energy of 32 ± 6 kJ/mol for oxidation of pure polycrystalline iron in dry O₂ gas over the temperature range 27–150°C. For oxidation of iron in air, Kubaschewski and Hopkins report an activation energy of 76 kJ/mol over the temperature range 600–1600°C [7], while Paidassi reports an activation energy of 40.5 kJ/mole over the temperature range 400–900°C [8].

Typical results for the effect of particle oxidation on rheological properties are illustrated in Fig. 4, where the yield stress scaled by the yield stress for pure iron particles is plotted as a function of the weight fraction of oxygen within the particles, w_{ox}, for 10 vol% suspensions at an applied flux density of 0.2 T. Also shown is the yield stress measured for a 10 vol% suspension of magnetite particles (10 μm diameter; Cerac Inc.) in Spectrasyn 2C. As expected, the yield stress decreases with increasing oxidation.

The effects of oxidation are also examined via a particle-level model, described in more detail elsewhere [9]. Motivated by the core-shell structures observed by Ulicny et al. [2], the particles are...
modeled as iron cores (radius $R_c$) surrounded by an iron oxide (magnetite) spherical shell (outer radius $R_s$), as illustrated in Fig. 5. The point-dipole approximation to the magnetic field-induced force between two magnetizable particles is [10]

$$F_{ij}^{\text{mag}} = F_0 \left( \frac{\sigma}{R_{ij}} \right)^4 \left[ (3 \cos^2 \theta_{ij} - 1) e_r + \sin 2\theta_{ij} e_\theta \right], \quad (1)$$

where $\sigma$ is the particle diameter. For core-shell particles such as that depicted in Fig. 5, the force magnitude $F_0$ in the limit of saturated magnetization is

$$F_0 = \frac{\pi}{12} \mu_0 R_s^2 \left[ M_{ss} + \left( \frac{R_c}{R_s} \right)^3 (M_{sc} - M_{ss}) \right]^2, \quad (2)$$

where $M_{sc}$ is the saturation magnetization of the core material, and $M_{ss}$ is the saturation magnetization of the shell material. The rheological properties of suspensions of such particles are determined by exploiting results of dipolar particle-level models. Here, the effect of oxidation appears as a reduction in the core radius and an increase in the shell radius, which results in an overall reduction particle
magnetization and thus the field-induced interparticle forces. The shear stress can be expressed

\[ \tau = -\frac{1}{V} \sum_{i=1}^{N} z_i F_{x,i} \]

\[ = \frac{F_0(f)}{R_s^2(f)} \tau^*(\phi) \]

where \( f \) is the degree of oxidation, and \( \tau^*(\phi) \) is the dimensionless yield stress determined, for example, from simulations or a chain model. This latter quantity depends only on the particle volume fraction. We note that the particle volume fraction will increase with time in an oxidizing suspension.

Results of this model presented along with the experimental data in Fig. 4. The model agrees well with the experimental data, with the stress decreasing with increasing oxide content (discrepancies are on the order of the experimental uncertainty). This behavior is consistent with results obtained for other systems with iron cores surrounded by nonmagnetizable shells, where the field-induced stress decreases with increasing shell thickness [11, 12, 13].

Figure 5. Schematic diagram of the core-shell structure employed in the model.

4. Conclusion

The oxidation of iron spheres in an aliphatic oil follows a linear growth law, suggesting that the oxide forms a nonadherent layer. The magnetic field-induced yield stress decreases with increasing extent of oxidation. The rheological behavior is consistent with that predicted using a core-shell model.

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