

# **Sedimentation Characterization of Zirconia coated Carbonyl Iron Based Suspensions for Magnetorheological Fluids**

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**Abstract:** The sedimentation rates of several different low-concentration (15 vol%) zirconia coated and uncoated carbonyl iron magnetorheological fluids are measured. The inductance of a constant volume of settling fluid is measured against time using a solenoid surrounding a test tube of fluid. This data are correlated to the sedimentation rate of each fluid. DAC and Glycerol are shown to be effective surfactants for reducing the sedimentation rate of both the coated and uncoated particles, reducing the sedimentation rates by 19% and 46% respectively when compared to a purely aqueous suspension. The results indicate that bi-disperse carbonyl iron suspensions have reduced sedimentation rates compared to mono-disperse carbonyl iron suspensions.

## 1. Introduction:

Magnetorheological finishing (MRF) is a deterministic precision polishing process which was developed in the 1990's at the Center for Optics Manufacturing in Rochester, NY [1]. MRF utilizes the properties of magnetorheological (MR) fluids, which vary from a liquid state to a semi-structured solid when a magnetic field is applied [2]. MR polishing fluids are typically composed of high-magnetic permeability, micron sized carbonyl iron (CI) particles suspended in water, surfactants to reduce agglomeration (clumping), and a hard polishing abrasive such as  $\text{CeO}_2$  or  $\text{ZrO}_2$  [1].

Standard magnetorheological slurries have several stability issues which limit the duration that the suspensions are able to polish surfaces. The carbonyl iron particles have a much higher density than water, thus gravity tends to force the particles to settle out of suspension. The aqueous carrier medium creates an environment which causes rapid corrosion without basic additives. Even with the basic additives, gradual lowering of pH from environmental absorption of  $\text{CO}_2$  will cause corrosion of the CI particles and agglomeration. [1]

An experimentally-verified solution to these stability problems is to layer the CI particles with a thin (~50 nm) zirconia coating using a sol-gel process. [1] The zirconia coating serves several purposes. The first is to act as an abrasive through the creation of nano-zirconia particles that result from the coating process, eliminating the need for hard abrasive particles and creating a bi-disperse system. The coating also serves to protect the particles from corrosion, allowing acidic slurries to exist without excessive agglomeration. [1] The zirconia coating changes the surface chemistry of the carbonyl iron particles, so alternative polymer surfactants are used to modify the electrostatic repulsive forces, such as Di-Ammonium Citrate (DAC) and Glycerol. [4] Thus, stable zirconia coated MR slurries are able to be created through the addition of polymer surfactants and pH control. [9]

An effective method of measuring the stability of a suspension is through the measurement of a sedimentation constant and sedimentation velocity data. [5] As the bulk of the MR fluid is in a non-magnetized state for the duration of polishing process, the offline (no magnetic field) sedimentation velocity is important in quantifying the in-use polishing duration for the given slurry. [4] While the rheological effects of the surfactants described above (DAC

and glycerol) have been examined through viscometric analysis, there have been no studies which investigated their effect on the sedimentation rate of carbonyl iron suspensions. [9] The zirconia coated particles are expected to behave differently when settling due to the modified surface chemistry of the coated particles as well as the bi-modal particle distribution in the zirconia coated suspension. [3] Thus, a comparison of sedimentation rates for several compositions of coated and uncoated carbonyl iron suspensions with and without surfactants will provide insight into the effectiveness of these surfactants.

## 2. Experimental Formulation and Procedure:

The MR suspension samples that will be tested are listed below in table 1:

Table 1: MR Sample Compositions

Sample No.	Description
1	15 vol% Zirconia coated Carbonyl Iron w/ 85 vol% DI Water
2	15 vol% Zirconia coated Carbonyl Iron, 1 vol% DAC, 2 vol% Glycerol, 82 vol% DI Water
3	15 vol% Zirconia coated Carbonyl Iron, 1 vol% Glacial Acetic Acid, 84 vol% DI Water
4	15 vol% Zirconia coated Carbonyl Iron, 1 vol% DAC, 2 vol% Glycerol, 1 vol% Glacial Acetic Acid, 81 vol% DI Water
5	15 vol% Uncoated Carbonyl Iron, 85 vol% DI Water
6	15 vol% Uncoated Carbonyl Iron, 1 vol% DAC, 2 vol% Glycerol, 82 vol% DI Water

The testing apparatus consisted of a 16.5 mm outer diameter and 200 mm high test tube mounted to a height-adjustable fitted stage with a digital height gage. A solenoid with a diameter matching the outer diameter of the test tube (having 70 turns with 22 gage insulated wire) was constructed and wrapped in a Co-Netic nickel permalloy shield. Both ends of the solenoid wires were connected to an INSTEK LCR-819 inductance meter. (Shown in Figure 1) Since this particular

inductance meter had no computer output a time-lapsing camera, taking a picture every 30 seconds, was used to capture inductance readings directly from the unit's screen. The pictures were then compiled and inductance readings were extracted and converted into usable Microsoft Excel data. The apparatus recorded the inductance as the carbonyl iron particles (with high magnetic permeability) settled to the bottom of the test tube, leaving only the carrier medium which has negligible inductance. [6] (Shown in Figure 1). As the inductance is measured with time, the particles settled at an approximately even rate, which gave the appearance of a "mudline" where the suspension is clear above that height. [6] Due to the lack of necessary chemicals and equipment on campus, each sample was created at the Laboratory for Laser Energetics by adding the carbonyl iron incrementally to the carrier medium mixed with surfactants in a 30 ml container. Each sample was mixed by hand in 20 ml batches after the addition of CI and surfactants. The samples were moved to campus with an average transport time of approximately 7.5 minutes. After arrival 10 ml of each sample was then transferred into the test tube using a 5 ml syringe to avoid splashing on the test tube walls.

To calibrate the apparatus, samples were placed into the inductor with a digital height meter resting on top as seen in Figure 1. The samples were then moved upward a few microns at a time while inductance readings were taken and recorded in Excel. This process produced the calibration curves (Figures 2 and 3) which were ultimately used in relating the changing inductance to the sedimentation rate. Only two calibration graphs were created as the magnetic permeability of the carbonyl iron particles is the only factor that changes the inductance readings. Since all samples were the same volume percentage of carbonyl iron, the experiment only required one calibration curve for coated CI and one for uncoated CI particles. The uncoated CI calibration curve has fewer data points because of the rapid sedimentation of the particles. The calibration had to be performed as quickly as possible to avoid settling during the process. Both calibration curves were best fit with a cubic polynomial function. The RMS error for the coated particle calibration was 0.40 mm and 0.75 mm for the uncoated CI particles. These errors are satisfactory when compared to the total magnitude of the mudline heights. After calibration, the samples were aligned in the inductor and allowed to settle. As the MRF settled the dropping inductance was recorded every 30 seconds by the camera using computer controlled software to time the camera pictures.



Figure 1: Experimental Set-up

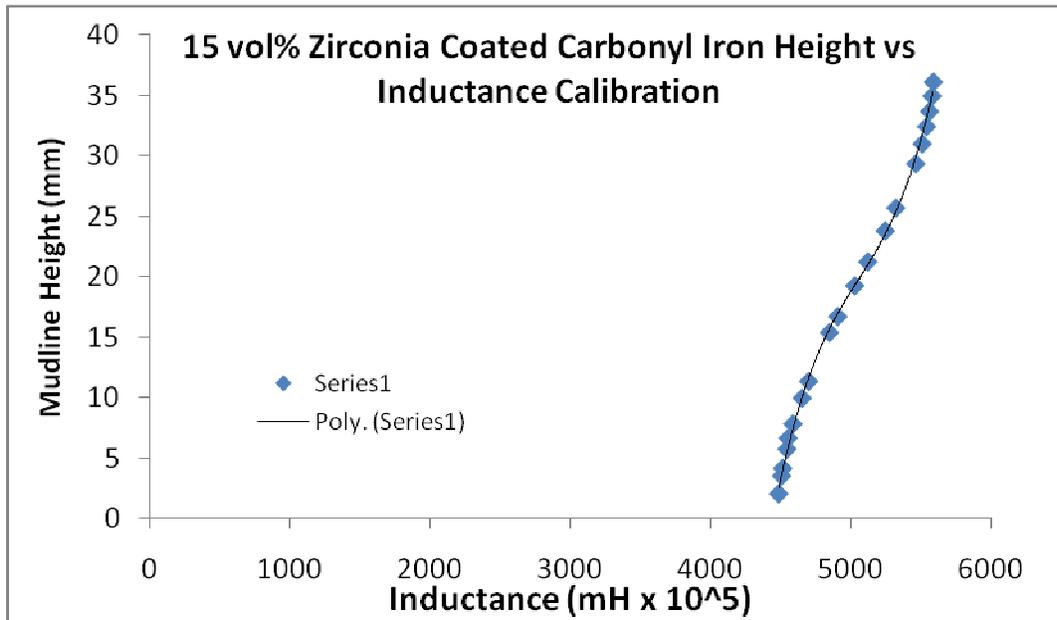
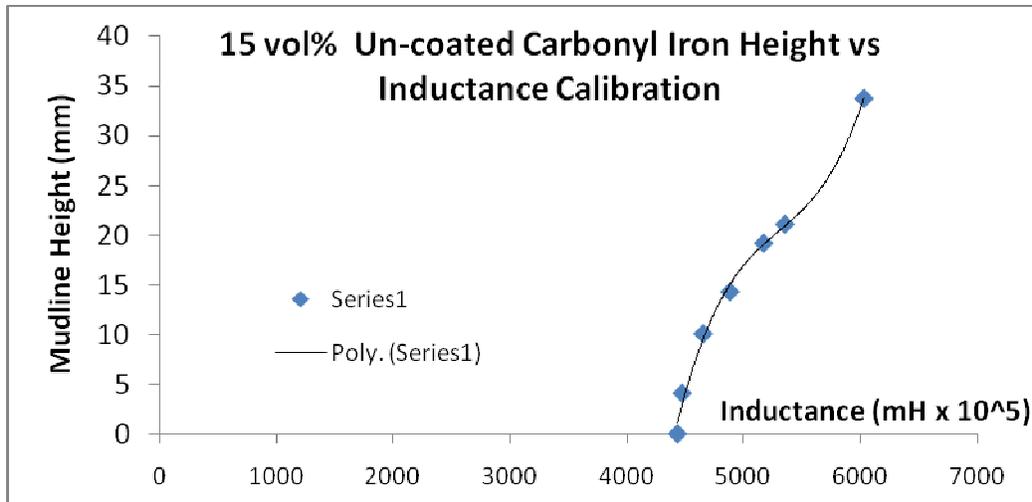


Figure 2: Calibration curve for the zirconia coated carbonyl iron particles



**Figure 3: Calibration curve for uncoated carbonyl iron particles**

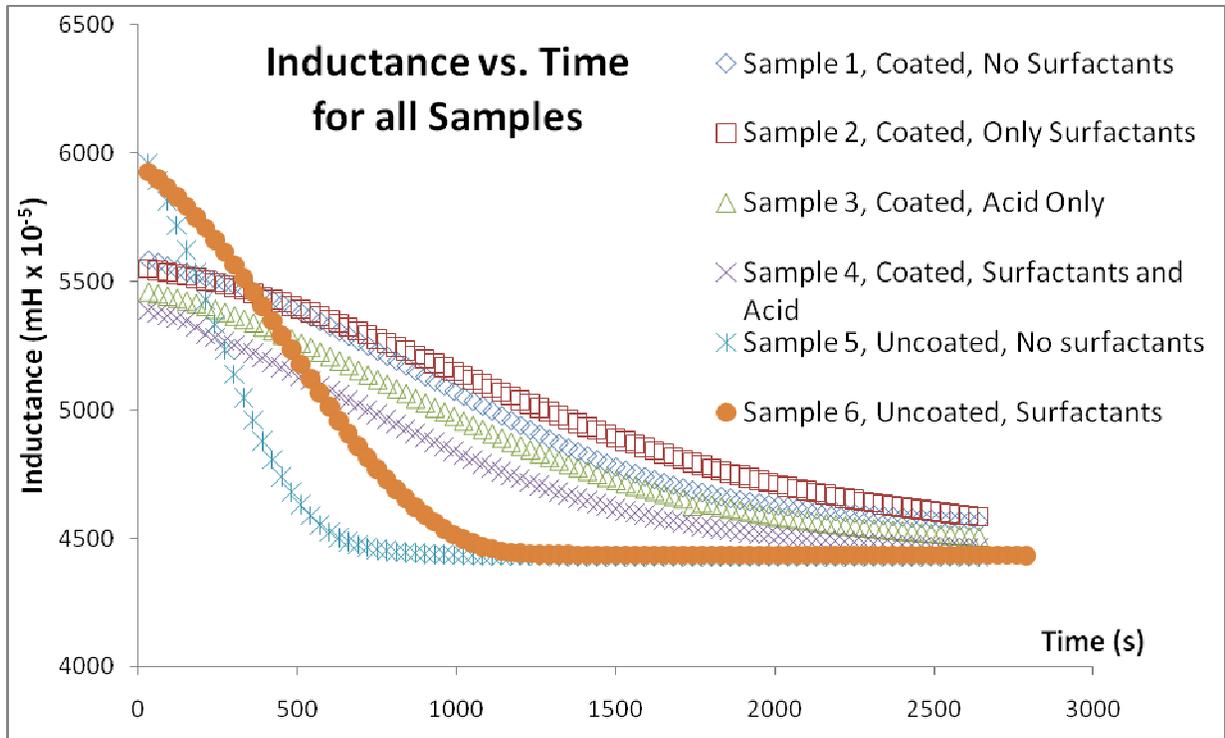
### 3. Results:

The inductance of each sample was measured over a period of approximately an hour after which the samples had all settled to a constant reading where the mudline was below the inductor itself. Figure 4 shows the inductance vs. time for each sample. The initial inductance readings are similar for each of the coated samples (1-4) and slightly higher for the uncoated particles (samples 5-6). This is due to the slight difference in magnetic permeability between coated and uncoated particles at the same volume percentage (15 vol%). [1] Each of the samples in Figure 4 has non-linear initial and final regions separated by a linear region. These non linear regions were observed in previous sedimentation experiments which measured the change in inductance through the varying magnetic permeability of the settling particles. They are attributed to “edge effects” as the mudline moves through the top and bottom of the inductor. [6]

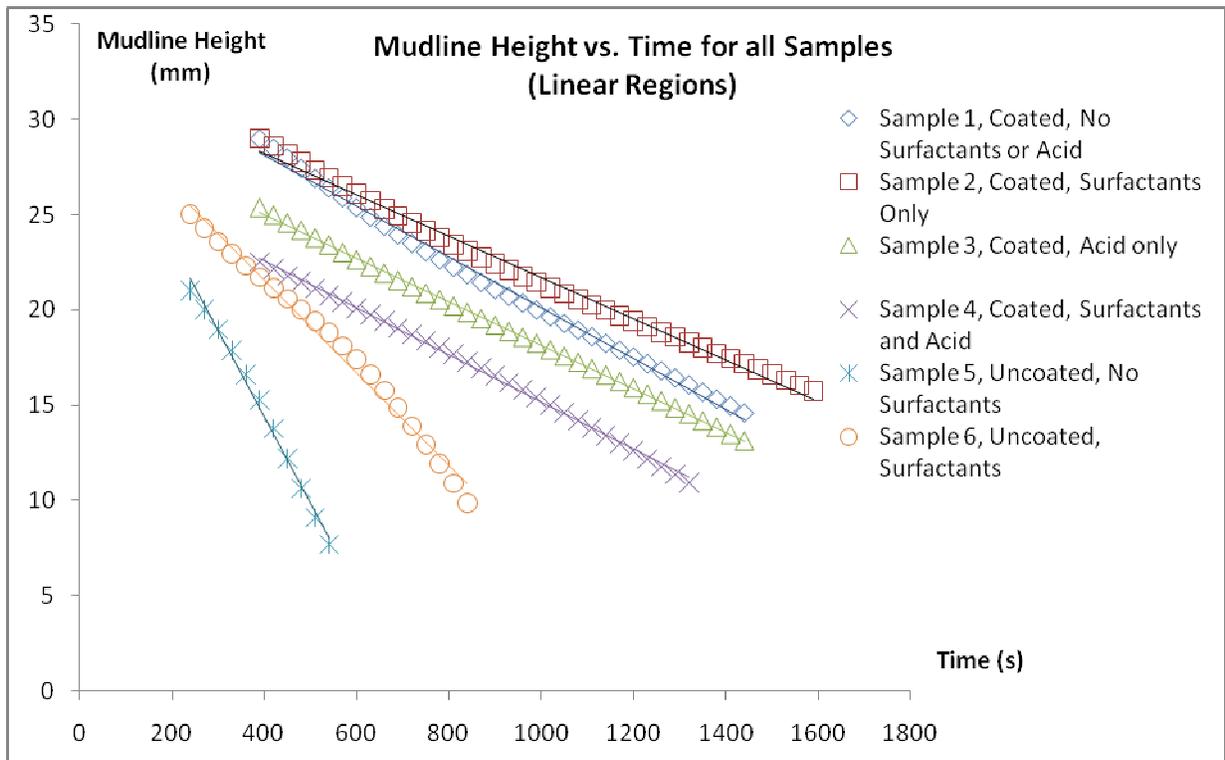
Figure 5 shows the cropped results after applying the calibration curves to convert from inductance to mudline height and removing the non-linear regions from each sample. Linear fits were applied to each sample and the mudline sedimentation rates were extracted as the slope of the linear sedimentation region. The samples did not all have the same starting height, which was difficult to control when setting up each test tube. However, the slopes of each linear fit were unaffected by the starting height. The RMS values for the linear fit were all satisfactory, approximately two orders of magnitude less than the mudline height magnitudes. A summary of these results can be found in table 2.

**Table 2: Summary of Sedimentation Results**

<b>Sample Composition</b>	<b>Linear Sedimentation Rate (mm/sec)</b>	<b>RMS from Linear Fit (mm)</b>	<b>Initial pH</b>
15 vol% Zirconia coated Carbonyl Iron w/ 85 vol% DI Water	0.0134	0.32	7.1
15 vol% Zirconia coated Carbonyl Iron, 1 vol% DAC, 2 vol% Glycerol, 82 vol% DI Water	0.0109	0.31	7.3
15 vol% Zirconia coated Carbonyl Iron, 1 vol% Glacial Acetic Acid, 84 vol% DI Water	0.0114	0.10	3.17
15 vol% Zirconia coated Carbonyl Iron, 1 vol% DAC, 2 vol% Glycerol, 1 vol% Glacial Acetic Acid, 81 vol% DI Water	0.0124	0.13	4.42
15 vol% Uncoated Carbonyl Iron, 85 vol% DI Water	0.0453	0.36	7.45
15 vol% Uncoated Carbonyl Iron, 1 vol% DAC, 2 vol% Glycerol, 82 vol% DI Water	0.0243	0.49	5.22



**Figure 4: Uncropped Inductance vs Time for all samples**



**Figure 5: Cropped Linear Sedimentation Results**

#### 4. Discussion/Conclusions

Several factors contributed to the modification of sedimentation rates achieved through pH control and the addition of DAC and glycerol. Both of the uncoated samples had higher sedimentation rates than any of the zirconia coated samples. It has been shown that bi-disperse suspensions that combine nano-sized particles with micron-sized particles are more stable and have slower sedimentation rates. [6] The zirconia coated carbonyl iron suspensions have a small volume percentage of nano-zirconia particles suspended amongst the CI that resulted from the coating process. [1] This large disparity in sedimentation rates between the coated and uncoated carbonyl iron suspensions can be attributed to the mono-disperse nature of the uncoated particle suspensions.

The sedimentation and rheological behavior of a particle suspension is highly dependent on the electro-chemical repulsive forces which result from the interaction between electrolytes adsorbed to the surface material of the suspended particle and the composition of the bulk carrier fluid. [8] A separation of charge exists at the surface of shear, which separates the more-concentrated adsorbed layer of electrolytes in solution from the typical electrolyte concentration throughout the bulk carrier solution. This forms an electric potential at the surface of shear known as the zeta potential of the surface material. A high magnitude of zeta potential implies that particles will be well dispersed from electro-chemical repulsive forces. [3] Since zeta potential is a function of the electrolyte concentration in the bulk carrier medium, it can be raised or lowered through pH modification via the addition of an acid or base. At the pH where a zeta potential of zero is reached, termed the Iso-electric point (IEP), the particles will experience no repulsive forces and experience attraction from short range van der Waals forces causing agglomeration which should increase sedimentation rates. [5] Thus the IEP was examined in each of the samples to determine the electro-chemical stability of each sample. In sample 5, the IEP for uncoated carbonyl iron particles was experimentally determined at a pH of 5.45. [7] The initial pH for sample 1 was 7.45, a difference of 2 from the IEP. For comparison, sample 1, which was merely zirconia coated carbonyl iron suspended in DI water, has an IEP of approximately 7.2. This is very close to the measured pH of 7.1, implying that the sample #4 was experiencing a high degree of agglomeration as seen at near neutral pH regions of several zirconia suspensions. [1] This demonstrates the strength of a bi-disperse system at reducing

sedimentation rates as even a highly agglomerated bi-disperse system (sample 1) settled more slowly than a less-agglomerated mono-disperse system (sample 5) when measured at the same carbonyl iron volume concentration.

Aside from pH control, the addition of surfactants is another way to improve the stability of a suspension. It can be seen that the addition of DAC and glycerol to Sample #6, slowed the sedimentation rate by 46%, demonstrating the effectiveness of the surfactants at providing repulsive forces between the carbonyl iron particles. The addition of DAC and glycerol was also successful in reducing the sedimentation rate of the zirconia coated suspension (as seen in sample 2) by 19%.

Acetic acid was added to samples 3 and 4 (zirconia coated samples) to modify the zeta potential of each suspension. Sample 3 contained only zirconia coated carbonyl iron and water, for which the IEP is around 7.2. [9] The acid lowered the pH to 3.17, improving the stability of suspension as can be demonstrated by the 15% reduction in sedimentation rate compared to the acid-less sample 1. Sample 4 contained DAC and Glycerol as surfactants as well as acetic acid to manipulate the surface chemistry of the suspension. The IEP for a zirconia coated carbonyl iron suspension with DAC and glycerol has been identified in previous work at a pH of approximately 4. [9] Unfortunately, the addition of acetic acid moved the pH to 4.42, very near the IEP of the suspension. This caused agglomeration and increased the sedimentation rate of the suspension, only reducing the sedimentation rate by 7.5% from sample 1. In future experiments, the sedimentation rate of a basic suspension with zirconia coated carbonyl iron particles, DAC, and Glycerol should be examined to move away from the IEP.

A possible source of error when identifying the sedimentation rates in the samples was in the difficulty of starting with a uniformly dispersed suspension when inductance measurements first began. Although the samples all had approximately equal times between creation and measurement, the samples were all shaken by hand, thus the level of dispersion was difficult to control or quantify. This may be the reason why there are such disparities in initial inductances and mudline heights in figure 4 and 5. A more rigid and prescribed mixing process may create more consistent results.

In conclusion, these results imply that the most important factor in reducing sedimentation in low volume concentration carbonyl iron suspensions is through the use of a bi-disperse system. The addition of DAC and Glycerol as surfactants had a larger effect at reducing the sedimentation rates than zeta potential manipulation through the addition of acid alone. The combined use of surfactants and pH control should allow for a higher degree of sedimentation rate reduction than demonstrated in this experiment, as a base should be used to move away from the suspension's natural IEP. Further experimentation should be performed to verify this hypothesis.

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